RAYMOND L. CARLSON, #138043
GRISWOLD, LaSALLE, COBB,
DOWD & GIN, L.L.P.
111 E. 7th St.
HANFORD, CA 93230
PHONE: (559) 584-6656
FAX: (559) 582-3106; (800) 947-1859
EMAIL: carlson@griswoldlasalle.com

Attorneys for Petitioners James G. Sweeney and Amelia M. Sweeney

STATE WATER RESOURCES CONTROL BOARD

In the Matter of the California Regional Water Quality Control Board – Central Valley Region, Adoption of Administrative Civil Liability Order No. R5-2015-0065 in the Matter of James G. and Amelia M. Sweeney, Sweeney Dairy, Tulare County	PETITION OF JAMES G. SWEENEY AND AMELIA M. SWEENEY FOR REVIEW OF ADMIISTRATIVE CIVIL LIABILITY ORDER NO. R5-2015-0065; REQUEST FOR HEARING; REQUEST FOR STAY

I. PETITION FOR REVIEW OF ADMINISTRATIVE CIVIL LIABILITY ORDER.

Pursuant to section 13320 of the California Water Code and section 2050 of Title 23 of the California Code of Regulations ("CCR"), James G. Sweeney and Amelia M. Sweeney ("Petitioners") petition the State Water Resources Control Board ("State Board") to review the June 4, 2015 Administrative Civil Liability Order adopted by the California Regional Water Quality Control Board, Central Valley Region ("Regional Board"), Order No. R5-2015-0065 ("Order"), for the Sweeney Dairy located at 30712 Road 170, Visalia, CA, Tulare County ("Site"). A true and correct copy of the Order is attached as **Exhibit 1** hereto.

Pursuant to Section 13320 of the California Water Code and Section 2053 of Title 23 of the California Code of Regulations, Petitioners also request that an order be issued staying the effect of the Order as to Petitioners, and request a hearing on this Petition.

Petitioners James G. Sweeney and Amelia M. Sweeney are doing business as Sweeney Dairy, 30712 Road 170, Visalia, CA 93292. Petitioners' dairy is a small dairy which milks fewer than 300 cows on a site where a dairy has operated continuously for over 80 years.

Petitioners take their commitment to environmental protection and stewardship seriously. Petitioners' believe their dairy has one of the lowest nitrate levels in the Central Valley. All of the domestic water and water for the dairy comes from wells on Petitioner's property. Petitioners' management practices insure that they preserve and protect the air, land and water resources for future generations. Petitioners have provided the highest quality milk possible for the past twenty five years. Petitioners' dairy has received the lowest somatic cell award from the Tulare DHIA for twenty one of the past twenty-two years. Petitioners have never had an antibiotic residue in meat or milk produced at their dairy.

It is important to keep in mind that Petitioners are not accused of a discharge violation. Rather, Petitioners are accused of violating a Regional Board order (the 2013 Order) requiring them to submit an annual report. Petitioners are not accused of actually discharging,[1] or threatening to discharge, any waste to the waters of the State, or of discharging any waste under circumstances that could affect the quality of the waters of the State.

Notwithstanding the above, the Regional Board, after the hearing on June 4, 2015, released a press release dated June 12, 2015, and immediately subsequently procured newspaper reportage putting Petitioners' and their dairy in a bad light, implying that not submitting the report harmed water quality.[2] The fact is that the Regional Board has no evidence of a discharge by Petitioners' dairy.

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[1] The Porter-Cologne Water Quality Control Act of 1969 (the "Act"), Water Code §§ 13000 et seq., establishes the State Board and the nine Regional Boards, and sets forth their jurisdiction and competence. Section 13050 provides definitions of various terms used in the Act, but does not include a definition of the term "discharge." This lack of definition makes its use vague and ambiguous under the facts of this case, if not void for vagueness, where there is no evidence that the Sweeneys have "discharged" or threatened to "discharge" anything to the waters of the State. There is no showing or evidence that anything the Sweeneys have done, or have not done, has impaired the quality of waters of the State. This proceeding reverses the normal order of proof, and the assumption is that the Sweeneys are subject to liability, and they have to prove that they are not.

[2] See Regional Board Press Release dated June 12, 2015 "Visalia Dairy Fined $34,650 for Failing to Provide Annual Report to Assess the Impacts of Dairy Operations on Water Quality;" "BREAKING: Leprino milk supplier fined $34,650," Hanford Sentinel, June 12, 2015; "Tulare County dairies [sic] fined $34,650," Visalia Times-Delta/Advance Register, June 13, 2015, p. 3A; "Dairy fined for missing report," Fresno Bee, June 13, 2015, p. 12A. The press release and articles are attached collectively hereto as **Exhibit 5**. None of the reporters contacted Petitioners. It is unknown whether the Regional Board has a formal policy for press releases, or is merely attempting to pressure Petitioners and put them and their dairy in a bad light.

II. SPECIFIC ACTION OF THE REGIONAL BOARD WHICH THE STATE BOARD IS REQUESTED TO REVIEW.

Petitioners request that the State Board review the Regional Board's issuance of Order No. R5-2015-0065.

III. THE DATE ON WHICH THE REGIONAL BOARD ACTED.

The Regional Board acted on June 4, 2015 when it issued the Order. The Order was not formally served, however, until June 19, 2015 when it was mailed to Petitioners by certified mail. The Order was received by Petitioners on Monday, June 22, 2015. The Order itself does not show what the Board member vote was on the Order, or which Board members were present when the vote on the Order occurred, or indeed even whether a quorum was present at that time.

IV. STATEMENT OF REASONS WHY THE REGIONAL BOARD'S ACTION WAS INAPPROPRIATE, IMPROPER and EXCEEDED THE AUTHORITY STATUTORY JURISDICTION COMPETENCE OF THE REGIONAL BOARD.

The Order to Petitioners is improper for the following principal reasons:

(1) The Regional Board failed to comply with Water Code § 13267(b)(1), which states, in relevant part: In conducting an investigation specified in subdivision (a), the regional board may require that any person who has discharged, discharges, or is suspected of having discharged or discharging, or who proposes to discharge waste within its region, [. . .] shall furnish, under penalty of perjury, technical or monitoring program reports which the regional board requires. The burden, including costs, of these reports shall bear a reasonable relationship to the need for the report and the benefits to be obtained from the reports. <u>In requiring those reports, the regional board shall provide the person with a written explanation with regard to the need for the reports, and shall identify the evidence that supports requiring that person to provide the reports</u>. (Emphasis added). The Regional Board has never complied with this requirement.

(2) The Regional Board is attempting to enforce the 2013 Order which has not been approved as a return on the writ issued on April 17, 2013, and that writ has yet to be

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111 E 7th St
HANFORD, CA 93230

discharged. The Regional Board remains under the mandate of the Court and may not enforce the 2013 Order until the Court's mandate has been discharged.

(3) Petitioners incorporate their arguments and evidence submitted in their Submission of Evidence and Policy Statement Regarding Hearing on Administrative Civil Liability Complaint No. R5-2015-0506, dated April 30, 2015, attached as **Exhibit 2** and incorporated herein by reference.

V. THE REGIONAL BOARD HAS FAILED TO COMPLY WITH WATER CODE § 13267(b)(1) WHICH IS A PRE-REQUISITE FOR PETITIONERS' BEING REQUIRED TO SUBMIT REPORTS DEMANDED BY THE REGIONAL BOARD.

Water Code § 13267(b)(1) provides in relevant part: In conducting an investigation specified in subdivision (a), the regional board may require that any person who has discharged, discharges, or is suspected of having discharged or discharging, or who proposes to discharge waste within its region, [. . .] shall furnish, under penalty of perjury, technical or monitoring program reports which the regional board requires. The burden, including costs, of these reports shall bear a reasonable relationship to the need for the report and the benefits to be obtained from the reports. <u>In requiring those reports, the regional board shall provide the person with a written explanation with regard to the need for the reports, and shall identify the evidence that supports requiring that person to provide the reports</u>. (Emphasis added).

The Regional Board is attempting to punish Petitioners for a non-discharge violation.

Petitioners are not accused of having discharged, discharging, proposing to discharge, or threatening to discharge, any waste to the waters of the State whether within or without the Central Valley Region, or of discharging any waste under circumstances that could affect the quality of the waters of the State either within or without the Central Valley Region. To the extent Petitioners are assumed to have engaged in any of such acts, they are deprived of due process of law in being denied the presumption of innocence until guilt or liability is proved, and denied due process of law by such shifting of the burden of proof from accuser to accused.

Petitioners are accused of failure to submit a report called for under the 2013 Order that is stayed until the Court's mandate is discharged in Asociacion de Gente Unida por Agua, et al., v. Central Valley Regional Water Quality Control Board, Sacramento County Superior Court Case No. 34-2008-00003604CU-WM-GDS.

Water Code § 13267(b)(1) imposes an affirmative mandatory statutory duty on the Regional Board to provide a person from whom a technical report is required with a written explanation with regard to the need for the report, and shall identify the evidence that supports requiring that person to provide the report.

The Regional Board never provided the Petitioners with the information required by section 13267(b)(1). There is no evidence that the Regional Board ever provided Petitioners with the information required by section 13267(b)(1). Therefore, Petitioners were not required to provide the report(s) demanded by the Regional Board and issuance of Administrative Civil Liability Order. No. R5-2015-0065 was improper and in excess of the jurisdiction of the Regional Board.

The plain language of section 13267(b)(1) requires Respondents to discharge the affirmative mandatory statutory duty stated in the statute.

Petitioners are not required to prepare and submit any technical reports to the Regional Board until it have discharged the affirmative mandatory statutory duty stated in the statute.

Petitioners cannot be made subject to administrative civil liability for alleged failure to prepare and submit any technical reports to the Regional Board until the Regional Board has discharged the affirmative mandatory statutory duty stated in the statute.

The Regional Board may not seek to impose administrative civil liability on Petitioners for alleged failure to prepare and submit any technical reports until the Regional Board has discharged the affirmative mandatory statutory duty stated in the statute.

The Regional Board engages in a pattern and practice of violation of Water Code § 13267(b)(1) in that it fails to provide persons from whom technical reports are demanded "with a written explanation with regard to the need for the report, and shall identify the evidence that supports requiring that person to provide the reports."

The Regional Board's violation of section 13267(b)(1) is continuous and on-going, and represents a policy and procedure of the Regional Board to deny Petitioners and all others similarly situated with the benefits and protection clearly intended by the Legislature when it enacted the statute.

VI. THE FACTUAL AND LEGAL BACKGROUND REGARDING THE 2007 ORDER AND THE 2013 ORDER SHOW THAT THE COURT ISSUED A WRIT OF MANDATE SETTING ASIDE THE 2007 ORDER IN ITS ENTIRETY AND THAT THE 2013 ORDER WAS PROFFERED AS A RETURN ON THE WRIT, OBJECTED TO, AND THAT TO DATE NO RETURN ON THE WRIT HAS BEEN MANDE AND THE WRIT HAS NOT BEEN DISCHARGED.

On May 3, 2007, the Regional Board adopted Order No. R5-2007-0035 entitled "Waste Discharge Requirements General Order for Existing Milk Cow Dairies," referred to herein as the "2007 Order."

Asociación de Gente Unida Por el Agua and others ("Ascociaón et al.") petitioned the State Board under Water Code § 13320 for review of the Regional Board's action in adopting the 2007 Order.

On January 16, 2008, the State Board through its Executive Director summarily and peremptorily dismissed the petition brought by Asociación et al., without notice or opportunity to be heard.

On February 15, 2008, Asociación et al. filed a petition for writ of mandate, Asociacion de Gente Unida por Agua, et al., v. Central Valley Regional Water Quality Control Board, Sacramento County Superior Court Case No. 34-2008-00003604CU-WM-GDS.

On September 10, 2010, the trial court denied the petition and entered judgment denying petition for writ of mandate.

On November 6, 2012, the Court of Appeal filed its opinion in Asociacion de Gente Unida por el Agua, et al., v. Central Valley Regional Water Quality Control Board (2012) 210 Cal. App. 4th 1255, in which the Court reversed the judgment of the trial court and remanded the matter to the trial court with "directions to grant the petition to require the Regional Board to comply with Resolution No. 68-16."

On April 17, 2013, the trial court filed its order granting writ of mandate in Asociacion de Gente Unida por Agua, et al., v. Central Valley Regional Water Quality Control Board, Sacramento County Superior Court Case No. 34-2008-00003604CU-WM-GDS, ordering Respondent Regional Board to "Set aside the Waste Discharge Requirements General Order for Existing 4 Milk Cow Diaries (Order No. R5-2007-0035) and reissue the permit only after application of, and compliance with, the State's anti-degradation policy (Resolution No. 68-16); as interpreted by the Court of Appeal in its opinion . . ."

The April 17, 2013 writ order set aside the 2007 Order in its entirety.

On October 3, 2013, the Regional Board adopted Order No. R5-2013- 0122, "Reissued Waste Discharge Requirements General Order for Existing Milk Cow Dairies" (2013 Order or Reissued Order).

On October 11, 2013, in Case No. 34-2008-00003604CU-WM-GDS, the Regional Board filed a Return to the Writ of Mandate indicating that it had rescinded the 2007 Order and adopted the 2013 Order.

On October 29, 2013, Petitioners filed their petition under Water Code § 13320 challenging the Regional Board's adoption of the 2013 Order, docket no. A-2283(a). Said petition remains still pending before the State Board.

On November 4, 2013, Petitioners Asociación et al. filed a Response to the Return to the Writ of Mandate, contending that the 2013 Order does not comply with the Writ of Mandate.

On November 5, 2013, Asociación et al. filed a petition under Water Code § 13320 challenging the Regional Board's adoption of the 2013 Order, docket no. A-2283(b). Said petition remains still pending before the State Board.

GRISWOLD, LaSALLE, COBB, DOWD & GIN, LLP
111 E. 7th St.
HANFORD, CA 93230

On November 22, 2013, Interveners Community Alliance for Responsible Environmental Stewardship ("CARES") filed a Reply to Petitioners' Asociación et al. Response to the Return to Writ of Mandate urging the Court to accept the Return and discharge the Writ.

On November 6, 2014, following a case management conference on October 14, 2014, the court entered its order to stay proceedings in Case No. 34-2008-00003604CU-WM-GDS to determine the adequacy of the Regional Board's Return to Writ of Mandate until such time as the State Board has issued a decision or an order of dismissal on the petition filed before the State Board by Petitioners Asociación et al., or until further order of the Court.

The writ issued April 17, 2013 setting aside the 2007 Order has not been discharged. The Regional Board proffered the 2013 Order as its return on the Writ. The court has not accepted the Regional Board's return on the writ, i.e., the 2013 Order. The 2013 Order may not be enforced for such reason; otherwise, the Regional Board could simply avoid the duty to comply with the mandate of the court.

The 2013 Order may not be enforced against Petitioners until the Regional Board ends its continuous and on-going policy and procedure of violating of section 13267(b)(1) to deny Petitioners and all others similarly situated with the benefits and protection clearly intended by the Legislature when it enacted the statute.

The Regional Board may not enforce against Petitioners the 2013 Order until the return is made on the writ issued in Case No. 34-2008-00003604CU-WM-GDS, and that writ is discharged. Advisory Counsel recognized that "The 2013 Order is still under the purview of the Superior Court, Sacramento Superior Court, due to the fact that there is a Petition pending at the State Water Board." Transcript [**Exhibit 3**] at p. 63, lines 18-22.

The administrative record for the 2013 Order has not been prepared. Mr. Sweeney requested the administrative record for the 2013 Order in October 2013. See e-mails attached as **Exhibit 6**. To date, the administrative record has not been received, nor been prepared so far as Petitioners know. The statement by Mr. Rodgers in his testimony [Transcript p. 57, line 23, to p. 58, line 9], that the administrative record for the 2013 Order was provided to Petitioners, is not correct. The e-mail exchange in **Exhibit 6** clearly shows that the administrative record for the 2013 Order did not exist at the time the 2013 Order was adopted on October 3, 2013; otherwise its size and scope would have been known.

VII. PETITIONERS REQUEST A HEARING ON THE ORDER.

Petitioners request a hearing on the Order. In support of this request, they make the following points:

A summary of the arguments that Petitioner wishes to make at the hearing is provided in the Petition above.

A summary of the testimony or evidence the petitioner wishes to introduce is provided in the Petition above, including all documents referenced in this Petition, although Petitioner may supplement the testimony or evidence at the hearing.

VIII. REQUEST FOR STAY.

Petitioner requests a stay of the Order pending resolution of the issues raised in this Petition.

Pursuant to Section 2053 of Title 23 of the California Code of Regulations, the effects of an order shall be stayed if the petitioner shows:

Substantial harm to Petitioner or to the public interest if a stay is not granted;

A lack of substantial harm to other interested parties and to the public if a stay is granted; and

Substantial questions of fact or law regarding the disputed action exist.

These requirements are met in this case.

1. <u>Petitioner Will Suffer Substantial Harm if a Stay Is Not Granted</u>.

The Order imposes fines that are approximately 34 times greater than the cost of compliance (report preparation) claimed by the Regional Board

The Order puts Petitioners in a prejudicial bind. If Petitioners comply with the Order pending appeal, it will have to spend significant sums with no hope of recouping them except through expensive cost recovery litigation. If Petitioners decline to expend the money, time, and resources in an effort to comply with the Order, they become exposed to potential civil enforcement action and further penalties for non-compliance. Therefore, if a stay is not granted, Petitioners would be faced with a no-win scenario: expend substantial sums to comply with an improperly issued Order, or face substantial monetary penalties for failure to comply. A stay until the State Board rules on the merits of the petition would solve this problem and save Petitioners from significant and substantial monetary harm.

2. <u>There is a lack of substantial harm to other interested parties and to the public if a stay is granted</u>.

Petitioners are charged with a non-discharge violation. The Petitioners are not accused of any discharge, and no evidence exists of any discharge by Petitioners to waters of the State. The only evidence regarding the water quality at the Sweeney Dairy was that presented by the testimony of Mr. Sweeney on direct examination by his counsel. The Regional Board offered no evidence of groundwater quality at or near Petitioners' dairy. Mr. Sweeney's testimony was that the water quality at his dairy is excellent with no nitrate or other problems. See Transcript [**Exhibit 3**], p. 33, line 23, to p. 38, line 15. Also note that the Petitioners' dairy is not near other dairies. The closest dairy on the north is five miles away, on the west two miles away, on the south five miles, and on the east, in Nevada. <u>Id</u>. at p. 33, lines 4-14. Data maintained by the State Board and accessible on its web site shows that no nitrate impaired well exists within 2000 feet of the Sweeney Dairy address. See **Exhibit 4** attached hereto. This fact is consistent with Mr. Sweeney's testimony, and supports the characterization that a nitrate water quality problem does not exist at the site of Petitioners' dairy. Therefore, there is a lack of substantial harm to other interested parties and to the public if a stay is granted.

3. <u>Substantial questions of fact or law regarding the disputed action exist</u>.

Here substantial questions exist regarding the failure of the Regional Board to comply with Water Code § 13267(b)(1) and whether the Regional Board exceeds its authority when engaging in enforcement actions without having so complied. There is no evidence in the record that the Regional

Board has complied with Water Code § 13267(b)(1). See Transcript, p. 29, line 22 to p. 8 (Mr. Rodgers admitting that no report was prepared for Petitioners' dairy, but claiming that the General Order contained analyses that discharged the Regional Board's duty under the statute). In further connection with the Regional Board's duty under Water Code § 13267(b)(1), an issue exists whether the Regional Board can discharge its duty under section 13267(b)(1) with an analysis contained in a general order or whether the statue requires an analysis for each person required to submit a report. The parties disagree on this point which is significant for further enforcement efforts by the Regional Board and for the regulated community.

A further substantial issue exists regarding the efficacy of the 2013 Order in view of the Regional Board's failure to make return on the writ issued on April 17, 2013.

An Exhibit list with the Exhibits is attached.

A copy of this Petition, together with all Exhibits, has been mailed to the Central Valley Regional Water Quality Control Board.

DATED: July 6, 2015.

GRISWOLD, LaSALLE, COBB,
DOWD & GIN, L.L.P.

By [signature]
RAYMOND L. CARLSON,
Attorneys for Petitioners

EXHIBIT LIST

EXHIBIT 1 Administrative Civil Liability Order No. R5-2015-0065, received June 22, 2015 (mailed June 19, 2015)
DATED JUNE 4, 2015

EXHIBIT 2 Submission of Evidence and Policy Statement Regarding Hearing on Administrative Civil Liability Complaint No. R5-2015-0506 with Exhibits A-N[3]
DATED APRIL 30, 2015

EXHIBIT 3 Transcript of Hearing of June 4, 2014
DATED CERTIFIED JUNE 23, 2015

EXHIBIT 4 Map showing Sweeney Dairy not within 2000 feet of Nitrate Impacted Well from State Board web site at: www.waterboards.ca.gov/water_issues/programs/nitrate_project/nitrate_tool/

EXHIBIT 5 Regional Board Press Release dated June 12, 2015 "Visalia Dairy Fined $34,650 for Failing to Provide Annual Report to Assess the Impacts of Dairy Operations on Water Quality;" "BREAKING: Leprino milk supplier fined $34,650," Hanford Sentinel, June 12, 2015; "Tulare County dairies [sic] fined $34,650," Visalia Times-Delta/Advance Register, June 13, 2015, p. 3A; "Dairy fined for missing report," Fresno Bee, June 13, 2015, p. 12A.

EXHIBIT 6 E-mails Friday, October 11, 2013 Jim Sweeney to Clay Rodgers requesting administrative record for 2013 Order; and Thursday, October 24, 2013, Doug Patteson to Jim Sweeney.

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[3]Exhibits M and N were submitted May 13, 2015, with Petitioners' Partial Response to Prosecution Team Rebuttal Argument and Rebuttal Evidence; Administrative Civil Liability Complaint No. R5-2105-0506. This was submitted to correct the impression in the prosecution's rebuttal that Petitioners had not petitioned the State Board for review of the 2103 Order.

GRISWOLD, LaSALLE, COBB, DOWD & GIN, LLP
111 E. 7th St.
HANFORD, CA 93230

PROOF OF SERVICE
CCP §§ 1011, 1013, 1013a; FRCP 5(b)

I am employed in the County of Kings, State of California. I am over the age of 18 years and not a party to the within action. My business address is 111 E. Seventh Street, Hanford, California 93230.

On July 6, 2015, I served the following document(s): **PETITION FOR REVIEW In the Matter of the California Regional Water Quality Control Board – Central Valley Region, Adoption of Administrative Civil Liability Order No. R5-2015-0065 in the Matter of James G. and Amelia M. Sweeney, Sweeney Dairy, Tulare County** on the interested parties in this action by placing a true and correct copy thereof enclosed in a sealed envelope addressed as follows:

SEE ATTACHED SERVICE LIST

[] (By Mail) I deposited such envelope in the United States mail at Hanford, California. The envelope was mailed with postage thereon fully prepaid.

[X] (By Mail) As follows: I am "readily familiar" with the firm's practice of collection and processing correspondence for mailing. Under the practice it would be deposited with the U.S. Postal Service on the same day with postage thereon fully prepaid at Hanford, California, in the ordinary course of business for delivery to the indicated recipient(s).

[X] (By Overnight Delivery) I deposited such envelope in the Federal Express/UPS Next Day Air/U.S. Mail Express Mail depository at Hanford, California. The envelope was sent with delivery charges thereon fully prepaid for delivery to the indicated recipient(s).

[] (By Personal Service) I caused such envelope to be hand delivered to the offices of the addressee(s) shown above.

[X] (By Electronic Mail) I caused such documents to be sent to the indicated recipients via electronic mail to the e-mail address(es) as stated herein.

[] (By Facsimile) I caused each document to be delivered by electronic facsimile to the offices listed above.

[X] (State) I declare under penalty of perjury, under the laws of the State of California, that the foregoing is true and correct.

[] (Federal) I declare that I am employed in the office of a member of the Bar of this Court at whose direction the service was made.

Executed on July 6, 2015, at Hanford, California.

Kato

KATIE ASKINS

SERVICE LIST

In re Matter of CVRWQCB Adoption of ACLC No. R5-2015-0065

BY UPS NEXT DAY AIR
TRACKING NO. 1ZF74R0191485945
BY E-MAIL jbashaw@waterboards.ca.gov

Jeanette L. Bashaw, Legal Analyst
State Water Resources Control Board
Office of Chief Counsel
1001 "I" Street, 22nd Floor
P. O. Box 100
Sacramento, CA 95812-0100

BY U.S. MAIL

Pamela Creedon, Executive Officer
Regional Water Quality Control Board
Central Valley Region
11020 Sun Center Drive, Suite 200
Rancho Cordova, CA 95670

CALIFORNIA
Water Boards

EDMUND G. BROWN JR.
GOVERNOR

MATTHEW RODRIQUEZ
SECRETARY FOR
ENVIRONMENTAL PROTECTION

Central Valley Regional Water Quality Control Board

19 June 2015

James G. and Amelia M. Sweeney (owner/operator)
Sweeney Dairy
30712 Road 170
Visalia, CA 93292

CERTIFIED MAIL
7014 1200 0000 3347 7449

TRANSMITTAL OF ADOPTED ADMINISTRATIVE CIVIL LIABILITY ORDER FOR SWEENEY DAIRY, WDID 5D545155N01, 30712 ROAD 170, VISALIA, TULARE COUNTY

Enclosed is an official copy of Order No. R5-2015-0065, as adopted by the California Regional Water Quality Control Board, Central Valley Region, at its 4 June 2015 meeting.

An official copy of the above Order has been posted on the Central Valley Water Board's website at:
http://www.waterboards.ca.gov/centralvalley/board_decisions/adopted_orders/

If you have any questions, please contact me at (559) 445-5093 or at dale.eessary@waterboards.ca.gov.

DALE E. ESSARY
Senior Engineer
Confined Animals Unit

Enclosure: Order No. R5-2015-0065

CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

ADMINISTRATIVE CIVIL LIABILITY ORDER R5-2015-0065

IN THE MATTER OF

JAMES G. AND AMELIA M. SWEENEY
SWEENEY DAIRY
TULARE COUNTY

This Order is issued to the James G. and Amelia M. Sweeney (hereafter Discharger) pursuant to California Water Code (Water Code) section 13268, which authorizes the imposition of Administrative Civil Liability. This Order is based on findings that the Discharger violated provisions of Reissued Waste Discharge Requirements General Order for Existing Milk Cow Dairies, Order R5-2013-0122 (hereinafter Reissued General Order).

The Central Valley Regional Water Quality Control Board (Central Valley Water Board or Board) finds the following:

1. The Discharger owns and operates the Sweeney Dairy (Dairy) located at 30712 Road 170, Visalia, California, County of Tulare.

2. The Dairy is regulated by the Reissued Waste Discharge Requirements General Order for Existing Milk Cow Dairies, Order R5-2013-0122 (Reissued General Order) and accompanying Monitoring and Reporting Program (MRP), which was adopted by the Central Valley Water Board on 3 October 2013. The Reissued General Order replaces the Waste Discharge Requirements General Order for Existing Milk Cow Dairies, Order R5-2007-0035 (hereinafter 2007 General Order) and accompanying MRP, which was issued by the Central Valley Water Board on 3 May 2007. The Reissued General Order and the MRP contain reporting requirements for dairies regulated by the Reissued General Order.

3. Water Code section 13267 authorizes the Regional Water Boards to require the submittal of technical and monitoring reports from any person who has discharged, discharges, or is suspected of having discharged or discharging, or who proposes to discharge to waters of the state.

4. The Reissued General Order and the MRP required the Discharger to submit a 2013 Annual Report by 1 July 2014 pursuant to the Central Valley Water Board's authority in accordance with Water Code section 13267.

5. The Discharger violated Water Code section 13267 by failing to submit the 2013 Annual Report required by the Reissued General Order and Monitoring and Reporting Program by the required deadline of 1 July 2014.

6. On 29 August 2014, the Central Valley Water Board staff issued a Notice of Violation notifying the Discharger that the 2013 Annual Report had not been received. The Notice of Violation requested that the delinquent report be submitted as soon as possible to minimize potential liability.

7. On 5 December 2014, the Central Valley Water Board staff issued a courtesy pre-filing settlement letter notifying the Discharger that staff was in the process of assessing civil liability for failure to submit the 2013 Annual Report.

8. On 11 March 2015, the Assistant Executive Officer, lead prosecutor for the Prosecution Team, issued Administrative Civil Liability Complaint (Complaint) No. R5-2015-0506 to the Discharger recommending that the Central Valley Water Board assess the Discharger an administrative civil liability in the amount of $34,650 pursuant to Water Code section 13268 for the failure to submit the 2013 Annual Report.

9. Issuance of this Administrative Civil Liability Order to enforce Water Code Division 7, Chapter 5.5 is exempt from the provisions of the California Environmental Quality Act (Pub. Resources Code § 21000 et seq.), in accordance with California Code of Regulations, title 14, section 15321(a)(2).

10. On 17 November 2008 the State Water Resources Control Board adopted Resolution No. 2009-0083 amending the Water Quality Enforcement Policy (Enforcement Policy). The Enforcement Policy establishes a methodology for assessing discretionary administrative civil liability. Use of the methodology addresses the factors used to assess a penalty under Water Code section 13327. The required factors under Water Code section 13327 have been considered using the methodology in the Enforcement Policy as explained in detail in Attachment A to this Order. Attachment A is attached hereto and incorporated herein by reference.

11. This Order is effective and final upon issuance by the Central Valley Water

12. Board. Payment must be received by the Central Valley Water Board no later than thirty (30) days from the date on which this Order is issued.

13. In the event that the Discharger fails to comply with the requirements of this Order, the Executive Officer or her delegee is authorized to refer this matter to the Attorney General's Office for enforcement.

14. Any person aggrieved by this action of the Central Valley Water Board may petition the State Water Board to review the action in accordance with Water Code section 13320 and California Code of Regulations, title 23, sections 2050 and following. The State Water Board must receive the petition by 5:00 p.m., 30 days after the date that this Order becomes final, except that if the thirtieth day following the date that this Order becomes final falls on a Saturday, Sunday, or state holiday, the petition must be received by the State Water Board by 5:00 p.m. on the next business day. Copies of the law and regulations applicable to filing petitions may be found on the Internet at: http://www.waterboards.ca.gov/public_notices/petitions/water_quality or will be provided upon request.

IT IS HEREBY ORDERED that pursuant to section 13323 of the Water Code, the Discharger is assessed an administrative civil liability in the amount of thirty-four thousand six hundred and fifty dollars ($34,650). Payment shall be made in the form of a check made payable to the State Water Pollution Cleanup and Abatement Account no later than thirty days from the date of issuance of this Order.

I Pamela C. Creedon, Executive Officer , do hereby certify that this Order is a full, true and correct copy of the Order adopted by the California Regional Water Quality Control Board , Central Valley Region, on 4 June, 2015.

PAMELA C. CREEDON, Executive Officer

Attachment A – ACL Complaint No. R5-2015-0506
Specific Factors Considered – Civil Liability
James G. & Amelia M. Sweeney
Sweeney Dairy

The Central Valley Water Board alleges that the Discharger failed to submit the 2013 Annual Report required to be submitted by 1 July 2014. For the purpose of applying the Enforcement Policy's administrative civil liability methodology, the alleged violation is a non-discharge violation. Each factor of the Enforcement Policy and its corresponding score for each violation are presented below:

Failure to submit 2013 Annual Report: In accordance with the Reissued Waste Discharge Requirements General Order for Existing Milk Cow Dairies, Order R5-2013-0122 (Reissued General Order) and the accompanying Monitoring and Reporting Program (MRP), a 2013 Annual Report must be submitted for regulated facilities by 1 July 2014. To date, the Owner/Operator (hereinafter the Discharger) has not submitted this report for the Sweeney Dairy.

Calculation of Penalty for Failure to Submit 2013 Annual Report

Step 1. Potential for Harm for Discharge Violations
This step is not applicable because the violation is a not a discharge violation.

Step 2. Assessment for Discharge Violations
This step is not applicable because the violation is a not a discharge violation.

Step 3. Per Day Assessment for Non-Discharge Violations

The per day factor is 0.35.

This factor is determined by using the potential for harm of the violation and the extent of the Discharger's deviation from requirements. The potential for harm was determined to be minor due to the following: The failure to submit the 2013 Annual Report did not increase the amount of pollution discharged or threatened to discharge into waters of the State. However, failing to submit the Annual Report to the Central Valley Water Board hinders the Board's ability to detect and address noncompliance. The Annual Report is a key means through which the Central Valley Water Board evaluates a Discharger's compliance with the Reissued General Order, including the assessment of proper manure application to fields and waste management in a dairy's production area. By failing to provide the information in the Annual Report, the Discharger frustrates the Board's efforts to assess the potential impacts and risks to water quality and circumvents the Board's ability to take necessary enforcement action to correct problems. The regulatory program is compromised when staff resources are directed toward bringing the Discharger into compliance and those resources are not available for other program activities. Since the violation thwarts the Board's ability to identify water quality risks, the violation has the potential to exacerbate the presence and accumulation of, and the related risks associated with, pollutants of concern. Failing to timely submit the Annual Report to the Central Valley Water Board hinders the Board's ability to address noncompliance. Those circumstances present at least a minor potential for harm.

The deviation from requirements was determined to be major, as the requirement to submit the Annual Report has been rendered ineffective. The failure to submit the required technical report undermines the Central Valley Water Board's efforts to prevent water quality degradation and implement the regulatory protection measures detailed in the Reissued General Order.

Initial Liability

The failure to submit an annual report is an enforceable violation under Water Code section 13268(b)(1) by civil liability in an amount which shall not exceed one thousand dollars ($1,000) for each day in which the violation occurs. The Discharger failed to submit a 2013 Annual Report by 1 July 2014 as required by the Reissued General Order and the MRP, and is 253 days late as of the issuance date of this Complaint. A pre-filing settlement letter issued to the Discharger on 5 December 2014 establishes a total of 157 days in which the Discharger has been out of compliance for failure to submit the 2013 Annual Report, and is the basis for determining the recommended civil liability amount.

Step 4. Adjustment Factors

The Enforcement Policy allows for multi-day violations to be consolidated provided certain findings can be made. The Enforcement Policy also describes three factors related to the Discharger's conduct that should be considered for modification of the initial liability amount: the Discharger's culpability, the Discharger's efforts to clean up or cooperate with regulatory authorities after the violation, and the Discharger's history of violations. After each of these factors is considered for the violation alleged, the applicable factor should be multiplied by the proposed liability amount for the violation.

a) *Multiple Day Violations*

The Enforcement Policy provides that, for violations lasting more than 30 days, the Central Valley Water Board may adjust the per-day basis for civil liability if certain findings are made and provided that the adjusted per-day basis is no less than the per-day economic benefit, if any, resulting from the violation.

For these cases, the Central Valley Water Board must make express findings that the violation: (1) is not causing daily detrimental impacts to the environment or the regulatory program; or (2) results in no economic benefit from the illegal conduct that can be measured on a daily basis; or (3) occurred without the knowledge or control of the violator, who therefore did not take action to mitigate or eliminate the violation. If one of these findings is made, an alternate approach to penalty calculation for multiple day violations may be used.

Here, the Central Valley Water Board finds that the Discharger's failure to submit a 2013 Annual Report is not causing daily detrimental impacts to the environment or the regulatory program. There is no evidence that the Discharger's failure to submit a 2013 Annual Report has detrimentally impacted the environment on a daily basis, since obtaining regulatory coverage does not result in an immediate evaluation of, or changes in, practices that could be impacting water quality. There is no daily detrimental impact to the regulatory program because information that would have been provided by the Discharger pursuant to the regulatory requirements would have been provided on an intermittent, rather than daily basis.

Moreover, the Discharger's failure to submit a 2013 Annual Report results in no economic benefit that can be measured on a daily basis. Rather, the economic benefit here is associated with avoided costs of preparing and submitting a 2013 Annual Report.

Either of the above findings justifies use of the alternate approach to penalty calculation for multiple day violations. The alternate approach assesses daily penalties for the first day of violation, plus an assessment for each five-day period of violation until the 30th day, plus an assessment of one day for each thirty days of violation thereafter. Applying this assessment method on the total 157 violation days gives the Board the discretion to reduce the assessed penalty days to a minimum number of 11 days. However, because this approach generates a Total Base Liability Amount that is not a sufficient deterrent, and because the Discharger's unwillingness to comply with the Revised General Order undermines the Central Valley Water Board's ability to protect water quality through its regulatory program, the Prosecution Team has increased the number of days of violation above the Minimum Approach to a total number of 22 days of violation.

A calculation of initial liability totals $7,700 (0.35 per day factor X 22 adjusted days of violation X $1,000 per day penalty).

b) *Culpability*: 1.5

Discussion: The Discharger was assessed a score of 1.5, which increases the liability amount. The Discharger is responsible for failing to submit the annual report alleged herein. The requirement to submit a 2013 Annual Report was detailed in the Reissued General Order. Despite the fact that the Discharger received multiple notices regarding the requirements set forth in the Reissued General Order, the Discharger continues to fail to comply. Thus, the

Discharger had knowledge of the requirement to submit the Annual Report and failed to meet the reasonable standard of care in that regard. Given the fact that the Discharger has chosen to willfully violate the legal requirement, the maximum culpability score of 1.5 has been applied.

c) *Cleanup and Cooperation*: 1.5

Discussion: The Discharger was assessed a score of 1.5, which increases the liability amount. The Discharger was issued a Notice of Violation on 29 August 2014, which requested that the report be submitted as soon as possible to minimize liability. The Discharger was unresponsive to the NOV, and did not cooperate with the Water Board to come back into compliance. The violation of Water Code section 13268(a), alleged herein, is a non-discharge violation, and thus cleanup is not applicable.

d) *History of Violations*: 2

Discussion: The Discharger was assessed the score of 2, which increases the fine. The Central Valley Water Board adopted Administrative Civil Liability Order No. R5-2011-0068 on 13 October 2011 for the Discharger's failure to submit the 2009 Annual Report and the Waste Management Plan by the required deadlines, as required by the Reissued General Order and the MRP. In addition, the Central Valley Water Board adopted Administrative Civil Liability Order No. R5-2012-0070 on 2 August 2012 for the Discharger's failure to submit the 2010 Annual Report by the required deadline, as required by the Reissued General Order and the MRP. In addition, the Central Valley Water Board adopted Administrative Civil Liability Order No. R5-2013-0091 on 25 July 2013 for the Discharger's failure to submit the 2011 Annual Report by the required deadline and for failure to comply with a Water Code 13267 Order issued to the Discharger on 4 May 2012, as required by the Reissued General Order and the MRP. In addition, the Central Valley Water Board adopted Administrative Civil Liability Order No. R5-2014-0119 on 9 October 2014 for the Discharger's failure to submit the 2012 Annual Report by the required deadline, as required by the Reissued General Order and the MRP. The Enforcement Policy requires that a minimum multiplier of 1.1 be used when there is a history of repeat violations.

Step 5. Determination of Total Base Liability Amount

The Total Base Liability is determined by applying the adjustment factors from Step 4 to the Initial Liability Amount determined in Step 3.

a) *Total Base Liability Amount:* **$34,650** [Initial Liability ($7,700) x Adjustments (1.5)(1.5)(2)].

Step 6. Ability to Pay and Continue in Business

The Enforcement Policy provides that if the Central Valley Water Board has sufficient financial information to assess the violator's ability to pay the Total Base Liability, or to assess the effect of the Total Base Liability on the violator's ability to continue in business, then the Total Base Liability amount may be adjusted downward.

a) *Adjusted Total Base Liability Amount:* **$34,650**

Discussion: The Discharger has the ability to pay the total base liability amount based on 1) the Discharger owns the Dairy, a significant asset, and 2) the Discharger operates a dairy, an ongoing business that generates profits.

Without additional information provided by the Discharger, based on this initial assessment of information available in the public record, it appears the Discharger has the assets to pay the Total Base Liability. Based on the reasons discussed above, no reduction in liability is warranted.

Step 7. Other Factors as Justice May Require

a) *Adjusted Combined Total Base Liability Amount:* $34,650 + $0 (Staff Costs) = **$34,650.**

b) *Discussion:* No staff costs have been assessed as part of this enforcement action.

Step 8. Economic Benefit

a) *Estimated Economic Benefit:* **$964**

Discussion: The Discharger has received an economic benefit from the costs saved in not drafting and preparing the 2013 Annual Report. This is based on the current consulting costs of producing an Annual Report, including the cost of any and all samples required under the Reissued Dairy General Order ($964). The adjusted combined total base liability amount of $34,650 is more than the economic benefit amount ($964) plus ten percent as required by the Enforcement Policy.

Step 9. Maximum and Minimum Liability Amounts

a) *Minimum Liability Amount:* ***$1,060.40***

Discussion: The Enforcement Policy requires that the minimum liability amount imposed not fall below the economic benefit plus ten percent. As discussed above, the Central Valley Water Board Prosecution Team's estimate of the Discharger's economic benefit obtained from the alleged violation is $964. Therefore, the minimum liability amount is $1,060.40 [Economic Benefit ($964) x Adjustment (1.1)].

b) *Maximum Liability Amount:* ***$157,000***

Discussion: The maximum administrative liability amount is the maximum amount allowed by Water Code section 13367(b)(1): one thousand dollars ($1,000) for each day in which the violation occurs. Without the benefit of the alternative approach for calculating liability for multiday violations under the Enforcement Policy, the Discharger could face penalties for the total number of days in violation (157 total days X $1,000 per day).

The proposed liability falls within these maximum and minimum liability amounts.

Step 10. Final Liability Amount

Based on the foregoing analysis, and consistent with the Enforcement Policy, the final liability amount proposed for the failure to submit the 2013 Annual Report Is **$34,650**.

Password for Workbook Protection: **enforcement**

Instructions
1. Select Potential Harm for Discharge Violations
2. Select Characteristics of the Discharge
3. Select Susceptibility to Cleanup or Abatement
4. Select Deviation from Standard
5. Click "Determine Harm & per Gallon/Day..."
6. Enter Values into the Yellow highlighted fields

Select Item [redacted]
Select Item [redacted]
Select Item [redacted]
Select Item [redacted]

Discharger Name/ID: James G. & Amelia M. Sweeney/5D545155N01

ATTACHMENT B

			Violation 1	
Discharge Violations	**Step 1**	Potential Harm Factor (Generated from Button)	[redacted]	
	Step 2	Per Gallon Factor (Generated from Button)	[redacted]	
		Gallons		
		Statutory / Adjusted Max per Gallon ($)		
		Total		$ -
		Per Day Factor (Generated from Button)	[redacted]	
		Days		
		Statutory Max per Day		
		Total		$ -
Non-Discharge Violations	**Step 3**	Per Day Factor	0.35	
		Days	22	
		Statutory Max per Day	$ 1,000	
		Total		$ 7,700.00
		Initial Amount of the ACL		$ 7,700.00
Add'l Factors	**Step 4**	Culpability	1.5	$ 11,550.00
		Cleanup and Cooperation	1.5	$ 17,325.00
		History of Violations	2	$ 34,650.00
	Step 5	**Total Base Liability Amount**		$ **34,650.00**
	Step 6	Ability to Pay & to Continue in Business	1	$ 34,650.00
	Step 7	Other Factors as Justice May Require	1	$ 34,650.00
		Staff Costs*		$ 34,650.00
	Step 8	Economic Benefit	$ 964	$ **34,650.00**
	Step 9	Minimum Liability Amount	$1,060	
		Maximum Liability Amount	$ 157,000	
	Step 10	**Final Liability Amount**		$ **34,650.00**

Penalty Day Range Generator

Start Date of Violation= 7/2/14
End Date of Violation= 12/5/14

Maximum Days Fined (Steps 2 & 3) = 157 Days
Minimum Days Fined (Steps 2 & 3) = 11 Days

Robert M. Dowd*
Robert W. Gin*†
Randy L. Edwards
Jim D. Lee
Jeffrey L. Levinson*
Raymond L. Carlson
Ty N. Mizote*
Michael R. Johnson*
Mario U. Zamora*
Janae D. Lopes

*A Professional Corporation
†Of Counsel

GRISWOLD LASALLE
COBB DOWD & GIN LLP

Lyman D. Griswold
(1914-2000)

Michael E. LaSalle
(Retired)

Steven W. Cobb
(1947-1993)

ATTORNEYS
A California Limited Liability Partnership including Professional Corporations

111 E. SEVENTH STREET
HANFORD, CA 93230

Telephone: (559) 584-6656
www.griswoldlasalle.com

Direct Facsimile: (800) 947-1859
carlson@griswoldlasalle.com

April 30, 2015

CENTRAL VALLEY REGIONAL
WATER QUALITY CONTROL BOARD
11020 Sun Center Drive, Suite 200
Rancho Cordova, CA 95670

Advisory Team

Pamela Creedon, Executive Officer
11020 Sun Center Drive, Suite 200
Rancho Cordova, CA 95670
Phone: (916) 464-3291

Patrick Pulupa, Senior Staff Counsel
State Water Resources Control Board
Office of Chief Counsel
Physical Address:
1001 I Street, Sacramento, CA 95814
Mailing Address:
P.O. Box 100, Sacramento, CA 95812
Phone: (916) 3 41-5189; fax (916) 341-5199
patrick.pulupa@waterboards.ca.gov

Prosecution Team

Andrew Altevogt, Assistant Executive Officer
11020 Sun Center Drive, Suite 200
Rancho Cordova, CA 95670
Phone: (916) 464-3291

Clay Rodgers, Assistant Executive Officer
Doug Patteson, Supervising WRC Engineer
Dale Essary, Senior WRC Engineer
1685 E Street, Fresno, CA 93706
Phone: (559) 445-5093; fax: (559) 445-5910
dale.essary@waterboards.ca.gov

Naomi Kaplowitz, Staff Counsel
State Water Resources Control Board
Office of Enforcement
Physical Address: 1001 I Street, Sacramento, CA 95814
Mailing Address: P.O. Box 100, Sacramento, CA 95812
Telephone: (916) 322-3227
Facsimile: (916) 341-5896
naomi.kaplowitz@waterboards.ca.gov

RE: **SUBMISSION OF EVIDENCE AND POLICY STATEMENT REGARDING HEARING ON ADMINISTRATIVE CIVIL LIABILITY COMPLAINT R5-2015-0506**

To the Prosecution Team, Advisory Team and the Honorable Members of the Central Valley Regional Water Quality Control Board:

A. INTRODUCTION.

This office represents James G. Sweeney and Amelia M. Sweeney, who do business as Sweeney Dairy. Mr. and Mrs. Sweeney are referred to as the "Dischargers" under Administrative Civil Liability Complaint R5-2015-0505 (2015 Complaint).

The Sweeneys' address is 30712 Road 170, Visalia, CA 93292. Their telephone number is (559) 280-8233. Their email address is jimsweeneydairy@gmail.com. The Central Valley Regional Water Quality Control Board is referred to below as the "Regional Board" or the "Board." The State Water Resources Control Board is referred to as the "State Board."

The Sweeneys are accused of violating a Board order requiring them to submit an annual report. The Sweeneys are not accused of actually discharging,[1] or threatening to discharge, any waste to the waters of the State, or of discharging any waste under circumstances that could affect the quality of the waters of the State. The Sweeneys are accused of failure to submit a report called for under a Board order that is stayed until the Court's mandate is discharged in *Asociacion de Gente Unida por Agua, et al., v. Central Valley Regional Water* Quality Control *Board*, Sacramento County Superior Court Case No. 34-2008-00003604CU-WM-GDS. **See EXHIBITS A and B.** Under these circumstances the proposed liability prayed for in the 2015 Complaint cannot be imposed. The remedy for the Board is to obtain discharge of the writ.

B. STATEMENT OF FACTS AND BACKGROUND OF PRESENT PROCEEDING.

1. Mr. and Mrs. Sweeney operate a small dairy at 30712 Road 170, Visalia, CA. They milk around 260 cows on a site where a dairy has continuously operated for over eighty years.

2. The Regional Board's Order No. R5-2007-0035 (2007 Dairy Order or 2007 Order) ordered the Sweeneys, along with all other dairymen, to prepare and file Annual Reports with the Regional Board by July 1 of the year following the year to which the Reports applied, commencing with July 1, 2010.

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[1]The Porter-Cologne Water Quality Control Act of 1969 (the "Act"), Water Code §§ 13000 et seq., establishes the State Board and the nine Regional Boards, and sets forth their jurisdiction and competence. Section 13050 provides definitions of various terms used in the Act, but does not include a definition of the term "discharge." This lack of definition makes its use vague and ambiguous under the facts of this case, if not void for vagueness, where there is no evidence that the Sweeneys have "discharged" or threatened to "discharge" anything to the waters of the State. There is no showing or evidence that anything the Sweeneys have done, or have not done, has impaired the quality of waters of the State. This proceeding reverses the normal order of proof, and the assumption is that the Sweeneys are subject to liability, and they have to prove that they are not.

3. Because of their financial inability and other legal grounds, the Sweeneys asked the Regional Board for relief from the obligation to file the 2009 Annual Report due on July 1, 2010. But these requests were ignored by the Board. The Sweeneys did not file the Report due on July 1, 2010.

4. On May 5, 2011 an Administrative Civil Liability Complaint, R5-2011-0562, (2011 Complaint) was mailed to the Sweeneys for failing to file the 2009 Annual Report due on July 1, 2010. The 2011 Complaint sought to assess a civil liability against the Sweeneys in the amount of $11,400.00.

5. On July 1, 2011, the 2010 Annual Report became due, but the Sweeneys did not file it because they were still seeking a hearing before the Regional Board to obtain relief from having to file these Annual Reports.

6. The Sweeneys appeared at the hearing on the 2011 Complaint before the Regional Board on October 13, 2011. At the end of the hearing, the Regional Board voted to adopt Order No. R5-2011-0068, assessing an administrative civil liability of $11,400.00 on the Sweeneys for failing to file the Report due July 1, 2010.

7. On November 9, 2011, the Sweeneys appealed the Regional Board's October 13, 2011 decision by filing a Petition for Review with the State Board (A-2190). Said petition remains pending before the State Board.

8. On May 4, 2012, the Regional Board mailed the Sweeneys a "Groundwater Monitoring Directive," ordering the Sweeneys to install either (a) an individual groundwater monitoring well system at their dairy, or (b) join a representative monitoring program (RMP) that will monitor groundwater at a set of representative facilities. The attempt to force persons into a representative monitoring program, under threat of imposing the more onerous and expensive requirements of and individual groundwater monitoring program and individual waste discharge requirement violates the First Amendment rights of associational freedom and represents compelled speech. The fact that an operator can avoid the individual requirements by joining a RMP or coalition militates against the efficacy and legitimacy of the regulatory effort. If it were true that all dairies posed unacceptable threats to water quality they would all be subject to individual WDRs, constantly monitored and enforced.

9. On May 9, 2012, an Administrative Civil Liability Complaint, R5-2012-0542 (2012 Complaint), was mailed to the Sweeneys for failing to file the 2010 Annual Report due on July 1, 2011. The 2012 Complaint sought to assess a civil liability against the Sweeneys in the amount of $7,650.00.

10. On May 30, 2012, the Sweeneys filed a Petition for Review with the State Board appealing the Regional Board's adoption of the foregoing Groundwater Monitoring Directive. (A-2213) Said petition remains pending before the State Board.

11. The Regional Board held its hearing on the 2012 Complaint on August 2, 2012. At the end of the hearing, the Regional Board voted to adopt Order No. R5-2012-0070, assessing an administrative civil liability of $7,650.00 on the Sweeneys for failing to file the 2010 Annual Report due July 1, 2011.

12. On August 26, 2012, the Sweeneys appealed the Regional Board's August 2, 2012 decision, including its Order No. R5-2012-0070, by filing a Petition for Review with the State Board. (A-2225) Said petition remains pending before the State Board.

13. On November 6, 2012, the Court of Appeal for the Third Appellate District reversed the trial court's decision regarding a challenge to the 2007 Dairy Order, and remanded it back to the trial court.[2] On April 16, 2013, the Trial Court ordered the 2007 Dairy Order set aside.[3]

14. On May 9, 2013, an Administrative Civil Liability Complaint, R5-2013-0539 (2013 Complaint), was mailed to the Sweeneys for failing to file the 2011 Annual Report due July 1, 2012. The Complaint sought to assess a civil liability against the Sweeneys in the amount of $20,400.00.

15. On July 25, 2013, the Regional Board held a hearing on the 2013 Complaint. At the end of the hearing, the Regional Board voted to adopt Order No. R5-2013-0091, assessing a civil liability of $15,000.00 on the Sweeneys for failing to file the 2011 Annual Report due July 1, 2012.

16. On August 21, 2013, the Sweeneys appealed the Regional Board's July 25, 2013 decisions, including its Order No. R5-2013-0091, by filing a Petition for Review with the State Board. (A-2267). Said petition remains still pending before the State Board.

17. On October 29, 2013, the Sweeneys filed their petition under Water Code § 13320 challenging the Board's adoption of the 2013 Order, also known as the 2013 Reissued Order, No. R5-2013-0122, to the State Board. Said petition remains still pending before the State

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[2] *Asociacion de Gente Unida por el Agua, et al., v. Central Valley Regional Water Quality Control Board* (2012) 210 Cal. App. 4th 1255.

[3] *Asociacion de Gente Unida por Agua, et al., v. Central Valley Regional Water* Quality Control *Board*, Sacramento County Superior Court Case No. 34-2008-00003604CU-WM-GDS. See **EXHIBIT A hereto**.

Board. This appeal was filed prior to the petition filed November 3, 2013 by Petitioners in *Asociation de Gente Unita por el Agua.*

18. On July 17, 2014, an Administrative Civil Liability Complaint, R5-2014-0543 (2014 Complaint), was mailed to the Sweeneys for failing to file the 2012 Annual Report due July 1, 2013. The 2014 Complaint asked to assess a civil liability against the Sweeneys in the amount of $ 18,564.00.

19. On October 9, 2014, the Board adopted Administrative Liability Order R5-2014-0119 imposing administrative civil liability on the Sweeneys and fining them $18,564.00.

20. On November 7, 2014, the Sweeneys filed their Petition under California Water Code § 13320 for Review by the State Board of the Regional Board's action on Administrative Civil Liability Complaint No. R5-2014-0543 and adoption of Administrative Liability Order No. R5-2014-0119. (A-2338). Said petition remains still pending before the State Board.

21. On March 11, 2015, an Administrative Civil Liability Complaint, R5-2015-0506 (2015 Complaint), was mailed to the Sweeneys for failing to file the 2013 Annual Report due July 1, 2014. The 2015 Complaint seeks to assess a civil liability against the Sweeneys in the amount of $34,650.00.

22. As already stated, the Sweeneys' appeals of the decisions/orders taken by the Regional Board in connection with the 2011 Complaint, 2012 Complaint, 2013 Complaint, 2014 Complaint, and of the Groundwater Monitoring Directive (A-2213), are still pending before the State Board. The Sweeneys had been waiting the exhaustion of their appeal rights to determine whether the Regional Board's 2007 Order was lawful and enforceable. It is their position that if the completion of the appeal process concluded with a determination that they had no legal grounds upon which not to file the Annual Reports for 2010, 2011, 2012, and 2013, then they would file them. The Sweeneys should not be treated as responsible for the State Board sitting on these appeals without acting upon them. It is the State Board that is depriving the Sweeneys of a resolution of these issues and is denying the Sweeneys due process.

C. DOCUMENTS AND EVIDENCE.

The Sweeneys are required to identify and provide all documents and other evidence that they intend to use or rely upon at the hearing. At the present time they intend to use or rely upon the following, which they identify and submit by reference because they are already in the files and records or otherwise in possession of the Regional Board:

1. Regional Board's Report of Compliance Inspection for Sweeney Dairy, dated December 31, 1998.

2. Regional Board's Inspection Report letter for Sweeney Dairy, dated April 7, 2003.

3. Letter from the Regional Board to the Sweeneys, dated October 15, 2003, regarding their groundwater supply well test results:

Irrigation Well #1	Nitrate (NO3)	2.0 mg/L
Domestic Well	" "	3.2 mg/L

4. Certificate of Analysis from BSK Laboratories to the Sweeneys, dated November 6, 2007, regarding their groundwater supply well test results:

Irrigation Well #1	Nitrate (NO3)	1.1 mg/L
Irrigation Well #2	" "	1.2 mg/L
Domestic Well	" "	3.2 mg/L

5. Reports from FGL Environmental to the Sweeneys, dated July 14, 2010, regarding their groundwater supply well test results:

Irrigation Well #1	Nitrate (NO3)	1.1 mg/L
Irrigation Well #2	" "	.2 mg/L
Domestic Well	" "	1.4 mg/L

6. Dairy Inventory Worksheet, dated December 12, 2009, prepared by the Sweeneys for Farm Credit West.

7. Jim Sweeney's letter to the Regional Board, dated March 28, 2010.

8. Jim Sweeney's letter to the Regional Board, dated April 7, 2010.

9. Regional Board's letter to the Sweeneys, dated June 15, 2010.

10. Jim Sweeney's letter to the Regional Board, dated June 27, 2010.

11. Regional Board's Notice of Violation sent to the Sweeneys on August 16, 2010.

12. Jim Sweeney's letter to the Regional Board dated August 22, 2010.

13. Regional Board's letter to the Sweeneys from Clay Rodgers dated May 5, 2011, regarding Administrative Civil Liability Complaint R5-2011-0562.

14. Administrative Civil Liability Complaint, R5-20011-0562, (2012 Complaint) against James G. and Amelia M. Sweeney, dated May 5, 2011 (together with attachments, including hearing procedures).

15. Jim Sweeney's letter to the Regional Board, dated May 15, 2011.

16. Jim Sweeney's letter to the Regional Board, dated May 31, 2011.

17. Sweeneys' Written Testimony and Arguments to the Regional Board, dated July 8, 2011, regarding 2011 Complaint.

18. Transcript of July 14, 2011 hearing before the Hearing Panel regarding the 2011 Complaint.

19. Jim Sweeney's letter to Alex Mayer (Regional Board's legal counsel) dated September 5, 2011.

20. Email from Alex Mayer to Jim Sweeney, dated September 20, 2011.

21. Jim Sweeney's letter to Alex Mayer, dated September 21, 2011.

22. Email from Alex Mayer to Jim Sweeney, dated September 29, 2011

23. Second email from Alex Mayer to Jim Sweeney, dated September 29, 2011.

24. Jim Sweeney's letter to Alex Mayer, dated September 30, 2011.

25. Sweeneys' Written Testimony and Arguments to the Regional Board, dated October 2, 2011.

26. Transcript of hearing held on October 13, 2011, before the Regional Board regarding the 2011 Complaint.

27. Email from Ken Landau to Jim Sweeney, dated October 25, 2011.

28. Sweeneys' Petition for Review to the State Board regarding the Regional Board's decisions at the October 13, 2011, hearing on the 2011 Complaint.

29. Groundwater Monitoring Directive from the Regional Board to Sweeneys, dated May 4, 2012.

30. Letter from Douglas Patteson to Sweeneys, dated May 23, 2012.

31. Email from Clay Rodgers to Jim Sweeney, dated May 27, 2012.

32. Sweeneys' Petition for Review to the State Board, dated May 30, 2012, regarding the Groundwater Monitoring Directive.

33. Sweeneys' Written Testimony and Arguments to the Regional Board, dated July 20, 2012, regarding the 2012 Complaint.

34. Transcript of hearing held on August 2, 2012, before the Regional Board regarding the 2012 Complaint.

35. The Sweeneys' Petition for Review to State Board, dated August 26, 2012, regarding the Regional Board's decision at the August 2, 2012, hearing on the 2012 Complaint.

36. The Sweeneys' Written Testimony and Arguments to the Regional Board, dated July 6, 2013, regarding the 2013 Complaint.

37. The Sweeneys' Petition for Review to the State Board, dated August 21, 2013, regarding an appeal of the Regional Board's decision at the July 25, 2013, hearing on the 2013 Complaint.

38. Order No. R5-2007-0035, "Waste Discharge Requirements General Order for Existing Milk Cow Dairies," (2007 Dairy Order)

39. Order No. R5-2013- 0122, "Reissued Waste Discharge Requirements General Order for Existing Milk Cow Dairies." (2013 Dairy Order)

40. The Administrative Record of all Public Hearings and Public Input, upon which Order Nos. R5-2007-0035 and R5-2013- 0122 were based and adopted.

41. Water Quality Control Plan for the Tulare Lake Basin (2nd ed., 1995) and subsequent amendments thereto and editions.

42. State Board Resolution No. 68-16, "Statement of Policy with Respect to Maintaining High Quality of Waters in California."

43. Final Report of Brown, Vence & Associates, "Review of Animal Waste Management Regulations – Task 4 Report (November 2004)."

44. Study Findings, Recommendations, and Technical Report (Parts I & II) of the University of California Extension, entitled "Manure Waste Ponding and Field Application Rates" (March, 1973).

45. NRCS Guidelines for Water Treatment Lagoons, Natural Resources Conservation Service Conservation Practice Standards, Code 359 (July 2000). Please advise if your agency does not have a copy.

46. "Impact of Dairy Operations on Groundwater Quality," a research project conducted and a report prepared by the Lawrence Livermore National Laboratory in cooperation with the State Water Resources Control Board. The report was submitted to the State Board in August 2009. The Sweeneys believe this report is in the possession of the Regional Board, and if it is not, it is **attached as Exhibit F**.

47. "Fate and Transport of Waste Water Indicators: Results from Ambient Groundwater and from Groundwater Directly Influenced by Wastewater," a report prepared by the Lawrence Livermore National Laboratory in connection with the State Water Resources Control Board. The Sweeneys believe this report is in the possession of the Regional Board, and if it is not, it is **attached hereto as Exhibit G**.

48. Jorge Bacca's (Regional Board) reporting data by herd size for both 2007 and 2010.

[The documents listed as 49 through 53 below were attached as exhibits to the Sweeneys' Submission of Evidence and Policy Statement submitted to the Regional Board on June 19, 2012 in connection with ACLC R5-2012-0542]

49. California Dairy Herd Improvement Association (DHIA) dairy herd size and numbers, Central Valley, 2011. (As Exhibit 1)

50. San Francisco Bay Regional Water Quality Control Board Resolution No. R2-2003-0094. (As Exhibit 2)

51. San Francisco Bay Regional Water Quality Control Board, Annual Certification Reporting Form, Dairy Waiver Compliance Documentation (As Exhibit 3)

52. North Coast Regional Water Quality Control Board Order No. R1-2012-0002. (As Exhibit 4).

53. North Coast Regional Water Quality Control Board Order No. R1-2012-0003. (As Exhibit 5)

[The documents listed as 54 through 67 below were attached as exhibits to the Sweeneys Petition for Review to the State Board, dated May 30, 2012. A copy of the same was mailed to the Regional Board on the same date.]

54. Letter to the Sweeneys from Dale Essary, dated August 22, 2011 (As Exhibit 1).

55. Letter from the Sweeneys to Dale Essary, dated September 30, 2011 (As Exhibit 2).

56. Letter to the Sweeneys from Douglas Patteson, dated November 9, 2011 (As Exhibit 3).

57. Letter from the Sweeneys to Dale Essary, Douglas Patteson, and Clay Rodgers, dated November 29, 2011 (As Exhibit 4).

58. Letter to the Sweeneys from Douglas Patteson, dated December 7, 2011 (As Exhibit 5).

59. Letter from the Sweeneys to Douglas Patteson, Dale Essary, and Clay Rodgers, dated January 17, 2012 (As Exhibit 6).

60. Certified letter to the Sweeneys from the Regional Board (Groundwater Monitoring Directive) (Pamela C. Creedon) dated May 4, 2012 (As Exhibit 7).

61. Letter from the Sweeneys to Clay Rodgers, dated May 11, 2012 (As Exhibit 8).

62. Letter to the Sweeneys from Douglas Patteson, dated May 23, 2012 (As Exhibit 9).

63. Email from Clay Rodgers to the Sweeneys, dated May 27, 2012 (As Exhibit 10).

64. Webpage of Dairy Cares Central Valley Dairy Representative Monitoring Program and Fact Sheet (http://www.dairycares.com/CVDRMP) (As Exhibit 11).

65. Letter from the Sweeneys to Douglas Patteson and Dale Essary, dated May 29, 2012 (As Exhibit 12).

66. Email to the Sweeneys from J. P. Cativiela of the Central Valley Dairy Representative Monitoring Program, dated May 29, 2012 (As Exhibit 13).

67. Letter to the Sweeneys from Dale Essary, dated July 19, 2012.

68. Opinion dated November 6, 2012 of the Court of Appeal in *Asociacion de Gente Unida por el Agua, et al. v. Central Valley Regional Water Quality Control Board*, (2012) 210 Cal. App. 4th 1255.

69. Letter from the Sweeneys to the Regional Board, dated March 26, 2013.

70. Order granting Writ of Mandate filed April 17, 2013 in *Asociacion de Gente Unida por el Agua, et al. v. Central Valley Regional Water Quality Control Board*, dated April 16, 2013, Case No. 34-2008-00003604CU-WM-GDS. **[Attached hereto as Exhibit A]** This Order granted a writ of mandate against the Regional Board setting aside in its entirety the 2007 Order. See Court Order at ¶ 1, p. 2:3-17.

71. Letter to the Sweeneys from the Regional Board, dated April 19, 2013.

72. Letter from the Sweeneys to the Regional Board, dated August 26, 2013.

73. Order to Stay Proceedings filed November 6, 2014, in Case No. No. 34-2008-00003604CU-WM-GDS. **[Attached hereto as Exhibit B]**. In this Order the Court stayed all proceedings: "IT IS ORDERED that this case and its proceedings to determine the adequacy of the Regional Board's Return to Writ of Mandate [the 2013 Reissued Order] be stayed until such time as the State Board has issued a decision or an order of dismissal on the petition filed before the State Board by Petitioners, or until further order of this Court." Court Order at 3:13-16. The Regional Board's Return to Writ of Mandate was nothing less than the 2013 Reissued Order, formally known as "Order No. R5-2013-0122, Reissued Waste Discharge Requirements General Order for Existing Milk Cow Dairies." See Court Order at 2:1-2. The 2013 Reissued Order cannot be enforced since its validity is at issue under the Petition pending before the State Board filed on November 5, 2013 (and also the Sweeneys prior filed Petition challenging the 2013 Order).

[Document # 74 was attached as Exhibit A to the Sweeneys' Petition for Review to the State Board, dated August 21, 2013; also mailed to the Board on the same date.]

74. A peer-reviewed paper entitled, "When Does Nitrate Become a Risk for Humans?," authored by David S. Powlson, Tom M. Addicott, Nigel Benjamin, Kenneth G. Cassman, Theo M. de Kok, Hans van Grinsvin, Jean-Louis L'hirondel, Alex A. Avery and Chris Van Kessel, and published in the *Journal of Environmental Quality* 37:291-295 (2008). **[Attached hereto as Exhibit C]**

75. A peer-reviewed paper entitled, "Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations." The paper was prepared by Lawrence Livermore National Laboratory and the University of California, Davis, and was published in *Environmental Science and Technology,* 41:759-765 (2007). The Sweeneys sent the Regional Board a copy of this paper on October 29, 2013. **[Attached hereto as Exhibit D]**

76. "Water Quality Regulations for Dairy Operators in California's Central Valley–Overview and Cost Analysis," November 2010, prepared by California Department of Food and Agriculture. **[Attached hereto as Exhibit E]**

77. Letter from Brian Pacheco dated April 23, 2015. Mr. Pacheco is a member of the Fresno County Board of Supervisors. **[Attached hereto as Exhibit H]**

78. Letter from John van Curen dated April 24, 2015. **[Attached hereto as Exhibit I]**

79. Letter from Jim Sullins dated April 29, 2015. **[Attached hereto as Exhibit J]**

80. "Model for Sustainability," Hoard's Dairyman, April 10, 2015. **[Attached hereto as Exhibit K]**

81. "Two Major Dairy States Aren't Ag Friendly," Hoard's Dairyman, May 27, 2014. **[Attached hereto as Exhibit L]**

D. WITNESSES.

The Sweeneys may call the following witnesses.

1. Jim Sweeney. His arguments are set forth herein. He will take approximately 20 minutes.
2. Clay L. Rodgers. He may be called to admit the facts regarding the Dairy Cares RMP. It will take 5 minutes.
3. Dale E. Essary. The same as above.
4. Douglas K. Patteson. The same as above.

The Sweeneys reserve the right to cross-examine all witnesses called or disclosed by Board staff. The Sweeneys object to de facto testimony by attorneys and other non-designated witnesses.

The Sweeneys also reserve their right to use other evidence and witnesses not listed above who come to light during the course of continuing to develop their case. They will notify you when such evidence or witnesses become known.

E. LEGAL ARGUMENT AND ANALYSIS.

1. The 2007 Order is presently invalid and unenforceable because the Sacramento Superior Court ordered the Order set aside in its entirety on April 6, 2013 and stayed all proceedings involving both the 2007 and 2013 Orders on November 6, 2014.

The 2014 Complaint alleges in paragraph 8 "that the Court's decision did not affect the reporting requirements of the 2007 General Order . . . ." The Sweeneys disagree. As of July 1, 2014, the deadline specified by the 2007 Dairy Order for submission of the 2013 Annual Report to the Regional Board, the Trial Court had already ordered that the 2007 Order be set aside. The Trial Court's order was occasioned by the Third District Court of Appeal finding on November 6, 2012, that "The 2007 Order's monitoring plan upon which the order relies to enforce its no degradation directive is inadequate" because "there is not substantial evidence to support the findings."[4] Hence, many of the elements to be reported in the Annual Report were based upon a monitoring plan in the 2007 Order that the Appellate Court determined was flawed and unlawful.

However, suppose a court were to conclude that the April 6, 2013 order of the Trial Court to the Regional Board to set aside the 2007 Order did not have the effect of barring the Regional Board from seeking a civil liability assessment for the Sweeneys failure to file the 2012 and later Annual Reports required under said Order. In such event, the Sweeneys contend that the 2007 Order was still unlawful and unenforceable for all of the following reasons:

2. The 2007 Order and 2013 Order are unlawful and unenforceable against the Sweeneys because they failed to comply with applicable law, including provisions of the Water Code and Government Code.

(a) The need for the 2007 and 2013 Dairy Order was not supported by substantial evidence.

[4] *Asociacion*, p. 1287.

It is fundamental administrative law that no rule or regulation of a state agency is valid and enforceable unless the administrative record shows that it is supported by substantial evidence. The Appellate Court in the *Asociacion* case confirmed the applicability of the foregoing precept.[5] Part of the reason the Appellate Court overturned the Trial Court's original decision was because "the Regional Board must ensure that sufficient evidence is analyzed to support its decision [to adopt the 2007 Dairy Order] and that the evidence is summarized in an appropriate finding."[6] It went on to add that "An administrative agency abuses its discretion where its order is not supported by the findings or where the findings are not supported by the evidence. (citation).[7] It concluded that "The 2007 Order's monitoring plan upon which the order relies to enforce its no degradation directive is inadequate" because "there is not substantial evidence to support the findings."[8]

Mr. Sweeney reviewed all 34,000 pages of the administrative record of the hearings held in connection with the adoption of the 2007 Dairy Order. He found no substantial evidence in the administrative record – in fact, no evidence whatsoever – that supports the need to replace the pre-2007 Order reporting requirements with the new reporting requirements adopted in the 2007 Order.

The Sweeneys found no substantial evidence in the record that the data, reports and information that the Regional Board staff obtained from or about dairies **prior** to its adoption of the 2007 Order were inadequate, insufficient, unreliable or otherwise flawed. And they have found no substantial evidence in the record that claimed or demonstrated that the new reporting requirements were necessary or needed to replace the pre-2007 Order requirements. They have made this argument to the Regional Board in connection with the 2011, 2012, 2013 and 2014 Complaints. This argument stands unchallenged and uncontroverted because, in each instance, the Regional Board staff has failed to argue or show otherwise.

(b) The Regional Board did not show the need for the reports specified in the 2007 Order or 2013 Order and did not justify their burden, as required under Water Code section 13267 (b)(1).

The "Monitoring and Reporting Program" of the 2007 Order recites that it is issued pursuant to Water Code § 13267. (2007 Dairy Order, p. MRP-1) Section 13267(b)(1) states that "the regional board may require that any person who ... discharges ... waste within its region ... shall furnish, under penalty of perjury, technical or monitoring program reports which the regional board requires."

Section 13267 (b) (1) further provides that "The burden, including costs, of the reports shall bear a reasonable relationship to the need for the reports and the benefits to be obtained from the reports. In requiring these reports, the regional board shall provide the person with a written

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[5] Ibid, p. 1282.

[6] Ibid.

[7] Ibid.

[8] Ibid., p. 1287.

explanation with regard to the need for the reports, and shall identify the evidence that supports requiring that person to provide the reports."

The Regional Board failed to comply with section 13267 in that the 2007 Order and 2013 Reissued Order do not contain "a written explanation with regard for the need for the reports," and it fails to "identify the evidence that supports requiring [the Sweeneys and parties similarly situated] to provide the reports." In addition, the Regional Board never provided the Sweeneys with "a written explanation with regard for the need for the reports," and it did not "identify the evidence that supports requiring [the Sweeneys] to provide the reports."

Over the years, the Regional Board's staff visited the Sweeney dairy site to inspect and obtain information about it. For example, staff member Ken Jones visited their dairy in 2003 and spent one day gathering information. He measured and calculated the storage capacity of the three waste water lagoons and concluded that their storage capacity exceeded what the Regional Board required. In fact, it was 128% of what was required. He also concluded that the Sweeneys had sufficient crop land for application of waste water. The Sweeneys have his letter dated April 17, 2003, confirming that their dairy was in full compliance with all Regional Board requirements. The Sweeneys are prepared to submit evidence that their dairy has essentially the same number of animals, the same lagoon capacity and even more crop land now than the dairy had in 2003.

A dairy has been continuously operating on the site for over eighty years. The Regional Board required the Sweeneys to provide it with water supply well test results. Indeed, its 2007 Order orders dairymen, on page MRP-7, to "sample each domestic and agricultural supply well" and to submit the test results for Nitrate-nitrogen to it on an annual basis.

In accordance with the Regional Board's requests, the Sweeneys submitted test results from water samples taken from each of their supply wells in 2003, 2007 and 2010. The results ranged between .2 and 3.4 mg/L, all extremely low levels. All well results were and are substantially below the state's maximum contaminant levels (MCL); in fact, they are substantially lower.

The Sweeneys argued to the Regional Board staff that these test results are compelling evidence that their dairy was and is not adversely impacting ground water, and therefore the cost of filing these reports did not and do not, in the words of Section 13267, "bear a reasonable relationship to the need for the reports and the benefits to be obtained from the reports."

Despite the Regional Board's prior requests for supply well test results and despite the 2007 Order requiring them, the Board's staff brushed off these results by telling the Sweeneys that "Groundwater supply wells are typically screened in deeper aquifer zones ... groundwater quality data collected from the Dairy's on-site supply wells do not necessarily represent the quality of first encountered groundwater beneath the Dairy." If this was the case, why did the Regional Board require them?

(c) The 2007 Order and 2013 Order fail to implement the most modern and meaningful scientific findings and technologies.

Section 13263(e) of the Water Code provides that "any affected person may apply to the regional board to review and revise its waste discharge requirements. All requirements shall be reviewed periodically." If new and more cost effective ways can accomplish the same purpose, the above section imposes on the Regional Board a mandatory statutory duty to review such issues and revise its requirements accordingly. In fact, the Appellate Court in the *Asociacion* case confirmed that "the agency [the Regional Board] should consider current technologies and costs …." [9]

New and old research and advanced technologies presently exist which may provide less expensive means for evaluating groundwater contamination risk, of determining non-contamination of groundwater, and of using less expensive practices that can still prevent such contamination.

At various times in the past, the Sweeneys provided the Regional Board with relevant research papers to consider. For example, Lawrence Livermore National Laboratory published two papers in *Environmental Science and Technology* (2007) 41:753-765 **(Exhibit D hereto)**. The authors state they discovered that soil bacteria break down and eliminate nitrates in dairy waste water in a substantial if not complete degree. They also ascertained that there are certain compounds and gasses in manure water that can be used to determine whether water from dairy lagoons or from waste applied in irrigation water has infiltrated into first encountered groundwater. There are also simple and inexpensive ways to show the amount of highly compacted clay layers sitting beneath a dairy site and whether they constitute an impervious barrier between the dairy and the groundwater. Yet, the 2007 and 2013 Orders contain a "one-size-fits-all" approach, and generally require reports that provide little to no meaningful information. Indeed, some of these reports are questionable, to say the least. One example is that the Sweeneys were required to provide monthly photos of their lagoons to show that the water level was not too high during the month. This is as ineffectual as requiring a person to photograph his speedometer once each month to prove he didn't drive over the speed limit during the month.

The Sweeneys have read all 34,000 pages of the administrative record compiled after the adoption of the 2007 Dairy Order. They found no substantial evidence in the record that supports or justifies the need to regulate nitrates, considering the levels found in the groundwater of the Central Valley. Indeed, a peer-reviewed paper entitled "When Does Nitrate Become a Risk for Humans?" **(Exhibit C hereto)**, co-authored by nine scientists from the U.S., the UK, France, Germany and the Netherlands, and published in 2008 in the *Journal of Environmental Quality,* have evaluated all the old studies done about the health impacts of nitrates on humans and it suggests that nitrates at the levels found in groundwater are not the health threat once believed. The paper further suggests that perhaps the current nitrate limits should be significantly raised because the health risks may be overstated.

In short, the 2007 Order's reporting requirements are excessive, unnecessary, overly burdensome, primitive, antiquated, obsolete, and provide nothing of value, except fees paid to engineers, consultants and laboratories. The Regional Board did not sufficiently examine and consider recent research results and advanced testing technologies, and it did not modify its 2007 Order accordingly. The Sweeneys have made these arguments to the Regional Board during the hearings on the 2011 Complaint, the 2012 Complaint and on the 2013 Complaint. In each instance, these arguments were never challenged, disputed or rebutted by the Regional Board staff or their counsel.

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[9] Ibid., p. 1283.

(d) The 2007 and 2013 Orders failed to take into account economic considerations.

The 2007 Order's (and 2013 Order's) waste discharge requirements as they relate to water quality objectives must take into account economic considerations.[10] (Water Code §§ 13241 and 13263 (a).) The 2007 Order does not do so. It specifically fails to set or implement water quality objectives that are within the economic means of smaller dairies – operations that have to deal with disproportionately higher per cow reporting costs. Indeed, the Order fails to address the special economic circumstances of smaller dairies in any way whatsoever.

Small dairies are under much greater economic stress than larger, more efficient dairies and, therefore, are less able to handle the high costs of complying with the 2007 Order's reporting requirements.

The administrative record (AR) of the 2007 Order consists of 34,000 pages of documents and testimony. A great deal of testimony was presented concerning how expensive the new reporting requirements would be, and how especially unbearable it would be for smaller dairies. (See AR 002089, AR 000384, AR 000444, AR 007297, AR 02397, AR 019632, AR 002163, and AR 000583)

As an example of how the 2007 Order adversely affected smaller dairies, Dairy Cares of Sacramento estimated the average cost for a dairy to install their own individual monitoring well system to be $42,000.00, and thousands of dollars each year thereafter for ongoing sampling, testing and reporting. The cost of monitoring well programs, both the installation and the periodic reporting costs, are for the most part the same for large dairies as they are for small dairies. This means that the costs, on a per cow basis, are dramatically higher for small dairies, and contribute to small dairies being at a competitive disadvantage. Section 13241 of the Water Code requires the Regional Boards to take into account "economic considerations" in connection with its water quality objectives.

The AR contains no economic analysis or evidence that disputed the abundant testimony that the proposed 2007 Order would be harmful, even fatal, to smaller dairies.

The Sweeneys requested data from the Regional Board staff that would reveal the report filing compliance rate of dairies, broken down by herd size. In response to their request, Jorge Baca, from the Regional Board, provided the Sweeneys with data concerning the dairies dealt with by its Fresno office. But the compliance rate is not what is most meaningful in this data. Rather it is the rate of loss of dairies, by herd size, since the adoption of the 2007 Order.

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[10]Hoard's Dairyman reports that although American agriculture has among the lowest input of pesticide and fertilizer per acre compared to the EU and other countries, but California rates an "F" grade on the Agribusiness Friendliness Index of Colorado State University professors Greg Perry and James Pritchett. See Hoard's Dairyman, "Model for Sustainability," April 10, 2015; "Two Major Dairy States Aren't Ag Friendly," May 27, 2014. See **Exhibits K and L**, respectively.

This data shows the following with respect to the dairies that provided reports to the Fresno office:

Herd Size	**2007**	**2010**	**Attrition**
Less than 400 cows	56	30	-26 = 46% attrition
400 to 700 cows	92	62	-30 = 32% attrition
Over 700 cows	485	455	-30 = .6% attrition
Total	633	547	-86 = 13% overall attrition

In other words, only about half the number of smaller dairies filed reports in 2010 as compared to the number of smaller dairies that filed reports in 2007.

Not only are small dairies less able to deal with the high regulatory costs, they pose a dramatically smaller threat to groundwater quality. California DHIA data shows that DHIA dairies in the San Joaquin Valley of the Sweeneys size or smaller represent less than 1/10 of 1% (.09%) of all DHIA cows in the San Joaquin Valley.

Other agencies recognize these facts. Both the North Coast Regional Water Quality Control Board and the San Francisco Bay Regional Water Quality Control Board have recognized how smaller dairies have a much smaller impact on groundwater, and how they are less able to bear the same regulatory expenses and burdens that larger dairies can. These Regional Boards saw fit to adopt special performance and reporting relief for dairies under 700 cows (See Orders R1-2012-003 and R2-2003-0094, respectively).

In the case of the North Coast Region's Order R1-2012-0003, it declares that "this Order applies to dairies that pose a low or insignificant risk to surface water or groundwater." The Order goes on to say that "economics were considered, *as required by law,* during the development of these objectives," and "that a waiver of WDRs [waste discharge requirements] for a specific type of discharge is in the public best interest."

The relative number of cows on different sized dairies in different regions is instructive. In 2012, Mr. Sweeney gathered information showing[11] that 69.8% of the total cows in the North Coast Region reside on dairies which milk less than 700 cows; 8.2% of the cows in the Central Valley Region reside on dairies with less than 700 cows, and 2.5% of the cows in Tulare County reside on dairies with less than 700 cows. 24.2% of the North Coast Region cows are on dairies with less than 300 cows, .87% of the Central Region's cows are milked on dairies with less than 300 cows, and .27% of the cows in Tulare County reside on these same, small, less than 300 cow dairies. Thus under the North Coast Region's Order the majority of cows are on less than 700 cow dairies, and these may obtain a waiver from the local Order.

The San Francisco Bay Region requires smaller dairies to complete and file a two-page "Reporting Form" which does not require the involvement or expense of hiring engineers.

[11]Information received from Tulare Dairy Herd Improvement Association April 13, 2012; CDFA 2011 California DHIA Member Herd Data April 2012.

The EPA likewise uses a 700 cow threshold. 40 C.F.R. § 122.23 (b)(4) defines a large dairy as an operation that stables or confines as many as, or more than, 700 mature dairy cows, whether milked or dry, or 10,000 sheep or lambs. In addition, the San Joaquin Valley Air Pollution Control District exempts smaller dairies from many of its requirements.

Significantly, the Regional Board adopted such an approach when it adopted its Irrigated Lands Orders in 2013. It put smaller farms into a special category.

Despite all of the foregoing, the Regional Board has refused to adopt any waivers, or make any special provisions for, or grant any reporting relief to smaller dairies, and none appeared in its 2007 Order or in the 2013 Order (the "Reissued Order"). Its refusal not only violated the law, but it put smaller dairies in the Central Valley region at a greater competitive disadvantage with larger dairies in the Central Valley, and at a competitive disadvantage with small dairies in the North Coast and San Francisco Bay regions.

(e) The Regional Board has failed to show the "need" for the Sweeneys to install an individual groundwater monitoring system on their dairy site, or to join a Representative Monitoring Program.

1. The 2015 Complaint alleges in paragraph 12 that "The Discharger is alleged to have violated the following sections of the Reissued General Order [2013 Dairy Order] and of the MRP:

   A) Provision G. 3 of the Reissued General Order, which states:

   'The Discharger shall comply with the attached Monitoring and Reporting Program R5-2013-0122 which is part of this Order, and future revisions thereto, or with an individual monitoring and reporting program, . . . '"

Although the allegation is ambiguous, it appears that the 2015 Complaint is charging the Sweeneys with failure to either (1) install an individual groundwater monitoring well system on their dairy site, or (2) to join a "Representative Monitoring Program."

2. The Regional Board's staff first informed the Sweeneys by letter dated August 22, 2011 that they would need to either install their own individual groundwater monitoring system at their dairy, or they would have to join a representative monitoring program (RMP) that would monitor groundwater at a set of representative facilities. In a letter they sent to staff on September 30, 2011, they pointed out that Water Code § 13267 obligates a regional board to "provide a person with a written explanation with regard to the need for the reports," and that "these reports shall bear a reasonable relationship to the need for the reports." In order to determine the "need" for these groundwater monitoring well test reports, the Sweeneys wanted to ascertain how meaningful they needed to be in order for them to be acceptable. For this reason, they asked, "Where are their [Central Valley Representative Monitoring Program – CVRMP] monitoring wells located that would serve as the basis of information for the Sweeneys site?"

3. The Board's staff responded to the Sweeneys' letter by letter dated November 9, 2011, but the letter never answered the Sweeneys' question about the locations of the CVRMP groundwater wells. They had to ask again in a letter they sent Mr. Essary on November 29,

2011 as to the location of these CVRMP wells. Yet, the responding letter to the Sweeneys dated December 7, 2011, again failed to answer this very specific and direct question. They sent Clay Rodgers a letter, dated May 11, 2012, which again called to his attention the obligations imposed by section 13267. In reply, the Sweeneys were sent yet another letter, this one dated May 23, 2012, that again failed to provide them with the locations of the CVRMP groundwater wells.

4. On May 4, 2012, the Regional Board issued a Directive, ordering the Sweeneys to implement groundwater monitoring at their dairy. The Directive claimed that it had the authority under Water Code § 13267 and under the 2007 Dairy Order (R5-2007-0035) to require them to do so. This Directive was communicated to the Sweeneys by letter dated, May 23, 2012. One of the allegations of this Complaint is that they have violated this Directive and the 2007 Dairy Order by failing to install a groundwater monitoring system.

The relevant language of section 13267 of the Water Code reads: "the regional board may require that any person ... who ... discharges ... within its region ... shall furnish ... monitoring program reports which the regional board requires. The burden, including costs, shall bear a reasonable relationship for the need for the report and the benefits to be obtained from the reports. In requiring these reports, the regional board shall provide the person with a written explanation with regard to the need for the reports, and shall identify the evidence that supports requiring the person to provide the reports."

The Regional Board also cited the following language found on page MRP-16 of the 2007 Order: "Pursuant to Section 13267, the Executive Officer will order Dischargers to install monitoring wells to comply with Monitoring and Reporting Program Order No. R5-2007-0035 based on an evaluation of the threat to water quality *at each dairy*. It is anticipated that this will occur in phases of 100 to 200 dairies per year." See also provisions in 2013 Order at MRP-17 [Groundwater Monitoring] and MRP-18 Table 6 [Additional Groundwater Monitoring].

Both provisions indicate that the determination of whether to require a given dairy to provide monitoring well reports is to be made on a dairy-by-dairy, individual basis. Before a dairy can be required to implement a monitoring well program, the Regional Board must be aware of specific and compelling evidence that there is a need for such a costly program, and it must inform the dairyman of what specific evidence regarding his/her dairy supports the requiring of such reports.

Despite the foregoing, the Regional Board expressed the position in its May 23, 2012, letter that the foregoing language in the 2007 Order gave it the right to require *all dairies*, in phases of "100 to 200 dairies," to install monitoring well systems. Indeed, the letter states that the Regional Board has issued directives to 260 dairymen to implement monitoring well programs, and that 1000 dairies have already joined "Representative Monitoring Programs." This statement implies that *all dairies* in the Central Valley region either already participate or are being ordered to do so, without any effort being made by the Regional Board to evaluate each dairy individually. Thus, it appears that the Regional Board engaged in a direct violation of the plain language of section 13267 and the 2007 Order, and violated its statutory duties and obligations under applicable law.

Section 13263 of the Water Code provides that a Regional Board may prescribe requirements for dischargers, which it did in adopting the 2007 Order and the 2013 Order. However, section 13269 states that the Regional Board can waive any of these requirements, including the monitoring requirements, as it applies to "an individual" by considering "relevant factors."

The Sweeneys have consistently called to Board staff's attention that their dairy has been continuously operating on the same site for over 80 years. They pointed out to the Regional Board's staff that the nitrate-nitrogen test results from their domestic and agricultural supply wells, which they began submitting in 2003. The results have ranged between .2 and 3.4 mg/L, all extremely low levels. Yet, the Regional Board brushed off these results by stating that "Groundwater supply wells are typically screened in deeper aquifer zones … groundwater quality data collected from the Dairy's on-site supply wells do not necessarily represent the quality of first encountered groundwater beneath the Dairy."

The Regional Board made this groundless statement after demanding for ten years that the Sweeneys test their supply wells and send the Board the results. The Board had the audacity to reject the Sweeney test results despite the 2007 Order, on page MRP-7, actually ordering dairymen to "sample each domestic and agricultural supply well," and submit the laboratory analysis for nitrate-nitrogen to it on an annual basis. After demanding these costly reports for over ten years they now tell the Sweeneys that they are meaningless. This behavior is arbitrary and capricious.

To make matters worse, the Regional Board has been advising dairymen, including the Sweeneys, that as an alternative, they can join a "Representative Monitoring Program," and the results from monitoring wells that are not even close to a particular individual dairy can be submitted and these results will be treated as satisfying the monitoring well requirement.

Mr. Sweeney wrote Douglas Patteson on May 27, 2012, and asked him what representative monitoring program the Regional Board would accept for his dairy. Clay Rodgers emailed Mr. Sweeney the same day and advised him that the Central Valley Dairy Representative Monitoring Program (CVDRMP), administered by Dairy CARES in Sacramento, covered Tulare County and that it would be an acceptable RMP for his dairy. Mr. Sweeney checked with Dairy CARES/CVDRMP and was advised by email dated May 29, 2012 that it would accept his application to join the program. Mr. Sweeney also discovered that the nearest CVDRMP monitoring wells were about 45 miles from his dairy. And this was going to be treated by the Regional Board as meaningful information for the Sweeney dairy?

5. Mr. Essary sent the Sweeneys a letter dated July 19, 2012 reminding the Sweeneys of their need to install groundwater monitoring wells on their dairy or join an RMP. He threatened the Sweeneys with action if they did not comply, and he completely ignored their previous request for the locations of the RMP wells. The Sweeneys responded with a letter dated March, 26, 2013, in which they again asked for the location of the CVRMP groundwater wells. He sent the Sweeneys a letter dated April 19, 2013, which completely ignored their question, but warned the Sweeneys that the Regional Board would issue a Complaint against them if they did not install a monitoring well system on their dairy or join an RMP. The Sweeneys petitioned the State Board for review of the Groundwater Monitoring Directive. (A-2213). This matter remains pending before the State Board.

6. The Regional Board's inconsistent behavior undermines its position. On the one hand, it has demanded supply well test results for over ten years, then rejects them as meaningless. It then demands that the Sweeneys install monitoring wells on their dairy because these results would be more "meaningful." Then it says that if the Sweeneys (and 1200 other dairymen) join an RMP, whose closest monitoring wells are many miles from their dairy, this would be an acceptable substitute and would satisfy the Board's monitoring well requirements.

7. The way in which the Regional Board's staff continuously dodged answering the Sweeneys' requests for the location of the CVRMP monitoring wells would make anyone suspicious. The reason they refused to answer questions about the location of the CVRMP groundwater wells is transparent: because these RMP wells are so far removed from most dairies they provide no meaningful information about what is going on at the dairy in question. In other words, the RMP with Dairy CARES is a fraud and a sham. Most significantly, however, by accepting enrollment in an RMP as a substitute for an individual groundwater monitoring well system on a dairy (as they have for over 1200 dairies), the Regional Board has revealed that it does not have the "need" required under Water Code § 13267(b)(1) for individual groundwater monitoring wells on the dairy site itself.

F. THE ASSESSMENT ANALYSIS IS FLAWED AND IMPROPER, AND THE 2015 COMPLAINT IS IN EXCESS OF THE BOARD'S JURISDICTION, A DENIAL OF DUE PROCESS AND A VIOLATION OF THE SWEENEY'S CIVIL RIGHTS.

The Board staff is asking that the civil liability assessment in the 2015 Complaint be enhanced because this is the fourth year the Sweeneys have failed to file Annual Reports. Indeed, the Complaint sought an initial liability[12] of "at least" $12,012.00, then adjusted this amount it upward to $34,650.00 based upon the Sweeneys' failure to file the earlier Annual Reports required under the 2013 "Reissued" Order[13] and the now-invalidated 2007 Order.

The Board staff knows that the Sweeneys opposed the earlier Complaints (2011, 2012, 2013 and 2014) — as they have every right to do, and it knows that the Sweeneys have appealed each of the Board's decisions to the State Board – as they have every right to do – by filing Petitions for Review, a recourse expressly afforded the Sweeneys under Water Code § 13320. Yet the attempt is made to punish the Sweeneys for exercising their rights, by enhancing the monetary penalty on the basis of prior violations, not one of which has reached a final adjudication.

The Sweeneys were prepared to comply with these reporting requirements if, after they had exhausted the appeal remedies afforded them by law, the 2007 Order's provisions had been upheld

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[12]Letter to the Sweeneys from Dale Essary dated December 5, 2014, p. 2, regarding "Forthcoming Assessment of Civil Liability for Failure to Submit the Annual Report for 2013."

[13]At this point it is important to recall and recognize that the 2013 "Reissued Order" is stayed as a result of the Court's Order to Stay Proceedings filed November 6, 2014. This stay is in effect until "The State Board has issued a decision or an order of dismissal of the petition filed before the State Board by Petitioners, or until further order of this Court." See November 6, 2014 Order at 3:14-16. **SEE EXHIBIT B HERETO.** Also recognize the the 2013 "Reissued Order" was adopted by the Board and then proffered to the Court as the Board's Return on the Court's Writ of Mandate filed April 17, 2013. See November 6, 2014 Order at 1:23 to 2:2.

as lawful and enforceable. They commenced the appeal process with the expectation that the State Board would decide their Petitions for Review in a timely manner, in accord with due process. Yet, almost four years after filing their first appeal, all four of the prior appeals are still pending before the State Board.

It is improper to assign fault to the Sweeneys because of the State Board's inaction in deciding the merits of their appeals. The Regional Board should complain to the State Board for its inaction in these matters, rather than repeatedly trying to punish the Sweeneys for the continued inaction by the State Board. Indeed, the State Board's failure to discharge its affirmative statutory duty to decide these administrative appeals denies appellants like the Sweeneys not only the due process provided for under administrative law, but of access to the courts entirely.

It is important to recognize that in 2013 the Trial Court's order in the *Asociacion* case set aside the *entire* 2007 Order. The 2013 Order stayed all proceedings involving the 2014 Order, which purported to "replace" the 2007 Order. Therefore, the Board remains subject to the Court's writ mandate. Until the Board makes a satisfactory return on this writ, and the Court discharges the writ, it remains in effect and the Board may not engage in proceedings which purport to enforce and impose liability for alleged violations of either the 2007 Order of the 2014 Order. If one claims the Sweeneys derive a benefit from that state of affairs, that is the fault of the Board for not diligently working to make a return on the writ and to obtain a discharge of the writ.

G. FILING THE 2007 AND 2008 REPORTS DO NOT CONSTITUTE A WAIVER OF OBJECTIONS TO THE FILING OF THE 2010 AND FOLLOWING YEARS' ANNUAL REPORT MANDATED UNDER THE 2007 ORDER AND THE 2013 REISSUED ORDER.

Prosecution counsel has argued that when the Sweeneys filed their 2007 and 2008 reports, they waived their objection to the filing of the 2010 (and presumably later years') Annual Report. This is not true.

The information the Sweeneys submitted to the Regional Board on June 25, 2008 (2007 Report) and on June 26, 2009 (2008 Report) was herd size and nutrient management information, the very same information the Board has been requiring for many years prior to its adoption of the 2007 Order and 2013 Reissued Order. This information did not need to be developed or certified by a "registered professional" (engineer), and was not costly to produce. In sharp contrast, the 2007 Order and now the 2013 Reissued Order impose an entirely new category of expensive reports that had to be prepared by licensed engineers. These are the reports that were unnecessary, and which the Sweeneys, as small dairymen, could not afford and did not file. To repeat, the Regional Board acknowledged in its 2009 Order that these reports were very expensive, and because of that, postponed their filing deadline by one year. In light of this, it cannot be argued that what the Sweeneys filed in 2008 and 2009 waived their objections to the new burdens imposed by the 2007 Order and now, the 2013 Reissued Order.

H. THE REGIONAL BOARD'S ATTORNEYS ARE ENGAGED IN A PROHIBITED CONFLICT OF INTEREST WHICH COMPROMISES THE LEGITIMACY OF THESE ADMINISTRATIVE PROCEEDINGS.

The attorney advising the Advisory Team and the attorneys advising the Prosecuting Team are all employees of the State Water Resources Control Board. In addition, the State Board is the public agency to which the Sweeneys must appeal any adverse ruling by the Regional Board. Such a situation constitutes a clear conflict of interest. Under the State Bar's Rules of Professional Conduct, attorneys employed by the same public agency are treated the same as attorneys working for the same private law firm. The Rules proscribe attorneys from the same "firm" representing and advising adverse interests.[14] Here attorneys from the same "firm" are representing and advising the complaining party (Board staff), the court (the Board), and the appeals court (the State Board).

This alignment of counsel and court is common in continental inquisitorial procedure with origins in Roman and Civil Law. It is in sharp contrast to Anglo-American adversarial procedure where the Court is an "umpire" adjudicating competing interests. Such conflicts of interest must be fully disclosed to all parties and are not permitted unless all parties to the matter expressly waive the conflict. The Sweeneys have not had this conflict disclosed to them, and do not waive it.

I. CONCLUSION.

In view of all of the circumstances shown above, the 2015 Complaint is in excess of the Board's jurisdiction, and constitutes an abuse of power and denial of due process, equal protection, and violates the Sweeneys'[15] civil rights including their rights under the fifth, sixth and eighth amendments to the U.S. Constitution. The Regional Board is violating their civil rights by increasing their fines without their being able to appeal any previous rulings.

Very truly yours,

GRISWOLD, LaSALLE, COBB,
DOWD & GIN, L.L.P.

By: [signature]
RAYMOND L. CARLSON

LIST OF ATTACHED EXHIBITS

EXHIBIT A Order granting Writ of Mandate in Asociacion de Gente Unida por el Agua, et al. v. Central Valley Regional Water Quality Control Board, filed April 16, 2013, Sacramento County Superior Court Case No. 34-2008-00003604-CU-WM-GDS

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[14] California State Bar Rules of Professional Conduct, Rules 1-100, 3-310 and 3-320.

[15] The Sweeneys' bona fides are attested by the letters of reference attached as **EXHIBITS H-J** attached hereto.

EXHIBIT B Order to Stay Proceedings filed November 6, 2014 in Case No. No. 34-2008-34-2008-00003604CU-WM-GDS

EXHIBIT C "When Does Nitrate Become a Risk for Humans?," Journal of Environmental Quality 37:291-295 (2008)

EXHIBIT D "Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations," Environmental Science and Technology, 41:759-765 (2007)

EXHIBIT E "Water Quality Regulations for Dairy Operators in California's Central Valley–Overview and Cost Analysis," November 2010, prepared by California Department of Food and Agriculture

EXHIBIT F California GAMA Program: Impact of Dairy Operations on Groundwater Quality, dated August 8, 2006 (Draft); August 17, 2009 (Final)

EXHIBIT G California GAMA Program: Fate and Transport of Wastewater Indicators: Results from ambient Groundwater and from Groundwater Directly Influenced by Wastewater, dated June 2006

EXHIBIT H Letter from Brian Pacheco, dated April 23, 2015

EXHIBIT I Letter from John van Curen, dated April 24, 2015

EXHIBIT J Letter from Jim Sullins, dated April 29, 2015

EXHIBIT K "Model for Sustainability," Hoard's Dairyman, April 10, 2015

EXHIBIT L "Two Major Dairy States Aren't Ag Friendly," Hoard's Dairyman, May 27, 2014

PROOF OF SERVICE
CCP §§ 1011, 1013, 1013a; FRCP 5(b)

I am employed in the County of Kings, State of California. I am over the age of 18 years and not a party to the within action. My business address is 111 E. Seventh Street, Hanford, California 93230.

On April 30, 2015, I served the following document(s): SUBMISSION OF EVIDENCE AND POLICY STATEMENT REGARDING HEARING ON ADMINISTRATIVE CIVIL LIABILITY COMPLAINT R5-2015-0506 on the interested parties in this action by placing a true and correct copy thereof enclosed in a sealed envelope addressed as follows:

SEE ATTACHED SERVICE LIST

[] (By Mail) I deposited such envelope in the United States mail at Hanford, California. The envelope was mailed with postage thereon fully prepaid.

[X] (By Mail) As follows: I am "readily familiar" with the firm's practice of collection and processing correspondence for mailing. Under the practice it would be deposited with the U.S. Postal Service on the same day with postage thereon fully prepaid at Hanford, California, in the ordinary course of business.

[] (By Overnight Delivery) I deposited such envelope in the Federal Express/UPS Next Day Air/U.S. Mail Express Mail depository at Hanford, California. The envelope was sent with delivery charges thereon fully prepaid.

[] (By Personal Service) I caused such envelope to be hand delivered to the offices of the addressee(s) shown above.

[X] (By Electronic Mail) I caused such documents to be sent to the indicated recipients via electronic mail to the e-mail address(es) as stated herein.

[] (By Facsimile) I caused each document to be delivered by electronic facsimile to the offices listed above.

[X] (State) I declare under penalty of perjury, under the laws of the State of California, that the foregoing is true and correct.

[] (Federal) I declare that I am employed in the office of a member of the Bar of this Court at whose direction the service was made.

Executed on April 30, 2015, at Hanford, California.

Kate

KATIE ASKINS

SERVICE LIST
ADMINISTRATIVE CIVIL LIABILITY COMPLAINT R5-2015-0506

Central Valley Regional
Water Quality Control Board
11020 Sun Center Drive, Suite 200
Rancho Cordova, CA 95670

Advisory Team
Pamela Creedon, Executive Officer
Central Valley Regional
Water Quality Control Board
11020 Sun Center Drive, Suite 200
Rancho Cordova, CA 95670
Telephone: (916) 464-3291

Patrick Pulupa, Senior Staff Counsel
State Water Resources Control Board
Office of Chief Counsel
Physical Address:
1001 I Street
Sacramento, CA 95814
Mailing Address:
P.O. Box 100
Sacramento, CA 95812
Telephone: (916) 341-5189
Facsimile: (916) 341-5199
E-mail: patrick.pulupa@waterboards.ca.gov

Prosecution Team
Andrew Altevogt, Assistant Executive Officer
11020 Sun Center Drive, Suite 200
Rancho Cordova, CA 95670
Phone: (916) 464-3291

Clay Rodgers, Assistant Executive Officer
Central Valley Regional
Water Quality Control Board
1685 E Street
Fresno, CA 93706

Doug Patteson, Supervising WRC Engineer
Central Valley Regional
Water Quality Control Board
1685 E Street
Fresno, CA 93706

Dale Essary, Senior WRC Engineer
Central Valley Regional
Water Quality Control Board
1685 E Street
Fresno, CA 93706
Telephone: (559) 445-5093
Facsimile: (559) 445-5910
dale.essary@waterboards.ca.gov

Naomi Kaplowitz, Staff Counsel
State Water Resources Control Board
Office of Enforcement
Physical Address:
1001 I Street
Sacramento, CA 95814
Mailing Address:
P.O. Box 100
Sacramento, CA 95812

Telephone: (916) 322-3227
Facsimile: (916) 341-5896
E-mail: naomi.kaplowitz@waterboards.ca.gov

EXHIBIT LIST

EXHIBIT A	Order granting Writ of Mandate in Asociacion de Gente Unida por el Agua, et al. v. Central Valley Regional Water Quality Control Board, filed April 16, 2013, Sacramento County Superior Court Case No. 34-2008-00003604-CU-WM-GDS
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EXHIBIT L	"Two Major Dairy States Aren't Ag Friendly," Hoard's Dairyman, May 27, 2014

James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT “A”

D-29

FILED
ENDORSED

APR 17 2013

By FRANK TEMMERMAN
Deputy Clerk

SUPERIOR COURT OF THE STATE OF CALIFORNIA
IN AND FOR THE COUNTY OF SACRAMENTO

ASOCIACION DE GENTE UNIDA POR EL AGUA, a California unincorporated association, and ENVIRONMENTAL LAW FOUNDATION, a California nonprofit organization, Petitioners, v. CENTRAL VALLEY REGIONAL WATER QUALITY CONTROL BOARD, a California state agency, Respondent. COMMUNITY ALLIANCE FOR RESPONSIBLE ENVIRONMENTAL STEWARDSHIP, a California corporation, Intervenor	Case No. 34-2008-00003604-CU-WM-GDS (Related Case No. 2008-00003603-CU-WM-GDS) ~~[PROPOSED]~~ **WRIT OF MANDATE** Honorable Timothy M. Frawley Dept. 29 **BY FAX**

RECEIVED APR 11 2013 CIVIL 29

To Defendant/Respondent Central Valley Regional Water Quality Control Board:

YOU ARE HEREBY COMMANDED, under seal of this Court, to do the following:

1. Set aside the Waste Discharge Requirements General Order for Existing Milk Cow Diaries (Order No. R5-2007-0035) and reissue the permit only after application of, and compliance with, the State's anti-degradation policy (Resolution No. 68-16), as interpreted by the Court of Appeal in its opinion, including, without limitation, adequate findings that any allowed discharges to high quality water:

a. Will be consistent with maximum benefit to the people of the State;

b. Will not unreasonably affect present and anticipated beneficial use of the affected waters;

c. Will not result in water quality less than that prescribed in applicable water quality objectives; and

d. That waste-discharging activities will be required to use the best practicable treatment or control of the discharge necessary to assure that:

i. A pollution or nuisance will not occur, and

ii. The highest water quality consistent with the maximum benefit to the people of the State will be maintained.

2. The writ further commands Defendant/Respondent to make and file a Return within 180 days, setting forth what they have done to comply.

3. Plaintiffs/Petitioners shall recover their costs on appeal in the amount of $3,485.63, as reflected in the Notice of Amended Costs on Appeal, filed February 22, 2013.

4. The Court retains jurisdiction to consider any motions for an award of attorneys' fees.

IT IS SO ORDERED, ADJUDGED, AND DECREED.

Dated: April 17, 2013

Timothy M. Frawley
Judge of the Superior Court of California
County of Sacramento

APPROVED AS TO FORM:

Date: ______________

Laurel Firestone
Community Water Center
Attorney for Petitioners Asociacion De Gente Unida El Agua and Environmental Law Foundation

Date: ______________

Lynne Saxton
Saxton & Associates
Attorney for Petitioners Asociacion De Gente Unida El Agua and Environmental Law Foundation

Date: ______________

Teri Ashby
Office of the Attorney General of California
Attorney for Respondent Central Valley Regional Water Quality Control Board

Date: ______________

Theresa Dunham
Somach Simmons & Dunn
Attorney for Intervenor Community Alliance for Responsible Environmental Stewardship

IT IS SO ORDERED, ADJUDGED, AND DECREED.

Dated: ________________

Timothy M. Frawley
Judge of the Superior Court of California
County of Sacramento

APPROVED AS TO FORM:

Date: ________________

Laurel Firestone
Community Water Center
Attorney for Petitioners Asociacion De Gente Unida El Agua and Environmental Law Foundation

Date: 4/8/2013

Lynne Saxton
Saxton & Associates
Attorney for Petitioners Asociacion De Gente Unida El Agua and Environmental Law Foundation

Date: 4/9/13

Teri Ashby
Office of the Attorney General of California
Attorney for Respondent Central Valley Regional Water Quality Control Board

Date: ________________

Theresa Dunham
Somach Simmons & Dunn
Attorney for Intervenor Community Alliance for Responsible Environmental Stewardship

Exhibit A

SOMACH SIMMONS & DUNN
A PROFESSIONAL CORPORATION
ATTORNEYS AT LAW
500 CAPITOL MALL, SUITE 1000, SACRAMENTO, CA 95814
OFFICE: 916-446-7979 FAX: 916-446-8199
SOMACHLAW.COM

April 9, 2013

Via Email and First Class U.S. Mail

Lynne Saxton, Esq.
Saxton & Associates
912 Cole Street, Suite 140
San Francisco, CA 94117
lynne@saxtonlegal.com

Re: *Asociacion de Gente Unida Por El Agua, et al. v. Central Valley Regional Water Quality Control Bd.*, Sacramento Superior Court Case No. 34-2008-00003604-CU-WM-GDS [Proposed] Writ of Mandate

Dear Ms. Saxton:

Thank you for providing the [Proposed] Writ of Mandate in the aforementioned case as directed by the Judgment After Remittitur issued by the Honorable Timothy M. Frawley on March 27, 2013. Pursuant to our conversation this afternoon, please consider this letter in response to the [Proposed] Writ of Mandate.

In accordance with Rule 3.1312 of the California Rules of Court, and on behalf of my client Community Alliance for Responsible Environmental Stewardship, I hereby provide my approval of the [Proposed] Writ of Mandate with the understanding that the reference to "discharges to high quality water" on page 2, line 7, is intended to qualify each of the following sub-paragraphs, including paragraph d with respect to reference to "waste-discharging activities" that "will be required to use best practicable treatment or control."

With that understanding, my signature page is enclosed for the Court. If my understanding is not correct, please consider this letter to constitute our disapproval. In that case, our disapproval would be based on the fact that the [Proposed] Writ of Mandate would then be inconsistent with Resolution No. 68-16, the Third Appellate District's opinion, and the Judgment After Remittitur. All findings in this matter need to be with respect to high quality waters, including findings regarding waste-discharging activities that will be required to use best practicable treatment or control. The [Proposed] Writ of Mandate must reflect this accordingly.

Thank you for your consideration.

Very truly yours,

Theresa A. Dunham

Enc.

cc (*via email only*): Teri H. Ashby, Esq. (Teri.Ashby@doj.ca.gov)
Laurel Firestone, Esq. (laurel.firestone@communitywatercenter.org)
Lori Okun, Esq. (lokun@waterboards.ca.gov)
Patrick Pulupa, Esq. (ppulupa@waterboards.ca.gov)
James Wheaton, Esq. (wheaton@envirolaw.org)

TAD:cr

IT IS SO ORDERED, ADJUDGED, AND DECREED.

Dated: ____________________

Timothy M. Frawley
Judge of the Superior Court of California
County of Sacramento

APPROVED AS TO FORM:

Date: ____________________

Laurel Firestone
Community Water Center
Attorney for Petitioners Asociacion De Gente Unida El Agua and Environmental Law Foundation

Date: 4/8/2013

Lynne Saxton
Saxton & Associates
Attorney for Petitioners Asociacion De Gente Unida El Agua and Environmental Law Foundation

Date: ____________________

Teri Ashby
Office of the Attorney General of California
Attorney for Respondent Central Valley Regional Water Quality Control Board

Date: 4-9-13

Theresa Dunham
Somach Simmons & Dunn
Attorney for Intervenor Community Alliance for Responsible Environmental Stewardship

PROOF OF SERVICE

I, Nicole Feliciano, hereby declare:

I am over the age of 18 years and am not a party to this action. I am employed in the county of Alameda. My business address is Environmental Law Foundation, 1736 Franklin Street, Ninth Floor, Oakland, CA 94612.

On April 11, 2013, I caused to be served the attached:

[PROPOSED] WRIT OF MANDATE

X **BY MAIL.** I caused the above identified document(s) addressed to the party(ies) listed below to be deposited for collection at the Public Interest Law Offices or a certified United States Postal Service box following the regular practice for collection and processing of correspondence for mailing with the United States Postal Service. In the ordinary course of business, correspondence is deposited with the United States Postal Service on this day.

I declare under penalty of perjury, under the laws of the State of California, that the foregoing is true and correct, and that this Declaration was executed at Oakland, California on April 11, 2013.

[signature]

Nicole Feliciano
DECLARANT

Service List

Lynne Saxton Saxton & Associates 912 Cole Street, #140 San Francisco, California 94117 Telephone: (415) 317-6713 Email: lynne@saxtonlegal.com	*Attorney for Petitioners AGUA, ELF*
Teri H. Ashby Attorney General of California Office of the Attorney General 1300 "I" Street Sacramento, CA 95814-2919 Tel: (916) 327-4254 Fax: (916) 327-2319 teri.ashby@doj.ca.gov	*Attorney for Respondent California Regional Water Quality Control Board, Central Valley Region*
Thomas Freeman Eric E. Bronson Gary S. Lincenberg Bird, Marella, Boxer, Wolpert, Nessim, Drooks & Lincenberg, P.C. 1875 Century Park East, 23rd Floor Los Angeles, California 90067-2561 Tel: (310) 201-2100 Fax: (310) 201-2110 trf@birdmarella.com eb@birdmarella.com gsl@birdmarella.com	*Attorney for Intervenor CARES*
Theresa A. Dunham Somach Simmons & Dunn 500 Capitol Mall, Suite 1000 Sacramento, CA 95814 Telephone: (916) 446-7979 Facsimile: (916)446-8199 tdunham@somachlaw.com	*Attorney for Intervenor CARES*
Laurel Firestone (SBN 234236) Rose Francis (SBN 248521) COMMUNITY WATER CENTER 311 W. Murray Ave. Visalia, CA 93291 Tel: 559-733-0219 Fax: 559-733-8219 laurel.firestone@communitywatercenter.org rose.francis@communitywatercenter.org	*Attorneys for Petitioners AGUA*

James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT “B”

FILED
ENDORSED
NOV - 6 2014
By FRANK TEMMERMAN
Deputy Clerk

James Wheaton (State Bar No. 115230)
Nathaniel Kane (State Bar No. 279394)
Lowell Chow (State Bar No. 273856)
ENVIRONMENTAL LAW FOUNDATION
1736 Franklin Street, 9th Floor
Oakland, CA 94612
Tel: (510) 208-4555
Fax: (510) 208-4562
Email: wheaton@envirolaw.org, nkane@envirolaw.org, lchow@envirolaw.org

Attorneys for Petitioners Environmental Law Foundation and
Asociacion de Gente Unida por el Agua

Additional counsel on next page

SUPERIOR COURT OF THE STATE OF CALIFORNIA

IN AND FOR THE COUNTY OF SACRAMENTO

ASOCIACION DE GENTE UNIDA POR EL AGUA, a California unincorporated association, and ENVIRONMENTAL LAW FOUNDATION, a California nonprofit organization, Petitioners, v. CENTRAL VALLEY REGIONAL WATER QUALITY CONTROL BOARD, a California state agency, Respondent. COMMUNITY ALLIANCE FOR RESPONSIBLE ENVIRONMENTAL STEWARDSHIP, a California corporation, Intervenor	Case No. 2008-00003604-CU-WM-GDS (Related Case No. 2008-00003603-CU-WM-GDS) **[PROPOSED] ORDER TO STAY PROCEEDINGS** Hon. Timothy M. Frawley Dept. 29 BY FAX

Additional counsel:

Lynne R. Saxton (State Bar No. 226210)
SAXTON & ASSOCIATES
912 Cole Street, Ste. 140
San Francisco, CA 94117
Tel: (415) 317-6713
Email: lynne@saxtonlegal.com
Attorneys for Petitioners Environmental Law Foundation and
Asociacion de Gente Unida por el Agua

Laurel Firestone (State Bar No. 234236)
COMMUNITY WATER CENTER
909 12th Street, Suite 200
Sacramento, CA 95814
Tel. (559) 789-7245
Fax (916) 706-2731
E-mail: laurel.firestone@communitywatercenter.org
Attorney for Petitioner Asociacion de Gente Unida por el Agua

Phoebe Seaton (State Bar No. 238273)
LEADERSHIP COUNSEL FOR JUSTICE AND ACCOUNTABILITY
764 P Street, Suite 12
Fresno, CA 93721
Telephone: (559) 369-2790
Email: pseaton@leadershipcounsel.org
Attorney for Petitioner Asociacion de Gente Unida por el Agua

WHEREAS, on April 17, 2013, the Court issued a Writ of Mandate directing Respondent Central Valley Regional Water Quality Control Board ("Regional Board") to set aside its Waste Discharge Requirements General Order for Existing Milk Cow Dairies (Order No. R5-2007-0035) ("the Permit"), and

WHEREAS, the Writ of Mandate directed the Regional Board to reissue the Permit only after application of, and compliance with, the State's anti-degradation policy as interpreted by the Court of Appeal in its decision in *Asociacion de Gente Unida por el Agua v. Central Valley Regional Water Quality Control Board* (2012) 20 Cal.App.4th 1244, and

WHEREAS, the Court directed the Regional Board to reissue the permit only after including, without limitation, adequate findings that any allowed discharges to high quality water (1) will be consistent with the maximum benefit to the people of the State, (2) will not unreasonably affect present and anticipated beneficial use of the affected waters, (3) will not result in water quality less than that prescribed in applicable water quality objectives, (4) that waste-discharging activities will be required to use the best practicable treatment or control of the discharge necessary to assure that (a) a pollution or nuisance will not occur, and (b) the highest water quality consistent with the maximum benefit to the people of the State will be maintained, and

WHEREAS, the Writ of Mandate further commanded the Regional Board to file a Return within 180 days, and

WHEREAS, on October 3, 2013, the Regional Board rescinded the Permit and issued Order R5-2013-0122, Reissued Waste Discharge Requirements General Order For Existing Milk Cow Dairies ("General Order"), and

WHEREAS, on October 11, 2013, the Regional Board filed a Return to the Writ of Mandate indicating that it had rescinded the Permit and adopted the General Order, and

WHEREAS, on November 4, 2013, Petitioners Asociacion de Gente Unida por el Agua ("AGUA") and Environmental Law Foundation ("ELF") (collectively referred to hereafter as "Petitioners") filed a Response to the Return to the Writ of Mandate, contending that the General Order does not comply with the Writ of Mandate because it (1) allows continued degradation, pollution, and/or nuisance, (2) does not require Best Practical Treatment and Control for existing manure ponds, and (3) fails to conduct the required antidegradation analysis because it fails to analyze any of the costs—whether economic or social, both tangible and intangible—of degradation to the population at large, especially those in communities most impacted by degradation, pollution and nuisance, and instead focuses solely on cost savings to the regulated industry by not requiring measures to stop the pollution, and

WHEREAS, on November 5, 2013, Petitioners filed a petition to the State Water Resources Control Board ("State Board") under Water Code § 13320 and California Code of Regulations, title 23, §§ 2050-68 challenging the General Order as adopted by the Respondents, which included among other issues, the three issues raised above, and

WHEREAS, Petitioners' Response to the Return to the Writ of Mandate asked the Court to stay any further action on the Regional Board's return until the completion of administrative procedures before the State Board, and

WHEREAS, Petitioners stated that if the State Board corrected the perceived deficiencies, Petitioners would so inform the Court and the case could be terminated and further stated that if the State Board does not correct the perceived deficiencies in the General Order, the Petitioners would seek a further order from the Court, and

WHEREAS, on November 22, 2013, Intervenors Community Alliance for Responsible Environmental Stewardship ("CARES") filed a Reply to Petitioner's Response to the Return to the Writ of Mandate urging the Court to accept the Return and discharge the Writ, and

WHEREAS, on May 14, 2014, the Court issued a Case Management Order setting a Case Management Conference for October 10, 2014, and

WHEREAS, on October 10, 2014, the Court held a Case Management Conference in Department 29, having heard argument from all parties and good cause appearing,

IT IS ORDERED that this case and its proceedings to determine the adequacy of the Regional Board's Return to Writ of Mandate be stayed until such time as the State Board has issued a decision or an order of dismissal on the petition filed before the State Board by Petitioners, or until further order of this Court.

IT IS FURTHER ORDERED that Petitioners shall serve and file notice of the State Board's decision promptly after receipt, which filing shall lift the stay. The Court will set a further Case Management Conference thereafter.

Dated: Nov. 6, 2014

SO ORDERED:

Timothy M. Frawley

Hon. Timothy M. Frawley

Approved as to form:

Nathaniel H. Kane

Nathaniel Kane
Environmental Law Foundation
Attorneys for Petitioners Asociacion de Gente Unida por el Agua and Environmental Law Foundation

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Teri H. Ashby
Attorney General of California
Office of the Attorney General
Attorneys for Respondent California Regional Water Quality Control Board, Central Valley Region

---

Theresa A. Dunham
Somach Simmons & Dunn
Attorneys for Intervenor CARES

Approved as to form:

Nathaniel H. Kane

Nathaniel Kane
Environmental Law Foundation
Attorneys for Petitioners Asociacion de Gente Unida por el Agua and Environmental Law Foundation

Teri H. Ashby

Teri H. Ashby
Attorney General of California
Office of the Attorney General
Attorneys for Respondent California Regional Water Quality Control Board, Central Valley Region

---

Theresa A. Dunham
Somach Simmons & Dunn
Attorneys for Intervenor CARES

Approved as to form:

Nathaniel Kane
Environmental Law Foundation
Attorneys for Petitioners Asociacion de Gente Unida por el Agua and Environmental Law Foundation

Teri H. Ashby
Attorney General of California
Office of the Attorney General
Attorneys for Respondent California Regional Water Quality Control Board, Central Valley Region

Theresa A. Dunham
Somach Simmons & Dunn
Attorneys for Intervenor CARES

PROOF OF SERVICE

I, Nicole Feliciano, hereby declare:

I am over the age of 18 years and am not a party to this action. I am employed in the county of Alameda. My business address is 1736 Franklin Street, Ninth Floor, Oakland, CA 94612.

On November 3, 2014, I caused to be served the attached:

[PROPOSED] ORDER TO STAY PROCEEDINGS

__X__ **BY MAIL.** I caused the above identified document(s) addressed to the party(ies) listed below to be deposited for collection at the Public Interest Law Offices or a certified United States Postal Service box following the regular practice for collection and processing of correspondence for mailing with the United States Postal Service. In the ordinary course of business, correspondence is deposited with the United States Postal Service on this day.

I declare under penalty of perjury, under the laws of the State of California, that the foregoing is true and correct, and that this Declaration was executed at Oakland, California on November 3, 2014.

Nicole Feliciano
DECLARANT

Service List

Lynne Saxton Saxton & Associates 912 Cole Street, #140 San Francisco, California 94117 Telephone: (415) 317-6713 lynne@saxtonlegal.com	*Attorney for Petitioners AGUA, ELF*
Teri H. Ashby Attorney General of California Office of the Attorney General 1300 "I" Street Sacramento, CA 95814-2919 Tel: (916) 327-4254 Fax: (916) 327-2319 teri.ashby@doj.ca.gov	*Attorney for Respondent California Regional Water Quality Control Board, Central Valley Region*
Theresa A. Dunham Somach Simmons & Dunn 500 Capitol Mall, Suite 1000 Sacramento, CA 95814 Telephone: (916) 446-7979 Facsimile: (916)446-8199 tdunham@somachlaw.com	*Attorney for Intervenor CARES*
Laurel Firestone COMMUNITY WATER CENTER 909 12th Street, Suite 200 Sacramento, CA 95814 Tel. (559) 789-7245 Fax (916) 706-2731 laurel.firestone@communitywatercenter.org	*Attorney for Petitioners AGUA*
Phoebe Seaton Leadership Counsel for Justice and Accountability 764 P Street, Suite 12 Fresno, CA 93721 Telephone: (559) 369-2790 pseaton@leadershipcounsel.org	*Attorney for Petitioners AGUA*

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GORDON D SCHABER COURTHOUSE
SUPERIOR COURT
OF CALIFORNIA
SACRAMENTO COUNTY

James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT "C"

1-1-2008

When Does Nitrate Become a Risk for Humans?

David S. Powlson
Rothamsted Research

Tom M. Addiscott
Rothamsted Research

Nigel Benjamin
Derriford Hospital

Kenneth G. Cassman
University of Nebraska - Lincoln, kcassman1@unl.edu

Theo M. de Kok
University Maastricht

See next page for additional authors

Authors
David S. Powlson, Tom M. Addiscott, Nigel Benjamin, Kenneth G. Cassman, Theo M. de Kok, Hans van Grinsven, Jean-Louis L'hirondel, Alex A. Avery, and Chris Van Kessel

When Does Nitrate Become a Risk for Humans?

David S. Powlson and Tom M. Addiscott Rothamsted Research
Nigel Benjamin Derriford Hospital
Ken G. Cassman University of Nebraska
Theo M. de Kok University Maastricht
Hans van Grinsven Netherlands Environmental Assessment Agency
Jean-Louis L'hirondel Centre Hospitalier Universitaire de Caen
Alex A. Avery Hudson Institute
Chris van Kessel* University of California–Davis

Is nitrate harmful to humans? Are the current limits for nitrate concentration in drinking water justified by science? There is substantial disagreement among scientists over the interpretation of evidence on the issue. There are two main health issues: the linkage between nitrate and (i) infant methaemoglobinaemia, also known as blue baby syndrome, and (ii) cancers of the digestive tract. The evidence for nitrate as a cause of these serious diseases remains controversial. On one hand there is evidence that shows there is no clear association between nitrate in drinking water and the two main health issues with which it has been linked, and there is even evidence emerging of a possible benefit of nitrate in cardiovascular health. There is also evidence of nitrate intake giving protection against infections such as gastroenteritis. Some scientists suggest that there is sufficient evidence for increasing the permitted concentration of nitrate in drinking water without increasing risks to human health. However, subgroups within a population may be more susceptible than others to the adverse health effects of nitrate. Moreover, individuals with increased rates of endogenous formation of carcinogenic N-nitroso compounds are likely to be susceptible to the development of cancers in the digestive system. Given the lack of consensus, there is an urgent need for a comprehensive, independent study to determine whether the current nitrate limit for drinking water is scientifically justified or whether it could safely be raised.

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*Corresponding author (cvankessel@ucdavis.edu).
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677 S. Segoe Rd., Madison, WI 53711 USA

Is nitrate harmful to humans? Are the current limits for nitrate concentration in drinking water justified by science? These questions were addressed at a symposium on "The Nitrogen Cycle and Human Health" held at the annual meeting of the Soil Science Society of America (SSSA). Although they sound like old questions, it became clear there is still substantial disagreement among scientists over the interpretation of evidence on the issue—disagreement that has lasted for more than 50 years.

This article is based on the discussion at the SSSA meeting and subsequent email exchanges between some of the participants. It does not present a consensus view because some of the authors hold strongly divergent views, drawing different conclusions from the same data. Instead, it is an attempt to summarize, to a wider audience, some of the main published information and to highlight current thinking and the points of contention. The article concludes with some proposals for research and action. Because of the divergent views among the authors, each author does not necessarily agree with every statement in the article.

Present Regulatory Situation

In many countries there are strict limits on the permissible concentration of nitrate in drinking water and in many surface waters. The limit is 50 mg of nitrate L^{-1} in the EU and 44 mg L^{-1} in the USA (equivalent to 11.3 and 10 mg of nitrate-N L^{-1}, respectively). These limits are in accord with WHO recommendations established in 1970 and recently reviewed and reconfirmed (WHO, 2004). The limits were originally set on the basis of human health considerations, although environmental concerns, such as nutrient enrichment and eutrophication of surface waters, are now seen as being similarly relevant. It is the health

D.S. Powlson and T.M. Addiscott, Soil Science Dep., Rothamsted Research, Harpenden, Herts AL5 2JQ, United Kingdom; N. Benjamin, Derriford Hospital, Brest Rd, Derriford, Plymouth, PL6 5AA, United Kingdom; K.G. Cassman, Dep. of Agronomy and Horticulture, Univ. of Nebraska, Lincoln, NE, 68583 USA; T.M. de Kok, Dep. of Health Risk Analysis and Toxicology, University Maastricht, P.O. Box 616, 6200 MD the Netherlands; H. van Grinsven, Netherlands Environmental Assessment Agency, P.O. Box 303, 3720 AH Bilthoven, the Netherlands; J.-L. L'hirondel, Service de rhumatologie, Centre Hospitalier Universitaire de Caen, 14033 Caen Cedex, France; A.A. Avery, Center for Global Food Issues, Hudson Inst., PO Box 202, Churchville, VA 24421 USA; C. van Kessel, Dep. of Plant Sciences, Univ. of California, Davis, CA, 95616 USA.

issues that are the main cause of disagreement; the contrasting views are set out in the following two sections.

Nitrate and Health

There are two main health issues: the linkage between nitrate and (i) infant methaemoglobinaemia, also known as blue baby syndrome, and (ii) cancers of the digestive tract. The evidence for nitrate as a cause of these serious diseases remains controversial and is considered below.

An Over-Stated Problem?

The link between nitrate and the occurrence of methaemoglobinaemia was based on studies conducted in the 1940s in the midwest of the USA. In part, these studies related the incidence of methaemoglobinaemia in babies to nitrate concentrations in rural well water used for making up formula milk replacement. Comly (1945), who first investigated what he called "well-water methaemoglobinaemia," found that the wells that provided water for bottle feeding infants contained bacteria as well as nitrate. He also noted that "In every one of the instances in which cyanosis (the clinical symptom of methaemoglobinaemia) developed in infants, the wells were situated near barnyards and pit privies." There was an absence of methaemoglobinaemia when formula milk replacements were made with tap water. Re-evaluation of these original studies indicate that cases of methaemoglobinaemia always occurred when wells were contaminated with human or animal excrement and that the well water contained appreciable numbers of bacteria and high concentrations of nitrate (Avery, 1999). This strongly suggests that methaemoglobinaemia, induced by well water, resulted from the presence of bacteria in the water rather than nitrate per se. A recent interpretation of these early studies is that gastroenteritis resulting from bacteria in the well water stimulated nitric oxide production in the gut and that this reacted with oxyhaemoglobin in blood, converting it into methaemoglobin (Addiscott, 2005).

The nearest equivalent to a present-day toxicological test of nitrate on infants was made by Cornblath and Hartmann (1948). These authors administered oral doses of 175 to 700 mg of nitrate per day to infants and older people. None of the doses to infants caused the proportion of heamoglobin converted to methaemoglobin to exceed 7.5%, strongly suggesting that nitrate alone did not cause methaemoglobinaemia. Furthermore, Hegesh and Shiloah (1982) reported another common cause of infant methaemoglobinaemia: an increase in the endogenous production of nitric oxide due to infective enteritis. This strongly suggests that many early cases of infant methaemoglobinaemia attributed at that time to nitrate in well water were in fact caused by gastroenteritis. Many scientists now interpret the available data as evidence that the condition is caused by the presence of bacteria rather than nitrate (Addiscott, 2005; L'hirondel and L'hirondel, 2002). The report of the American Public Health Association (APHA, 1950) formed the main basis of the current recommended 50 mg L^{-1} nitrate limit, but even the authors of the report recognized that it was compromised by unsatisfactory data and methodological bias. For example, in many cases, samples of water from wells were only taken for nitrate analysis many months after the occurrence of infant methaemoglobinaemia.

About 50 epidemiological studies have been made since 1973 testing the link between nitrate and stomach cancer incidence and mortality in humans, including Forman et al. (1985) and National Academy of Sciences (1981). The Chief Medical Officer in Britain (Acheson, 1985), the Scientific Committee for Food in Europe (European Union, 1995), and the Subcommittee on Nitrate and Nitrite in Drinking Water in the USA (NRC, 1995) all concluded that no convincing link between nitrate and stomach cancer incidence and mortality had been established.

A study reported by Al-Dabbagh et al. (1986) compared incidence of cancers between workers in a factory manufacturing nitrate fertilizer (and exposed to a high intake of nitrate through dust) and workers in the locality with comparable jobs but without the exposure to nitrate. There was no significant difference in cancer incidence between the two groups.

Based on the above findings showing no clear association between nitrate in drinking water and the two main health issues with which it has been linked, some scientists suggest that there is now sufficient evidence for increasing the permitted concentration of nitrate in drinking water without increasing risks to human health (L'hirondel et al., 2006; Addiscott, 2005).

Space does not permit here to discuss other concerns expressed about dietary nitrate, such as risk to mother and fetus, genotoxicity, congenital malfunction, enlarged thryroid gland, early onset of hypertension, altered neurophysiological function, and increased incidence of diabetes. For differing views of other possible health concerns, see L'hirondel and L'hirondel (2002) and Ward et al. (2006).

Nitrate is made in the human body (Green et al., 1981), the rate of production being influenced by factors such as exercise (Allen et al., 2005). In recent years it has been shown that body cells produce nitric oxide from the amino acid L-arginine and that this production is vital to maintain normal blood circulation (Richardson et al., 2002) and protection from infection (Benjamin, 2000). Nitric oxide is rapidly oxidized to form nitrate, which is conserved by the kidneys and concentrated in the saliva. Nitrate can also be chemically reduced to nitric oxide in the stomach, where it can aid in the destruction of swallowed pathogens that can cause gastroenteritis.

Evidence is emerging of a possible benefit of nitrate in cardiovascular health. For example, the coronaries of rats provided water for 18 mo that contained sodium nitrate became thinner and more dilated that the coronaries of the rats in the control group (Shuval and Gruener, 1977). Nitrate levels in water showed a negative correlation coefficient with the standardized mortality ratio for all cardiovascular diseases (Pocock et al., 1980). In healthy young volunteers, a short-term increase in dietary nitrate reduced diastolic blood pressure (Larsen et al., 2006). Based on these data, one could hypothesize that nitrate might also play a role in the cardiovascular health benefit of vegetable consumption (many vegetables contain high concentrations of nitrate) (Lundberg et al., 2004).

The Need for Caution

Although there is little doubt that normal physiological levels of nitric oxide play a functional role in vascular endothelial function and the defense against infections (Dykhuizen et al., 1996), chronic exposure to nitric oxide as a result of chronic inflammation has also been implicated, though not unequivocally identified, as a critical factor to explain the association between inflammation and cancer (Sawa and Oshima, 2006; Dincer et al., 2007; Kawanishi et al., 2006). Nitric oxide and NO-synthase are known to be involved in cancer-related events (angiogenesis, apoptosis, cell cycle, invasion, and metastasis) and are linked to increased oxidative stress and DNA damage (Ying and Hofseth, 2007). Rather than nitrate, the presence of numerous classes of antioxidants is generally accepted as the explanation for the beneficial health effects of vegetable consumption (Nishino et al., 2005; Potter and Steinmetz, 1996).

A recent review of the literature suggests that certain subgroups within a population may be more susceptible than others to the adverse health effects of nitrate (Ward et al., 2005). Although there is evidence showing the carcinogenity of N-nitroso compounds in animals, data obtained from studies that were focused on humans are not definitive, with the exception of the tobacco-specific nitrosamines (Grosse et al., 2006). The formation of N-nitroso compounds in the stomach has been connected with drinking water nitrate, and excretion of N-nitroso compounds by humans has been associated with nitrate intake at the acceptable daily intake level through drinking water (Vermeer et al., 1998). The metabolism of nitrate and nitrite, the formation of N-nitroso compounds, and the development of cancers in the digestive system are complex processes mediated by several factors. Individuals with increased rates of endogenous formation of carcinogenic N-nitroso compounds are likely to be susceptible. Known factors altering susceptibility to the development of cancers in the digestive system are inflammatory bowel diseases, high red meat consumption, amine-rich diets, smoking, and dietary intake of inhibitors of endogenous nitrosation (e.g., polyphenols and vitamin C) (de Kok et al., 2005; De Roos et al., 2003; Vermeer et al., 1998). In 1995, when the Subcommittee on Nitrate and Nitrate in Drinking Water reported that the evidence to link nitrate to gastric cancer was rather weak (NRC, 1995), the stomach was still thought to be the most relevant site for endogenous nitrosation. Previous studies, such as those reviewed in the NRC (1995) report, which found no link between nitrate and stomach cancer, concentrated on the formation of nitrosamines in the stomach. Recent work indicates that larger amounts of N-nitroso compounds can be formed in the large intestine (Cross et al., 2003; De Kok et al., 2005).

Some scientists argue that there are plausible explanations for the apparent contradictive absence of adverse health effects of nitrate from dietary sources (Van Grinsven et al., 2006; Ward et al., 2006). Individuals with increased rates of endogenous formation of carcinogenic N-nitroso compounds are more likely to be at risk, and such susceptible subpopulations should be taken into account when trying to make a risk-benefit analysis for the intake of nitrate. In view of these complex dose-response mechanisms, it can be argued that it is not surprising that ecological and cohort studies (e.g., Van Loon et al., 1998) in general do not provide statistically significant evidence for an association between nitrate intake and gastric, colon, or rectum cancers. The experimental design of most of these studies may not have been adequate to allow for the determination of such a relationship.

Population studies have the problem that factors influencing health tend to be confounded with each other. This necessitates molecular epidemiological studies aimed at improving methods for assessing exposure in susceptible subgroups. This approach requires the development of biomarkers that enable the quantification of individual levels of endogenous nitrosation and N-nitroso compounds exposure and methods for accurate quantification of exposure-mediating factors.

Nitrate, Food Security, and the Environment

It is beyond dispute that levels of nitrate and other N-containing species have increased in many parts of the ecosystem due to increased use of fertilizers and combustion of fossil fuels. At present, 2 to 3% of the population in USA and the EU are potentially exposed to public or private drinking water exceeding the present WHO (and USA and EU) standard for nitrate in drinking water. The proportion of the exposed population in the emerging and developing economies is probably larger and increasing (Van Grinsven et al., 2006).

The environmental impacts of reactive N compounds are serious, and continued research on agricultural systems is essential to devise management practices that decrease losses and improve the utilization efficiency of N throughout the food chain. At the same time, the central role of N in world agriculture must be considered. Agriculture without N fertilizer is not an option if the 6.5 billion people currently in the world and the 9 billion expected by 2050 are to be fed (Cassman et al., 2003). Losses of reactive N compounds to the environment are not restricted to fertilizers: losses from manures and the residues from legumes can also be large (Addiscott, 2005). Research indicates that simply mandating a reduction in N fertilizer application rates does not automatically reduce N losses because there is typically a poor relationship between the amount of N fertilizer applied by farmers and the N uptake efficiency by the crops (Cassman et al., 2002; Goulding et al., 2000). Instead, an integrated systems management approach is needed to better match the amount and timing of N fertilizer application to the actual crop N demand in time and space. Such an approach would lead to decreased losses of reactive N to the environment without decreasing crop yields. Many of the potential conflicts between the agricultural need for N and the environmental problems caused by too much in the wrong place are being studied within the International Nitrogen Initiative (INI; http://initrogen.org/), a networking activity sponsored by several international bodies.

The adverse environmental impact of reactive N species (i.e., all N-containing molecules other than the relatively inert N_2 gas that comprises 78% of the atmosphere) deserves attention. Some of these molecules, such as nitrogen oxides, come from combustion of fossil fuels in automobiles and power plants. Agriculture, however, is the dominant source through the cultivation of N_2–fixing crops and the manufacture and use of N fertilizers (Turner and Rabalais, 2003). Both have increased greatly over the last few decades, and the trend is set to continue (Galloway et al., 2003; 2004). The subsequent N enrichment causes changes to terrestrial and aquatic ecosystems and to the environmental services they provide. Examples include nitrate runoff to rivers causing excessive growth of algae and associated anoxia in coastal and estuarine waters (James et al., 2005; Rabalais et al., 2001) and deposition of N-containing species from the atmosphere causing acidification of soils and waters and N enrichment to forests and grassland savannahs (Goulding et al., 1998). All of these impacts can radically change the diversity and numbers of plant and animal species in these ecosystems. Other impacts almost certainly have indirect health effects, such as nitrous oxide production, which contributes to the greenhouse effect and the destruction of the ozone layer, thereby allowing additional UV radiation to penetrate to ground level with the associated implications for the prevalence of skin cancers.

Losses of nitrate to drinking water resources are also associated with leaky sewage systems. Leaky sewage systems need to be improved for general hygiene considerations. This need is especially important in developing countries and poor rural areas that do not have well developed sewage and waste disposal infrastructure.

Returning Question

In considering the management of nitrogen in agriculture and its fate in the wider environment, the debate keeps returning to the original question: "Is nitrate in drinking water really a threat to health?" Interpretations of the evidence remain very different (L'hirondel et al., 2006; Ward et al., 2006). The answer has a significant economic impact. The current limits established for ground and surface waters require considerable changes in practice by water suppliers and farmers in many parts of the world, and these changes have associated costs. If nitrate in drinking water is not a hazard to health, could the current limit be relaxed, perhaps to 100 mg L^{-1}? The relaxation could be restricted to situations where the predominant drainage is to groundwater. Such a change would allow environmental considerations to take precedence in the case of surface waters where eutrophication is the main risk, and N limits could be set to avoid damage to ecosystem structure and function. Phosphate is often the main factor limiting algal growth and eutrophication in rivers and freshwater lakes, so a change in the nitrate limit would focus attention on phosphate and its management—correctly so in the view of many environmental scientists (Sharpley et al., 1994). It is possible that a limitation on phosphate might lead to even lower nitrate limits in some freshwater aquatic environments to restore the diversity of submerged plant life (James et al., 2005). It could be argued that setting different limits, determined by health or environmental considerations as appropriate, is a logical response to the scientific evidence.

Given the criticisms of the scientific foundation of present drinking water standards and the associated cost-benefits of prevention or removal of nitrate in drinking water, we propose the need to consider the following issues in discussing an adjustment of the nitrate standards for drinking water:

- Nitrogen intake by humans has increased via drinking water and eating food such as vegetables.
- There is circumstantial and often indirect evidence of the enhanced risk of cancers of the digestive system after an increase in the concentration of nitrate in drinking water. There is an urgent need to synthesize existing data and understanding, or to carry out additional research if necessary, to reach clear and widely accepted conclusions on the magnitude of the risk. This will require greater collaboration between scientists who hold opposing views over the interpretation of currently available data. The possibility that subgroups within the population respond differently requires quantification and critical examination.
- Nitrogen oxides have a functional role in normal human physiology, but they are also involved in the induction of oxidative stress and DNA damage. The challenge is to quantify and evaluate these risks and benefits of nitric oxide exposure in relation to the intake of nitrate in drinking water. If humans have a mechanism to combat infectious disease with nitric oxide, produced from nitrate consumed in drinking water and food, what are the long-term effects of the nitric oxide benefits compared with the potential negative health effects from higher intake of nitrate?
- If the evaluation of potential adverse health effects from chronic exposure to nitrate levels in drinking water above 50 mg L^{-1} demonstrates that these adverse effects can be considered minor compared with other issues of health loss associated with air pollution or life style, would the removal of nitrate from drinking water to meet the current allowable concentration standards be cost-efficient relative to other potential investments in health improvement?

Although science may not provide society with unequivocal conclusions about the relationship between drinking water nitrate and health over the short term, there are good reasons to further explore the issue (Ward et al., 2005). Unfortunately, it remains difficult to predict the health risks associated with chronic nitrate consumption from water that exceeds the current WHO drinking water standard. One complication is the endogenous production of nitrate, which makes it more difficult than previously realized to relate health to nitrate intake in water or food.

Practical management strategies to overcome inefficient use of nitrogen by crops and to minimize losses of nitrate and other N-containing compounds to the environment have to be developed for agricultural systems worldwide.

Given the lack of consensus, there is an urgent need for a comprehensive, independent study to determine whether the current nitrate limit for drinking water is scientifically justified or whether it could safely be raised. Meta-analyses are valuable tools for generating conclusions about specific chronic health effects (e.g., stomach cancer, colon cancer, bladder cancer, specific reproductive outcomes). Unfortunately, the number of suitable studies for any particular health effect is likely too small to be detected by meta-analyses (Van Grinsven et al., 2006). Empirical studies focused on susceptible subgroups, development of biomarkers for demonstration of endogenous nitrosation, and methods for accurate quantification of mediating factors may provide part of the answers. Moreover, there is also a separate need for determining water quality standards for environmental integrity of aquatic ecosystems. It is time to end 50 yr of uncertainty and move forward in a timely fashion toward science-based standards.

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James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT "D"

Environ. Sci. Technol. **2007**, *41*, 759–765

Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations

M. J. SINGLETON,*,† B. K. ESSER,† J. E. MORAN,† G. B. HUDSON,† W. W. MCNAB,‡ AND T. HARTER§

Chemical Sciences Division, Lawrence Livermore National Laboratory, Environmental Restoration Division, Lawrence Livermore National Laboratory, and Department of Land, Air, and Water Resources, University of California at Davis

We present results from field studies at two central California dairies that demonstrate the prevalence of saturated-zone denitrification in shallow groundwater with $^3H/^3He$ apparent ages of <35 years. Concentrated animal feeding operations are suspected to be major contributors of nitrate to groundwater, but saturated zone denitrification could mitigate their impact to groundwater quality. Denitrification is identified and quantified using N and O stable isotope compositions of nitrate coupled with measurements of excess N_2 and residual NO_3^- concentrations. Nitrate in dairy groundwater from this study has $\delta^{15}N$ values (4.3–61‰), and $\delta^{18}O$ values (−4.5–24.5‰) that plot with $\delta^{18}O/\delta^{15}N$ slopes of 0.47–0.66, consistent with denitrification. Noble gas mass spectrometry is used to quantify recharge temperature and excess air content. Dissolved N_2 is found at concentrations well above those expected for equilibrium with air or incorporation of excess air, consistent with reduction of nitrate to N_2. Fractionation factors for nitrogen and oxygen isotopes in nitrate appear to be highly variable at a dairy site where denitrification is found in a laterally extensive anoxic zone 5 m below the water table, and at a second dairy site where denitrification occurs near the water table and is strongly influenced by localized lagoon seepage.

Introduction

High concentrations of nitrate, a cause of methemoglobinemia in infants (*1*), are a national problem in the United States (*2*), and nearly 10% of public drinking water wells in the state of California are polluted with nitrate at concentrations above the maximum contaminant level (MCL) for drinking water set by the U.S. Environmental Protection Agency (*3*). The federal MCL is 10 mg/L as N, equivalent to the California EPA limit of 45 mg/L as NO_3^- (all nitrate concentrations are hereafter given as NO_3^-). In the agricultural areas of California's Central Valley, it is not uncommon to have nearly half the active drinking water wells produce groundwater with nitrate concentrations in the range considered to indicate anthropogenic impact (>13–18 mg/L) (*2, 4*). The major sources of this nitrate are septic discharge, fertilization using natural (e.g., manure) or synthetic nitrogen sources, and concentrated animal feeding operations. Dairies are the largest concentrated animal operations in California, with a total heard size of 1.7 million milking cows (*5*).

Denitrification is the microbially mediated reduction of nitrate to gaseous N_2, and can occur in both unsaturated soils and below the water table where the presence of NO_3^-, denitrifying bacteria, low O_2 concentrations, and electron donor availability exist. In the unsaturated zone, denitrification is recognized as an important process in manure and fertilizer management (*6*). Although a number of field studies have shown the impact of denitrification in the saturated zone (e.g., *7, 8–11*), prior to this study it was not known whether saturated zone denitrification could mitigate the impact of nitrate loading at dairy operations. The combined use of tracers of denitrification and groundwater dating allows us to distinguish between nitrate dilution and denitrification, and to detect the presence of pre-modern water at two dairy operations in the Central Valley of California, referred to here as the Kings County Dairy (KCD) and the Merced County Dairy (MCD; Figure 1). Detailed descriptions of the hydrogeologic settings and dairy operations at each site are included as Supporting Information.

Materials and Methods

Concentrations and Nitrate Isotopic Compositions. Samples for nitrate N and O isotopic compositions were filtered in the field to 0.45 μm and stored cold and dark until analysis. Anion and cation concentrations were determined by ion chromatography using a Dionex DX-600. Field measurements of dissolved oxygen and oxidation reduction potential (using Ag/AgCl with 3.33 mol/L KCl as the reference electrode) were carried out using a Horiba U-22 water quality analyzer. The nitrogen and oxygen isotopic compositions ($\delta^{15}N$ and $\delta^{18}O$) of nitrate in 23 groundwater samples from KCD and MCD were measured at Lawrence Berkeley National Laboratory's Center for Isotope Geochemistry using a version of the denitrifying bacteria procedure (*12*) as described in Singleton et al. (*13*). In addition, the nitrate from 17 samples was extracted by ion exchange procedure of (*14*) and analyzed for $\delta^{15}N$ at the University of Waterloo. Analytical uncertainty (1σ) is 0.3‰ for $\delta^{15}N$ of nitrate and 0.5‰ for $\delta^{18}O$ of nitrate. Isotopic compositions of oxygen in water were determined on a VG Prism isotope ratio mass spectrometer at Lawrence Livermore National Laboratory (LLNL) using the CO_2 equilibration method (*15*), and have an analytical uncertainty of 0.1‰.

Membrane Inlet Mass Spectrometry. Previous studies have used gas chromatography and/or mass spectrometry to measure dissolved N_2 gas in groundwater samples (*16–19*). Dissolved concentrations of N_2 and Ar for this study were analyzed by membrane inlet mass spectrometry (MIMS), which allows for precise and fast determination of dissolved gas concentrations in water samples without a separate extraction step, as described in Kana et al. (*20, 21*). The gas abundances are calibrated using water equilibrated with air under known conditions of temperature, altitude, and humidity (typically 18 °C, 183 m; and 100% relative humidity). A small isobaric interference from CO_2 at mass 28 (N_2) is corrected based on calibration with CO_2-rich waters with known dissolved N_2, but is negligible for most samples. Samples are collected for MIMS analysis in 40 mL amber

* Corresponding author address: P.O. Box 808, L-231, Livermore, California, 94550; phone: (925) 424-2022; fax: (925) 422-3160; e-mail: singleton20@llnl.gov.

† Chemical Sciences Division, Lawrence Livermore National Laboratory.

‡ Environmental Restoration Division, Lawrence Livermore National Laboratory.

§ University of California at Davis.

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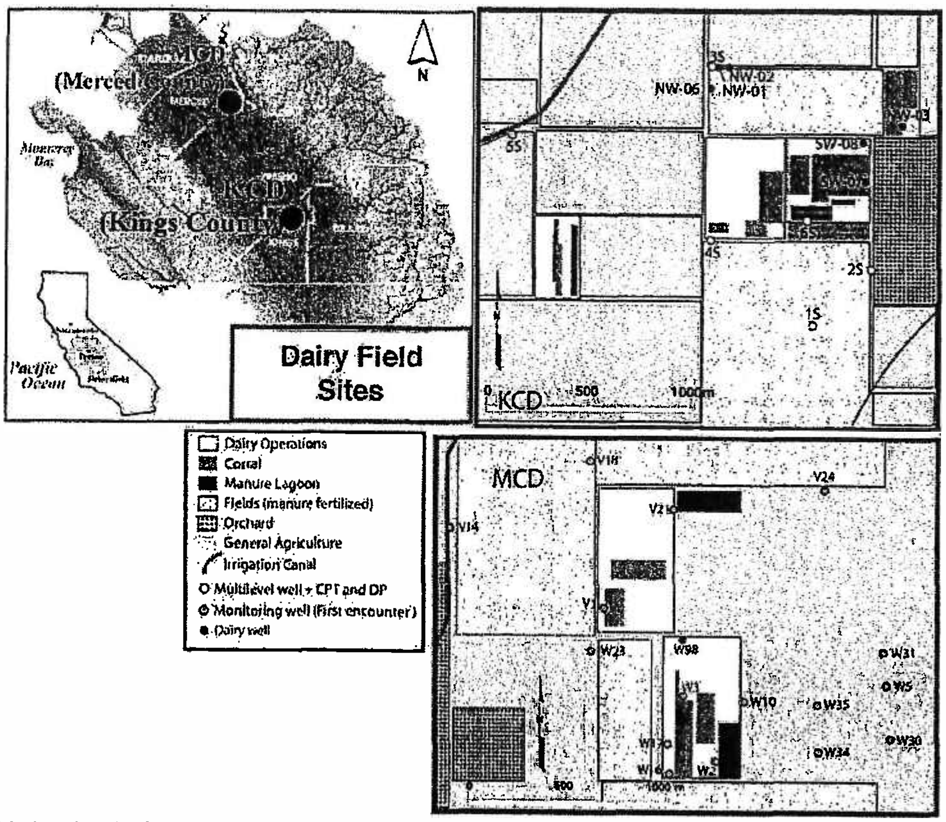

FIGURE 1. Location of dairy study sites, and generalized maps of each dairy showing sample locations relative to lagoons and dairy operations.

glass VOA vials with no headspace that are kept cold during transport, and then analyzed within 24 h.

Noble Gases and $^3H/^3He$ Dating. Dissolved noble gas samples are collected in copper tubes, which are filled without bubbles and sealed with a cold weld in the field. Dissolved noble gas concentrations were measured at LLNL after gas extraction on a vacuum manifold and cryogenic separation of the noble gases. Concentrations of He, Ne, Ar, and Xe were measured on a quadrupole mass spectrometer. The ratio of ^3He to ^4He was measured on a VG5400 mass spectrometer. Calculations of excess air and recharge temperature from Ne and Xe measurements are described in detail in Ekwurzel (*22*), using an approach similar to that of Aeschbach-Hertig et al. (*23*).

Tritium samples were collected in 1 L glass bottles. Tritium was determined by measuring ^3He accumulation after vacuum degassing each sample and allowing 3–4 weeks accumulation time. After correcting for sources of ^3He not related to ^3H decay (*24, 25*), the measurement of both tritium and its daughter product ^3He allows calculation of the initial tritium present at the time of recharge, and apparent ages can be determined from the following relationship based on the production of tritiogenic helium ($^3He_{trit}$):

$$\text{Groundwater Apparent Age (years)} = -17.8 \times \ln(1 + {}^3He_{trit}/{}^3H)$$

Groundwater age dating has been applied in several studies of basin-wide flow and transport (*25–27*). The reported groundwater age is the mean age of the mixed sample, and furthermore, is only the age of the portion of the water that contains measurable tritium. Average analytical error for the age determinations is ±1 year, and samples with ^3H that is too low for accurate age determination (<1 pCi/L) are reported as >50 years. Significant loss of ^3He from groundwater is not likely in this setting given the relatively short residence times and high infiltration rates from irrigation. Apparent ages give the mean residence time of the fraction of recently recharged water in a sample, and are especially useful for comparing relative ages of water from different locations at each site. The absolute mean age of groundwater may be obscured by mixing along flow paths due to heterogeneity in the sediments (*28*).

Results and Discussion

Nitrate in Dairy Groundwater. Nitrate concentrations at KCD range from below detection limit (BDL, <0.07 mg/L) to 274 mg/L. Within the upper aquifer, there is a sharp boundary between high nitrate waters near the surface and deeper, low nitrate waters. Nitrate concentrations are highest between 6 and 13 m below ground surface (BGS) at all multilevel wells (0.5 m screened intervals), with an average concentration of 98 mg/L. Groundwater below 15 m has low nitrate concentrations ranging from BDL to 2.8 mg/L, and also has low or nondetectable ammonium concentrations. The transition from high to low nitrate concentration corresponds to decreases in field-measured oxidation–reduction potential (ORP) and dissolved oxygen (DO) concentration. ORP values are generally above 0 mV and DO concentrations are >1 mg/L in the upper 12 m of the aquifer, defining a more oxidizing zone (Figure 2). A reducing zone is indicated below

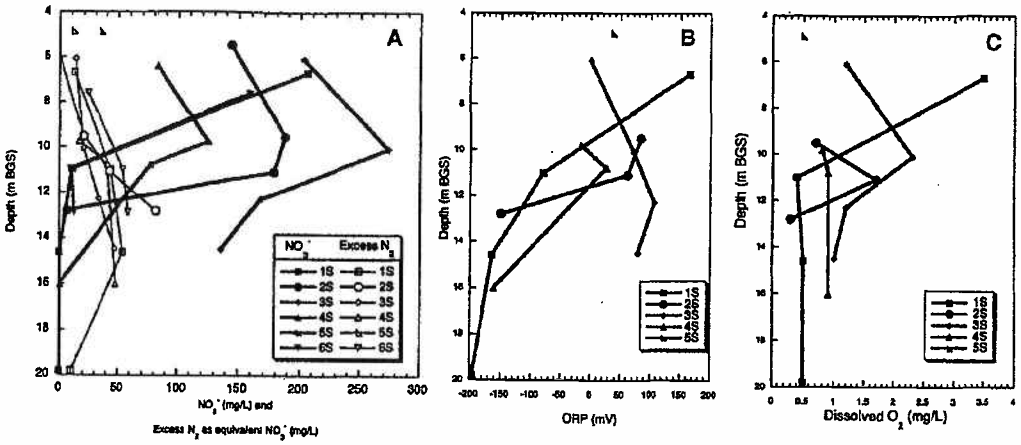

FIGURE 2. (A) Average excess N_2 and nitrate concentrations, (B) oxidation–reduction potential (ORP), and (C) dissolved oxygen in multilevel monitoring wells at the KCD site.

12 m by ORP values as low as −196 mV and DO concentrations <1.2 mg/L. Vertical head varies by less than 10 cm in the upper aquifer multilevel wells.

Nitrate concentrations at MCD monitoring wells sampled for this study range from 2 to 426 mg/L with an average of 230 mg/L. Several wells (W-02, W-16, and W-17) located next to a lagoon and corral have lower nitrate but high ammonium concentrations (Table 1 in Supporting Information). The MCD wells are all screened at the top of the unconfined aquifer except W98, a supply well that is pumped from approximately 57 m BGS. Nitrate concentrations observed for this deeper well are <1 mg/L.

Dissolved Gases. Nitrogen gas, the comparatively conservative product of denitrification, has been used as a natural tracer to detect denitrification in the subsurface (*16–18*). Groundwater often also contains N_2 beyond equilibrium concentrations due to incorporation of excess air from physical processes at the water table interface (*23, 29, 30*). In the saturated zone, total dissolved N_2 is a sum of these three sources:

$$(N_2)_{dissolved} = (N_2)_{equilibrium} + (N_2)_{excess\ air} + (N_2)_{denitrification}$$

By normalizing the measured dissolved concentrations as N_2/Ar ratios, the amount of excess N_2 from denitrification can be calculated as

$$(N_2)_{denitrification} = \left(\left(\frac{N_2}{Ar}\right)_{measured} - \left(\frac{N_{2equilibrium} + N_{2excess\ air}}{Ar_{equilibrium} + Ar_{excess\ air}}\right)\right) Ar_{measured}$$

where the N_2 and Ar terms for equilibrium are calculated from equilibrium concentrations determined by gas solubility. The N_2/Ar ratio is relatively insensitive to recharge temperature, but the incorporation of excess air must be constrained in order to determine whether denitrification has shifted the ratio to higher values (*19*). Calculations of excess N_2 based on the N_2/Ar ratio assume that any excess air entrapped during recharge has the ratio of N_2/Ar in the atmosphere (83.5). Any partial dissolution of air bubbles would lower the N_2/Ar ratio (*30, 31*), thus decreasing the apparent amount of excess N_2.

For this study, Xe and Ne derived recharge temperature and excess air content were determined for 12 of the monitoring wells at KCD and 9 wells at MCD. For these sites, excess N_2 can be calculated directly, accounting for the contribution of excess air and recharge temperature. Site representative mean values of recharge temperature and excess air concentration are used for samples without noble gas measurements. Mean annual air temperatures at the KCD and MCD sites are 17 and 16 °C, respectively (*32*), and the Xe-derived average recharge temperatures for the KCD and MCD sites are 19 and 18 °C. Recharge temperatures are most likely higher than mean annual air temperature because most recharge is from excess irrigation during the summer months. The average amount of excess air indicated by Ne concentrations is 2.2×10^{-3} cm^3(STP)/g H_2O for KCD and 1.7×10^{-3} cm^3(STP)/g H_2O for MCD. From these parameters, we estimate the site representative initial N_2/Ar ratios including excess air to be 41.2 for KCD and 40.6 for MCD. Measured N_2/Ar ratios greater than these values are attributed to production of N_2 by denitrification.

The excess N_2 concentration can be expressed in terms of the equivalent reduced nitrate that it represents in mg/L NO_3^- based on the stoichiometry of denitrification. Considering excess N_2 in terms of equivalent NO_3^- provides a simple test to determine whether there is a mass balance between nitrate concentrations and excess N_2. From Figure 2, there does not appear to be a balance between nitrate concentrations and excess N_2 in KCD groundwater, since nitrate concentrations in the shallow wells are more than twice that of equivalent excess N_2 concentrations in the anoxic zone. There are multiple possible causes of the discrepancy between NO_3^- concentrations and excess N_2 concentrations including (1) the NO_3^- loading at the surface has increased over time, and denitrification is limited by slow vertical transport into the anoxic zone, (2) mixing with deeper, low initial NO_3^- waters has diluted both the NO_3^- and excess N_2 concentrations, or (3) some dissolved N_2 has been lost from the saturated zone. All three processes may play a role in N cycling at the dairies, but we can shed some light on their relative importance by considering the extent of denitrification and then constraining the time scale of denitrification as discussed in the following sections.

Isotopic Compositions of Nitrate. Large ranges in $\delta^{15}N$ and $\delta^{18}O$ values of nitrate are observed at both dairies (Figure 3). Nitrate from KCD has $\delta^{15}N$ values of 4.3–61.1‰, and $\delta^{18}O$ values of −0.7–24.5‰. At MCD, nitrate $\delta^{15}N$ values range from 5.3 to 30.2‰, and $\delta^{18}O$ values range from −0.7 to 13.1‰. The extensive monitoring well networks at these sites increase the probability that water containing residual nitrate from denitrification can be sampled.

Nitrate $\delta^{15}N$ and $\delta^{18}O$ values at both dairies are consistent with nitrification of ammonium and mineralized organic N

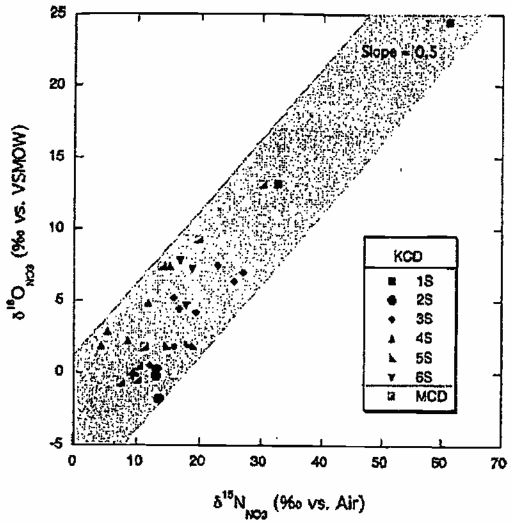

FIGURE 3. Oxygen and nitrogen isotopic composition of nitrate in dairy groundwater from multilevel monitoring wells at KCD and first encounter wells at MCD. The shaded region indicates a slope of 0.5 for a range of starting compositions. Calculated slopes for linear fits to multilevel wells at KCD and first encounter wells at MCD range from 0.47 to 0.60.

compounds from manure-rich wastewater, which is stored and used as a fertilizer at both dairy sites. At some locations, nitrification has been followed by denitrification. Prior to nitrification, cow manure likely starts out with a bulk $\delta^{15}N$ value close to 5‰, but is enriched in ^{15}N to varying degrees due to volatile loss of ammonia, resulting in $\delta^{15}N$ values of 10−22‰ in nitrate derived from manure (*33, 34*). Culture experiments have shown that nitrification reactions typically combine 2 oxygen atoms from the local pore water and one oxygen atom from atmospheric O_2 (*35, 36*), which has a $\delta^{18}O$ of 23.5‰ (*37*). Different ratios of oxygen from water and atmospheric O_2 are possible for very slow nitrification rates and low ammonia concentrations (*38*), however for dairy wastewater we assume that the 2:1 relation gives a reasonable prediction of the starting $\delta^{18}O$ values for nitrate at the two dairies based on the average values for $\delta^{18}O$ of groundwater at each site (−12.6‰ at KCD and −9.9‰ at MCD). Based on this approach, the predicted initial values for $\delta^{18}O$ in nitrate are −0.7‰ at KCD and 1.1‰ at MCD. Samples with the lowest nitrate $\delta^{15}N$ values have $\delta^{18}O$ values in this range, and are consistent with nitrate derived from manure. There is no strong evidence for mixing with nitrate from synthetic nitrogen fertilizers, which are used occasionally at both sites, but typically have low $\delta^{15}N$ values (0−5‰) and $\delta^{18}O$ values around 23‰ (*39*).

Denitrification drives the isotopic composition of the residual nitrate to higher $\delta^{15}N$ and $\delta^{18}O$ values. The stable isotopes of nitrogen are more strongly fractionated during denitrification than those of oxygen, leading to a slope of approximately 0.5 on a $\delta^{18}O$ vs $\delta^{15}N$ diagram (*34*). Nitrate $\delta^{15}N$ and $\delta^{18}O$ values at individual KCD multilevel well sites are positively correlated with calculated slopes ranging from 0.47 to 0.60; the slope of first encounter well data at MCD is 0.66 (Figure 3). These nitrate $\delta^{15}N$ and $\delta^{18}O$ values indicate that denitrification is occurring at both sites. Because a wide range of fractionation factors are known to exist for this process (*40*), it is not possible to determine the extent of denitrification using only the isotopic compositions of nitrate along a denitrification trend, even when the initial value for manure-derived nitrate can be measured or calculated.

Extent of Denitrification. The concentrations of excess N_2 and residual nitrate can be combined with the isotopic composition of nitrate in order to characterize the extent of denitrification. In an ideal system, denitrification leads to a regular decrease in nitrate concentrations, an increase in excess N_2, and a Rayleigh-type fractionation of N and O isotopes in the residual nitrate (Figure 4). In the Rayleigh fractionation model (*41*) the isotopic composition of residual nitrate depends on the fraction of initial nitrate remaining in the system ($f = C/C_{initial}$), the initial $\delta^{15}N$, and the fractionation factor (α) for denitrification:

$$\delta^{15}N = (1000 + \delta^{15}N_{initial})\, f^{(\alpha-1)} - 1000$$

The fractionation factor α is defined from the isotopic ratios of interest ($R = {}^{15}N/{}^{14}N$ and $^{18}O/^{16}O$):

$$\alpha = \frac{(R)_{Product}}{(R)_{Reactant}}$$

This fractionation can also be considered as an enrichment factor (ε) in ‰ units using the approximation $\epsilon \approx 1000 \ln \alpha$. The extent of denitrification can be calculated as $1 - f$. Rather than relying on an estimate of initial nitrate concentration, the parameter f is determined directly using field measurements of excess N_2 in units of equivalent reduced NO_3^-:

$$f = C_{NO_3^-}/(C_{NO_3^-} + C_{excess\ N2})$$

Heterogeneity in groundwater systems can often complicate the interpretation of contaminant degradation using a Rayleigh model (*42*). Denitrified water retains a proportion of its excess N_2 concentration (and low values of f) during mixing, but the isotopic composition of nitrate may be disturbed by mixing since denitrified waters contain extremely low concentrations of nitrate (<1 mg/L). The sample from 1S with a f value close to zero and a $\delta^{15}N$ value of 7.6‰ was likely denitrified and is one example of this type of disturbance. However, in general, groundwater samples from the same multilevel well sites at KCD fall along similar Rayleigh fractionation curves, indicating that the starting isotopic composition of nitrate and the fractionation factor of denitrification vary across the site (Figure 4).

Values of $\delta^{15}N$ and f calculated from nitrate and excess N_2 fall along Rayleigh fractionation curves with enrichment factors (ε) ranging from −57‰ to −7‰ for three multilevel well sites at KCD and first encounter wells at MCD. As expected for denitrification, the enrichment factors indicated for oxygen are roughly half of those for nitrogen. The magnitude of these enrichment factors for N in residual nitrate are among the highest reported for denitrification, which typically range from −40‰ to −5‰ (*34, 40*). Partial gas loss near the water table interface at MCD could potentially increase the value of f, resulting in larger values of ε. Gas loss is unlikely to affect fractionation factors at KCD since most excess N_2 is produced well below the water table. Considering the large differences observed for denitrification fractionation factors within and between the two dairy sites, it is not sufficient to estimate fractionation factors for denitrification at dairies based on laboratory-derived values or field-derived values from other sites. The appropriate fractionation factors must be determined for each area, and even then the processes of mixing and gas loss must be considered in the relation between isotopic values and the extent of denitrification. Nevertheless, direct determination of the original amount of nitrate using dissolved N_2 values significantly improves our ability to determine the extent of denitrification in settings where the initial nitrate concentrations are highly variable.

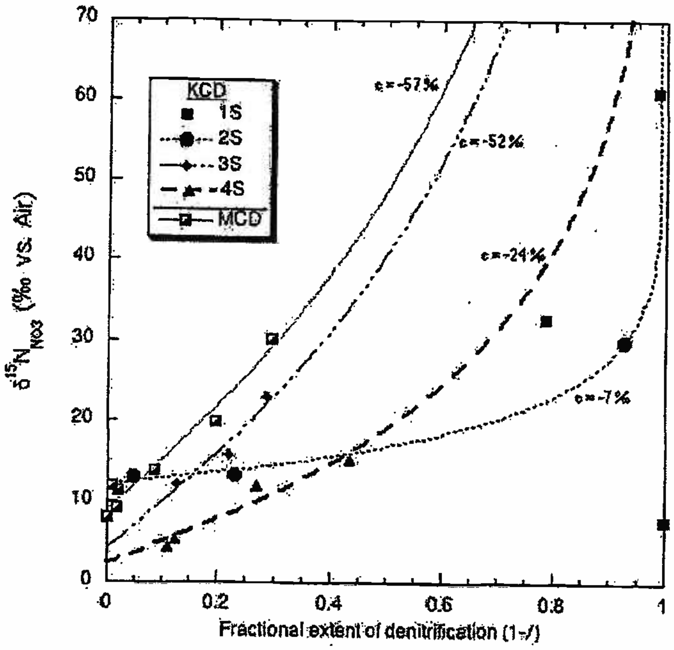

FIGURE 4. Nitrate $\delta^{15}N$ values plotted against the fractional extent of denitrification $(1 - f)$ based on excess N_2 and residual nitrate. Enrichment factors (ϵ) are calculated by fitting the Rayleigh fractionation equation to data from three multilevel well sites at KCD and wells at MCD.

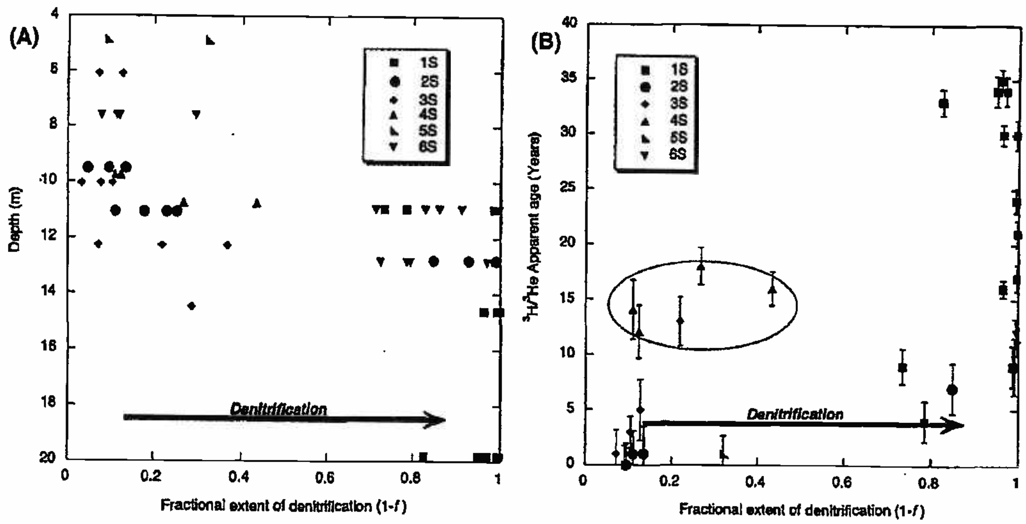

FIGURE 5. Sample depth (A) and $^3H/^3He$ apparent age (B) plotted against the fractional extent of denitrification $(1 - f)$. Samples at two sites have experienced less denitrification than is typical for samples with $^3H/^3He$ apparent age >8 years (circled, see text).

Time Scale of Denitrification. Modern water (i.e., groundwater containing measurable tritium) is found at all multilevel wells completed in the upper aquifer at KCD, the deepest of which is 20 m BGS. The upper aquifer below KCD has $^3H/^3He$ apparent ages of <35 years. At well 1D1 (54 m BGS), the lower aquifer has no measurable NO_3^- and tritium below 1 pCi/L, indicating a groundwater age of more than 50 years. The sum of nitrate and excess N_2 is highest in the young, shallow dairy waters at KCD. Samples with $^3H/^3He$ ages >29 years were below the MCL for nitrate prior to denitrification. These results are consistent with an increase in nitrate loading at the surface, which followed the startup of KCD operations in the early 1970s.

The extent of denitrification at KCD is related to both depth and groundwater residence times based on $^3H/^3He$ apparent ages (Figure 5). There is a sharp transition from high nitrate waters to denitrified waters between 11 and 13 m depth across the KCD site. This transition is also related to the apparent age of the groundwater, as the high nitrate waters typically have apparent ages of between 0 and 5 years, and most samples with ages greater than 8 years are significantly or completely denitrified. There are five samples that do not follow this pattern. These outliers are from sites 3S and 4S where the shallow groundwater has much higher $^3H/^3He$ apparent ages due to slow movement around clay zones at the screened intervals for these samples. The existence of older water that is not significantly impacted by denitrification indicates that it is the physical transport of water below the transition from oxic to anoxic conditions rather than the residence time that governs denitrification in this system.

At the MCD site, groundwater $^3H/^3He$ apparent ages indicate fast transit rates from the water table to the shallow monitoring wells. Most of the first encounter wells have apparent ages of <3 years, consistent with the hydraulic analysis presented by Harter et al. (*5*). The very fast transit times to the shallow monitoring wells at MCD allow for some constraints on minimum denitrification rates at this site. Based on the comparison of the calculated ages with the initial tritium curve, these shallow wells contain a negligible amount of old, ^3H-decayed water. In shallow wells near lagoons (e.g., W-16 and V-21), the observed excess N_2 (equivalent to 71 and 40 mg/L of reduced NO_3^-) accumulated over a duration of less than 1 year, indicating that denitrification rates may be very high at these sites. Complete denitrification of groundwater collected from well W-98 (excess N_2 equivalent to 51 mg/L NO_3^-) was attained within approximately 31 years, but may have occurred over a short period of time relative to the mean age of the water.

Occurrence of Denitrification at Dairy Sites. The depth at which denitrified waters are encountered is remarkably similar across the KCD site. This transition is not strongly correlated with a change in sediment texture. The denitrified waters at all KCD wells coincide with negative ORP values and generally low dissolved O_2 concentrations. Total organic carbon (TOC) concentration in the shallow groundwaters range from 1.1 to 15.7 mg/L at KCD, with the highest concentrations of TOC found in wells adjacent to lagoons. The highest concentrations of excess N_2 are found in nested well-set 2S, which is located in a field downgradient from the lagoons. However, sites distal to the lagoons (3S and 4S) that are apparently not impacted by lagoon seepage (*43*) also show evidence of denitrification, suggesting that direct lagoon seepage is not the sole driver for this process.

The chemical stratification observed in multilevel wells at the KCD site demonstrates the importance of characterizing vertical variations within aquifers for nitrate monitoring studies. Groundwater nitrate concentrations are integrated over the high and low nitrate concentration zones by dairy water supply wells, which have long screened intervals from 9 to 18 m BGS. Water quality samples from these supply wells underestimate the actual nitrate concentrations present in the uppermost oxic aquifer. Similarly, first encounter monitoring wells give an overestimate of nitrate concentrations found deep in the aquifer, and thus would miss entirely the impact of saturated zone denitrification in mitigating nitrate transport to the deep aquifer.

Monitoring wells at MCD sample only the top of the aquifer, so the extent of denitrification at depth is unknown, except for the one deep supply well (W98), which has less than 1 mg/L nitrate and an excess N_2 content consistent with reduction of 51 mg/L NO_3^- to N_2. This supply well would be above the MCL for nitrate without the attenuation of nitrate by denitrification. The presence of ammonium at several of the wells with excess N_2 indicates a component of wastewater seepage in wells located near lagoons, where mixing of oxic waters with anoxic lagoon seepage may induce both nitrification and denitrification. Wells that are located in the surrounding fields have high NO_3^- concentrations, and do not have any detectable excess N_2, a result consistent with mass-balance models of nitrate loading and groundwater nitrate concentration (*5*).

While dairy operations seem likely to establish conditions conducive to saturated zone denitrification, the prevalence of the phenomenon is not known. Major uncertainties include the spatial extent of anaerobic conditions, and transport of organic carbon under differing hydrogeologic conditions and differing nutrient management practices. Lagoon seepage may also increase the likelihood of denitrification in dairy aquifers. The extent to which dairy animal and field operations affect saturated zone denitrification is an important consideration in determining the assimilative capacity of underlying groundwater to nitrogen loading associated with dairy operations.

Acknowledgments

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Supporting Information Available

A table of chemical, isotopic, and dissolved gas results from this study, a plot of apparent age with depth, and detailed descriptions of the study sites. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information for "Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations" by M. J. Singleton[1*], B. K. Esser[1], J. E. Moran[1], G. B. Hudson[1], W. W. McNab[2], and T. Harter[3]

Contents: 7 Pages, 1 Figure, and 1 Table

Description of Dairy Sites

Study Site 1:

Study Site #1 is located at a dairy operation in Kings County, CA (KCD). Manure management practices employed at KCD, with respect to corral design, runoff capture and lagoon management are typical of practices employed at other dairies in the region. KCD has close to the 1000-cow average for dairies in the area, and operates three clay-lined wastewater lagoons that receive wastewater after solids separation. Wastewater is used for irrigation of 500 acres of forage crops (corn and alfalfa) on the dairy and on neighboring farms; dry manure is exported to neighboring farms.

KCD is located in the Kings River alluvial fan, a sequence of layered sediments transported by the Kings River from the Sierra Nevada to the low lying southern San Joaquin Valley of California (*1, 2*). The site overlies an unconfined aquifer, which has been split into an upper aquifer from 3m to 24m below ground surface (BGS) and a lower aquifer (>40 m BGS) that are separated by a gap of unsaturated sediments. Both aquifers are predominantly composed of unconsolidated sands with minor clayey sand layers. The lower unsaturated gap was likely caused by intense regional groundwater pumping, and a well completed in this unsaturated zone has very low gas pressures. There are no persistent gradients in water table levels across the KCD site, but in general, regional groundwater flow is from the NW to SE due to topographic flow on the Kings River fan. The water table is located about 5 m BGS. Local recharge is dominated by vertical fluxes from irrigation, and to a lesser extent, leakage from adjacent unlined canals. Transient cones of depression are induced during groundwater pumping from dairy operation wells.

The regional groundwater is highly impacted by agricultural activities and contains elevated concentrations of nitrate and pesticides (*3, 4*).

KCD was instrumented with five sets of multi-level monitoring wells and one "up-gradient" well near an irrigation canal. These wells were installed in 2002, and sampled between Feb. 2002 and Aug. 2005. The multi-level wells have short (0.5 m) screened intervals in order to detect heterogeneity and stratification in aquifer chemistry. One monitoring well was screened in the lower aquifer, 54m BGS. The remaining monitoring wells are screened in the upper aquifer from 5m to 20m BGS. In addition, there are eight dairy operation wells that were sampled over the course of this study. These production wells have long screens, generally between 9 to 18 meters below ground surface (BGS).

Study Site 2:

The second dairy field site is located in Merced County, CA. The Merced County dairy (MCD) lies within the northern San Joaquin Valley, approximately 160 km NNW from the KCD site. The site is located on the low alluvial fans of the Merced and Tuolumne Rivers, which drain the north-central Sierra Nevada. Soils at the site are sand to loamy sand with rapid infiltration rates. The upper portion of the unconfined alluvial aquifer is comprised of arkosic sand and silty sand, containing mostly quartz and feldspar, with interbedded silt and hardpan layers. Hydraulic conductivities were measured with slug tests and ranged from 1×10^{-4} m/s to 2×10^{-3} m/s with a geometric mean of 5×10^{-4} m/s (*5*). Regional groundwater flow is towards the valley trough with a gradient of approximately 0.05% to 0.15%. Depth to groundwater is 2.5 m to 5 m BGS. The climate is Mediterranean with annual precipitation of 0.5 m, but groundwater recharge is on the order of 0.5–0.8 m per year with most of the recharge originating from excess irrigation water (*3*). Transit times in the unsaturated zone are relatively short due to the shallow depth to groundwater and due to low water holding capacity in the sandy soils. Shallow water tables are managed through tile drainage and groundwater pumping specifically for drainage. The MCD site is instrumented with monitoring wells that are screened from 2-3 m BGS to a depth of 7-9 m BGS. The wells access the upper-most part of the unconfined aquifer, hence, the most recently recharged groundwater (*6*). Recent investigations showed strongly elevated nitrate levels in this shallow groundwater originating largely from applications of liquid dairy manure to field crops, from corrals, and from manure storage lagoons (*6*). For this study, a subset of 18 wells was sampled. A deep domestic well was also sampled at MCD. This domestic well is completed to 57 m BGS, and thus samples a deeper part of the aquifer than the monitoring well network.

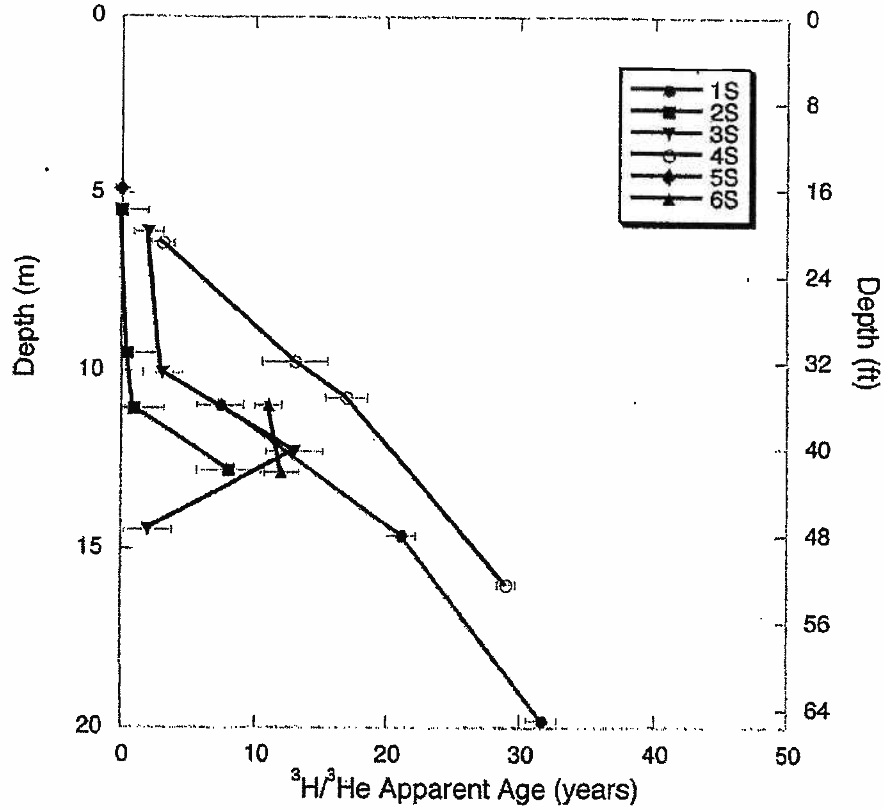

Figure S1. Groundwater $^{3}H/^{3}He$ apparent ages from multilevel monitoring wells at KCD. Error bars show analytical error.

Table 51. Chemical, dissolved gas, and isotopic compositions for multilevel groundwater monitoring wells and lagoons. Average values are given for wells sampled more than onc
Excess N_2 values in bold are fully constrained by noble gas determinations of excess air and recharge temperature.

Site	Depth of multi-level well (m)	Cl^- (mg/L)	NO_3^- (mg/L)	NH_4^+ (mg/L)	ORP	DO (mg/L)	TOC (mg/L)	$\delta^{18}O$ H_2O (‰ SMOW)	$\delta^{15}N$ NO_3^- (‰ Air)	$\delta^{18}O$ NO_3^- (‰ SMOW)	$^3H/^3He$ age (yr)	+/- (yr)	Excess air determined from Ne (cc STP/g)	Recharge Temp. from Xe (°C)	+/- (°C)	^3H pCi/L	+/- (pCi/L)	N_2/Ar
KCD-CANAL-1		1.5	1.2	0.2		10.0		-12.9								13.3	0.6	
KCD-LAGOON-1		304.5	28.6	360.8		0.4	480.0	-10.2										68
KCD-LAGOON-2		265.2	13.9	292.1		0.5	490.0	-10.0										58
KCD-LAGOON-3		212.2	22.4	181.3		0.5	420.0	-9.9										41
KCD-1D1	54.3	1.9	0.2	<0.1	-264	0.2	0.8	-13.7	7.1		>50		3.40E-03	15	1.2	0.5	0.1	41
KCD-1S1	6.7		206.0		166	3.5		-12.7										46
KCD-1S2	11.0	52.5	11.1	0.3	-79	0.4	2.5	-12.8	46.9	18.8	7.3	1.8	<1E-4	16	1.1	32.0	1.2	62
KCD-1S3	14.6	36.0	0.5	1.3	-164	0.5	1.3	-12.9	7.6		21.1	1.1	2.82E-03	14	1.1	31.4	1.2	63
KCD-1S4	19.8	9.8	0.4	2.5	-196	0.5	1.1	-13.3			31.7	1.1	4.02E-03	16	1.1	28.3	1.1	46
KCD-2S1	5.5	107.7	144.5	<0.1			5.0	-12.3			0.0	2.0	1.70E-03	19	1.0	21.9	0.9	39
KCD-2S2	9.5	95.0	187.2	0.6	84	0.7	4.2	-12.2	13.1	-0.2	0.5	2.2	1.78E-03	22	1.1	19.5	0.8	49
KCD-2S3	11.1	101.1	178.2	0.1	62	1.7	3.0	-12.1	13.2	0.2	1.0	2.1	<1E-4	21	1.1	19.3	0.8	62
KCD-2S4	12.8	72.7	7.1	1.0	-149	0.3	1.8	-12.4	29.9		8.0	2.4	<1E-4	23	1.8	19.8	0.8	10[illegible]
KCD-3S1	6.1	170.4	203.1	0.4	0	1.2	5.3	-11.7	14.5	2.4	2.0	1.0	1.42E-03	19	1.1	17.8	0.7	46
KCD-3S2	18.1	255.6	273.6	<0.1	72	2.3	14.2	-11.2			3.0	1.4	6.35E-04	21	1.1	21.2	0.9	49
KCD-3S3	12.3	162.7	167.8	0.5	107	1.2	9.0	-11.9	15.8	5.2	13.0	2.2	1.30E-03	18	1.0	16.4	0.8	53
KCD-3S4	14.5	194.0	136.4	<0.1	79	1.0	5.6	-11.8	22.9	7.4	2.0	1.7	<1E-4	20	1.0	18.6	0.7	59
KCD-4S1	6.4	127.0	83.3	<0.1					8.6	2.2	3.0	0.8	3.35E-04	20	1.0	35.6	1.4	
KCD-4S2	9.8	32.1	125.4	0.4	-16	0.8	1.1	-11.8	4.7	2.3	13.0	2.5	5.07E-03	18	1.3	20.3	0.8	51
KCD-4S3	10.8	42.3	77.1	0.5	27	0.9	1.1	-12.0	13.5	6.1	17.0	1.6	3.54E-03	19	1.2	22.7	0.9	60
KCD-4S4	16.0	35.0	0.9	1.8	-161	0.9	3.5	-13.0			29.0	0.7		18	1.0	46.5	1.7	61
KCD-5S1	4.9	14.5	35.4	1.3	37	0.5	1.5	-13.4	18.9	1.8	<1		<1E-4	18	1.0	12.5	0.6	46
KCD-6S1	12.9	129.3	12.7	20.4		1.0	15.7	-11.9	12.1		12.0	1.3	<1E-4			29.1	1.1	70
KCD-6S2	11.0	140.6	10.1	3.2		1.2	14.6	-11.8			11.0	1.0	<1E-4			33.3	1.2	67
KCD-6S3	7.6	129.5	159.3	0.9			6.7	-11.6	19.0	7.7			2.13E-04			33.9	1.3	51
KCD-NW-01	9-18	140.8	114.7	1.9		1.9		-12.0	15.0									54
KCD-NW-02	9-18	163.4	75.2	3.4		1.3		-12.0	18.2							17.0	0.9	71
KCD-NW-03	9-18	100.3	67.2	<0.1														
KCD-NW-04	9-18	2.8	2.0	<0.1				-13.7			>50		7.72E-04	12	0.9	0.2	0.2	
KCD-NW-06	9-18	92.8	48.6	2.8				-12.2	17.2							22.9	1.2	61
KCD-SW-02	9-18	52.6	91.0	<0.1				-12.7	23.5							24.8	1.4	
KCD-SW-03	9-18	45.1	29.2	1.9		1.5		-12.4	27.3							30.4	1.3	57
KCD-SW-07	9-18	165.5	25.8	<0.1														
KCD-SW-08	9-18	184.1	116.6	2.3		3.8		-10.9	16.9							19.7	0.8	53
MCD-LAGOON		514.0	<0.1	691.8														62
MCD-V-01	7.0	317.8	425.1	<0.1	111	5.6	12.7	-9.3	13.9	7.4	12.0	1.7	<1E-4	25	1.2	36.0	1.4	61
MCD-V-14	7.6	71.4	316.0	<0.1			5.8		11.2	1.7	2.0	2.9	1.26E-03	18	1.0	12.4	0.5	41
MCD-V-18	6.1	77.2	195.5	1.7	193	3.3	8.1		10.1	-0.9						12.2	0.5	39
MCD-V-21	9.1	145.5	163.1	<0.1	147	1.4	22.6	-9.1	19.9	9.2	<1					15.3	0.6	61
MCD-V-24	9.1	30.2	201.5	<0.1	161	7.0	5.4	-10.5	7.4	-0.7	<1		4.31E-04	20	1.0	13.8	0.6	37
MCD-V-99		73.0	303.2	2.4			12.2		10.3	0.4	1.0	2.1	<1E-4	19	1.0	14.5	0.6	39
MCD-W-02	7.0	226.1	2.0	148.5		0.6	12.7	-9.1								17.9	0.7	12[illegible]
MCD-W-03	7.0	82.2	341.8	0.7		0.8	14.5	-10.5			3.0	3.1	2.13E-03	17	1.0	13.7	0.6	45
MCD-W-05	7.0	48.3	230.6	<0.1				-10.7	6.8							14.5	0.8	39
MCD-W-10	9.1	55.5	426.1	<0.1	171		11.7	-10.3	9.1	0.0	3.0	3.4	2.52E-03	19	1.1	13.5	0.6	44
MCD-W-16	9.1	298.9	6.1	113.9	176	0.7	9.1	-8.1			<1	0.7	<1E-4			18.9	0.9	13[illegible]
MCD-W-17	9.1	136.9	171.7	26.7	208	0.7	9.8	-9.4	30.2	13.1			<1E-4			15.9	0.7	90
MCD-W-23	9.1	80.9	356.1	1.9	121	1.1	10.4	-10.2			2.0	2.8	1.65E-03	20	1.0	13.9	0.5	43
MCD-W-30	9.1	49.1	324.8	<0.1				-9.9	5.3		1.0	2.3	1.23E-03	17	0.8	16.3	0.9	38
MCD-W-31	9.1	40.8	187.9	<0.1				-10.9	8.0		<1		1.82E-03			15.9	0.7	40
MCD-W-34	7.3	63.4	185.6	<0.1				-10.8	7.9		1.0	3.6	2.77E-03	17	0.8	13.7	0.7	41
MCD-W-35	7.3	159.6	304.4	<0.1				-9.7	11.8		<1		1.52E-03	17	0.8	16.3	0.8	41
MCD-W-98	57	69.6	0.4	<0.1			2.1	-10.6			31.0	0.6	1.76E-03	18	1.0	21.8	0.9	64

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James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT "E"

Water Quality Regulations for Dairy Operators in California's Central Valley – Overview and Compliance Cost Analysis

Casey Walsh Cady and Mike Francesconi[1]
November 2010

Table of Contents

1. Executive Summary
2. Introduction and Background
3. Study Scope and Methodology
4. Dairying in California's Central Valley
5. Consultants Addressing the General Order
6. Requirements of the General Order Waste Discharge Requirements
7. Dairy Operators' Time
8. Capital Investment
9. Technical and Financial Assistance
10. Analysis and Conclusions
11. References and Acknowledgements

1. Executive Summary

To protect beneficial uses of surface waters and groundwater, the Central Valley Regional Water Quality Control Board adopted a general Waste Discharge Requirements order for dairies (the General Order) in May 2007. Approximately 1,600 dairies were initially covered under the General Order which established a timeline for operators to develop and implement both a waste management plan (WMP) and a nutrient management plan (NMP). The General Order includes a monitoring and reporting program (MRP) that identifies mandatory sampling and reporting. The General Order also requires that registered professionals perform specified tasks. To comply with the General Order, dairy operators have become much more sophisticated at using the nutrients in manure to match crop needs.

CDFA analyzed the costs of compliance with the General Order by interviewing dairy operators and their consultants. Dairy operators are incurring significant costs to comply with the General Order requirements for a NMP, WMP, and MRP. Future costs related to groundwater monitoring and infrastructure improvement are uncertain at this time but will significantly increase compliance costs in 2011 and beyond. These costs are not offset by the increased efficiency of using manure for crop production, although some financial and technical assistance is available to operators to help them comply with the General Order and offset some of the initial costs of implementation.

Results from the survey show that from 2007 - 2010 total compliance costs for individual dairy operators (not including additional groundwater monitoring) in the Central Valley vary widely from $11,768 to $162,804 with an average of $54,975. One time costs range from $2,250 to $34,000 with an average of $11,575 without additional groundwater monitoring. The average annual estimated costs of compliance is $14,136.

[1] Casey Walsh Cady is Staff Environmental Scientist, Division of Marketing Services, California Department of Food and Agriculture. Mike Francesconi, is Supervising Auditor, Dairy Marketing Branch, California Department of Food and Agriculture. Corresponding author: ccady@cdfa.ca.gov

The amount spent ranges widely based on dairy size location, number of fields, herd size and other factors. This report was prepared in response to a November, 2009 request from the California Department of Food and Agriculture (CDFA).

2. Introduction and Background

The Central Valley of California is over 500 miles long and extends from the Oregon border to the Tehachapi Mountains south of Bakersfield. The region currently has approximately 1,400 dairies. Herd size (mature cows) for dairies permitted under the General Order vary widely, from 58 to 10,925 Nitrates and salts from dairies can result in contamination of surface water and groundwater, and so dairies are regulated by the Central Valley Regional Water Quality Control Board (RB5). Other sources of nitrate such as irrigated agriculture and septic systems are also regulated by RB5.

Prior to May 2007, most of the approximately 1,600 dairies operating in the Central Valley were not regulated under a formal order issued by RB5. In May 2007, RB5 adopted Order R5-2007-0035 "*Waste Discharge Requirements General Order for Existing Milk Cow Dairies*" (the General Order). The General Order applies to dairies that submitted a complete Report of Waste Discharge (ROWD) by October 17, 2005, have not expanded their herd size by more than fifteen percent since they submitted their ROWD, do not discharge wastes that originate outside the dairy, and do not discharge manure or process water to waters of the State. The purpose of the General Order is to regulate the discharge of wastes from the dairy production area and associated cropland. Such wastes are generated from the storage and use of manure, and may transport nutrients, pathogens, and/or salts that can adversely affect the quality of surface water and groundwater.

The General Order applies to both the dairy production area and land application area. The General Order defines requirements for land application of manure based on nutrient budgets developed in a site-specific Nutrient Management Plan (NMP) and requires dairies to have sufficient storage capacity to contain all wastewater generated at the dairy, including rainfall runoff that has contacted manure or feed, until the wastewater can be applied to cropland pursuant to an NMP or is otherwise properly managed. Wastewater is not allowed to be discharged to waters of the State unless the dairy obtains a National Pollutant Discharge Elimination System (NPDES) permit that allows certain discharges following storms that exceed a 25-year, 24-hour storm event. However, stormwater runoff from cropland where manure was applied pursuant to an NMP may also be allowed if receiving water is not significantly affected. The General Order also prohibits further degradation of groundwater, but does not address the cleanup of groundwater degraded by past dairy operations.

The General Order incorporates a phased compliance schedule that gives operators time to make necessary changes in their facilities and practices, take advantage of opportunities for education, and obtain funding for needed facility improvements. The General Order imposes complex requirements on dairy operators including submission of annual reports; development and implementation of an NMP with annual updates, development and implementation of a WMP; daily, weekly and monthly monitoring; and specific sampling of process wastewater, manure, irrigation water, plant tissue, soils, supply wells, tile drainage, etc.. The General Order requires each dairy to fully implement their NMP and WMP by July 1, 2011. More information on the requirements in the General Order is presented below along with an analysis of the compliance costs.

This report examines the cost of complying with the General Order based on data for some of the approximately 1,400 dairies that are covered by the General Order. The data covers the years when facility assessments, planning, and implementation first began. It is anticipated that for most dairies these costs will increase as the monitoring program is implemented and infrastructure upgrades are made.

3. Study Scope and Methodology

No two California dairies are exactly alike; dairy operators have different resources and production facilities. Therefore, this report provides a range of compliance costs based on a number of factors including dairy herd size, location, number and size of crop fields, facility wells, age of the dairy, physical layout, lagoon size, options for nutrient export, choice of consultants, soil types, etc. Where appropriate, average compliance costs are presented.

This report evaluates the cost of compliance for dairy operators covered under the General Order. It does not analyze costs for dairies covered under National Pollutant Discharge Elimination System (NPDES) permits or covered under individual Waste Discharge Requirements (WDR) orders (e. g., dairies that did not file a ROWD by October 17, 2005 or those that have expanded their herd size more than fifteen percent after October 17, 2005).

To prepare this report, CDFA staff interviewed personnel from eight consulting firms (one of these firms also provides engineering services), two agricultural laboratories and two engineering firms. These firms work with approximately 77% of the dairy operators in the Central Valley. CDFA also collected information on time spent on compliance and infrastructure costs from 62 dairy operators who participate in CDFA's Cost of Production studies. They represent 4% of Central Valley dairy operators and 5% of Central Valley milking cow population.

4. Dairy Production in California's Central Valley

Milk and associated dairy products (cheese, dry milk powder, butter, ice cream etc.) are California's top grossing agricultural products and California leads the nation in milk production (CDFA, 2010). California produces 21% of the nation's milk supply (CDFA, 2010) and the Central Valley houses an estimated 89% of California's dairy cows. However, in 2009, dairy operators in California were faced with historic low prices for milk and unusually high cost of production, including the cost of compliance with environmental regulations. There was a net loss of 100 dairies across California in 2009, eighty one dairies were located in the Central Valley (CDFA, 2009).

California dairies are complex, advanced operations, especially those facilities with a large herd size. Most all the dairies are family run, and the operators strive for production efficiencies through use of advanced technologies in genetics, nutrition, reproduction, animal housing, and animal welfare. Because the California dairy industry is so large, various entrepreneurs have developed niche markets to provide assistance to dairy operators. So instead of relying on employees, many dairy operators hire consultants who specialize in providing information, services, or trouble shooting. That option doesn't exist in most other states.

5. Consultants Addressing the General Order

The General Order has an intensive monitoring and reporting program. Operators may choose to do none, some, or all of the monitoring on their own, or hire consultants to do it. Components of the WMP such as storage capacity calculations and flood protection must be signed off by a appropriately registered professional. Likewise, only a trained professional can sign off on backflow prevention on well heads. Some components of the NMP such as the Sampling and

Analysis Plan and Nutrient Budget must be signed off by a Professional Soil Scientist, Professional Agronomist, or Crop Advisor certified by the American Society of Agronomy, or by a Technical Service Provider certified in nutrient management in California by the Natural Resources Conservation Service.

Consultants have varied knowledge and understanding of dairy operations. Some consultants have been conducting nutrient management at dairies for years. Other firms are new to nutrient management. Some consulting firms have a long history of service to the dairy industry, including addressing compliance with regulations. Some consultants provide all required services, while others provide only limited services. Some firms serve 300 or more dairies while others may serve fewer than 15 dairies.

This report presents a range of compliance costs that reflect different approaches on structuring services and fees. Some consultants charge a flat fee, while others charge based on herd size. Some focus on a particular aspect of the General Order – such as the record keeping or preparing an NMP or WMP.

6. Requirements of the General Order

The General Order requires that each dairy operation accomplish the following tasks:

A. Inspection of dairy production area
B. Annual report (submitted annually, July 1)
C. Sampling and analysis of wastewater, plant tissue, solid manure, irrigation water , and soil
D. Sampling and analysis of unauthorized off-site discharges, supply wells, tile drains, some tailwater discharges, and stormwater discharges
E. Nutrient management plan (completion date July 1, 2009)
F. Waste management plan (completion date July 1, 2010)
G. Additional groundwater monitoring (some dairies ordered to begin February 1, 2010)
H. Implementation of the NMP and WMP by July 1, 2011

In this analysis various compliance costs were examined, including:

- Reporting and documentation required by RB5
- Dairy operators (and staff) time associated with implementing the General Order
- Fees paid to consultants
- Laboratory costs
- Infrastructure I Upgrades to dairy
- Annual fees paid to RB5

A. Monthly Inspections/Servicing of Samples

The General Order requires a number of inspections of production and land application areas by the dairymen or a consultant, including:

- Inspection of waste storage areas (weekly or monthly depending on the time of year);
- Inspections of storm water containment structures (after significant storm events);
- Pond inspection with photo documentation showing current freeboard (monthly).
- Inspections of land application areas when process wastewater is being applied (daily).

Many of the consultants report that operators do the daily, weekly, and monthly inspections themselves. For the consultants who do this service, the fee is typically bundled with annual reporting and/or an NMP. Also some consultants charge a separate fee to travel and conduct water and soil sampling (see Subsection C below). These costs are termed "servicing of samples". Six consultants provided cost data for monthly inspections. Costs range from $600 to $9600 per year with an average annual cost of $5,148.

B. Annual Report

An annual report (AR) is due by July 1 of each year, and includes a General Section, Groundwater Reporting Section, and a Storm Water Reporting Section. Table 1 provides a comprehensive list of the AR requirements.

Six consultants provided cost data for AR preparation. Costs range from $150 to $3,000. Some consultants reported that in general the costs to prepare the annual report increase with an increase in the number of fields utilized by the dairy. Larger dairies tend to have more fields for land application of manure.

Each application of nutrients, water, or soil amendments to each field for each crop must be tracked, recorded and data submitted within the AR. Some consultants report that they have been able to lower the fees for the AR as their staff have increased their proficiency, and some consultants alter their fee structure based on herd size. Consultants report that larger dairies may have more skilled staff who are more proficient at handling the paperwork requirements. Some consultants have raised their fees to address poor record keeping. Consultants with numerous clients generally achieve an organizational structure that permits rapid entry and review of all required data.

Table 1 - Annual Report Requirements
An annual monitoring report is due by 1 July of each year and represents activities from the previous calendar year.

A. General Section:

1. Information on crops harvested
2. An Annual Dairy Facility Assessment (an update to the Preliminary Dairy Facility Assessment
3. Number and type of animals, whether in open confinement or housed under roof;
4. Estimated amount of total manure and process wastewater generated by the facility,
5. Estimated amount of total manure and process wastewater applied – with calculations of the nitrogen, phosphorus, potassium and total salt content.
6. Estimated amount of total manure and process wastewater transferred to other persons – with calculations of the nitrogen, phosphorus, potassium and total salt content.
7. Total number of acres for all and actual application areas used during the reporting period for application of manure and process wastewater;
8. Summary of all manure, process wastewater discharges from the production area
9. Summary of all storm water discharges from the production area
10. Summary of all discharges from the land application area to surface water
11. A statement regarding NMP update
12. Copies of all manure/process wastewater tracking manifests and written agreements for transfer of process wastewater
13. Copies of laboratory analyses of all discharges
14. Tabulated analytical data for samples of manure, process wastewater, irrigation water, soil, and plant tissue
15. Results of the Record-Keeping Requirements for the production and land application areas

B. Groundwater Reporting Section
Laboratory data for annual results from supply well and subsurface (tile) drainage systems. Additional sampling and reporting is required once groundwater monitoring wells are required and installed. For those dairies that currently have groundwater monitoring results shall be included with the annual reports.

C. Stormwater monitoring results
The report shall include a map showing all sample locations for all land application areas, rationale for all sampling locations, a discussion of how storm water flow measurements were made, the results (including the laboratory analyses, chain of custody forms, and laboratory quality assurance/quality control results) of all samples of storm water, and any modifications made to the facility or sampling plan in response to pollutants detected in storm water.

C. Sampling and Analysis of Wastewater, Manure, Plant Tissue, Soil and Irrigation Water, Supply Well, Storm Water Discharges and Unauthorized Discharges

The General Order calls for a significant amount of sampling and analyses. – including

- Sampling of solid manure
- Process wastewater (liquid manure)
- Irrigation water
- Plant tissue
- Soil
- Domestic and agricultural supply wells
- Subsurface (tile) drainage systems

Discharge Monitoring

- Unauthorized discharges of manure or process wastewater
- Stormwater discharges to surface water from production area
- Stormwater discharges to surface water from land application area
- Tail water discharges to surface water from land application area

For a detailed list of sampling frequency and minimum analyses required, see guidance from the California Dairy Quality Assurance Program (http://www.cdqa.org/docs/1.4_sampling_requirements_crib_sheetv3_9-30-07.pdf).

The General Order identifies sample handling procedures, completion of chain-of-custody documents, and approved analytical methods.

Some dairy operators hire consultants to collect samples and record appropriate information others collect samples and deliver them to the laboratory for analysis. CDFA interviewed two laboratories that conduct sampling. The reported annual costs for sampling and analysis range from $1,500 per year for a smaller dairy to $15,000 per year for very large dairies. The reported average annual cost was $3,350.

One of the primary factors influencing the cost of the sampling is irrigation water source. Those dairies that are served by canal water may use data from irrigation districts (if available). For those dairies with multiple wells, each well must be sampled annually.

D. Nutrient Management Plan

The NMP is a collection of documents detailing how nutrients will be managed to prevent contamination of groundwater or discharges of nutrients to surface water. All dairies under the General Order were required to certify their NMP completed in the AR due 1 July 2009. The NMP is not required to be submitted to RB5; however, operators were required to submit numerous statements of completion during the first 30 months after the adoption of the General Order and to maintain documents and all records at the dairy for at least five years. The NMP must be made available to RB5 staff upon request during an inspection. Updates to the NMP are required when changes are made in manure management practices, including changes to crop rotation.

One of the key objectives of the NMP is to ensure that nitrogen application rates do not exceed 1.4 times the nitrogen removal rates of crops and thus be protective of groundwater quality. According to the General Order:

> *The purpose of the NMP is to budget and manage the nutrients applied to the land application area(s) considering all sources of nutrients, crop requirements, soil types, climate, and local conditions in order to prevent adverse impacts to surface water and groundwater quality. The NMP must take the site-specific conditions into consideration in identifying steps that will minimize nutrient movement through surface runoff or leaching past the root zone* (RB5, 2007).

Required information in the NMP includes:

a) Land application area map identifying: each field, application of solid manure or process wastewater, infrastructure for irrigation, nearby water conveyances and waterways, etc.,
b) Written agreements for third parties receiving wastewater (including updates in each annual report),
c) Sampling and analysis plan that documents protocols for sample collection, identifies material to be sampled and frequency of sampling, and identifies the field and laboratory data required,
d) Nutrient budgets for each field with planned rates of nutrient applications for each crop. Nutrient budgets include: 1) rate of manure and process wastewater for each crop in each field; 2) application timing, 3) method of application of manure and process wastewater; and 4) review of P and K application rates to avoid build-up of these nutrients in the soil,
e) Setbacks, buffers and other alternatives to protect surface water,

f) Field risk assessment to evaluate the effectiveness of management practices used to prevent off site discharges of waste constituents,
g) Detailed record keeping,
h) Nutrient management plan review.

The Sampling and Analysis Plan and the Nutrient Budget require signatures of a certified nutrient management specialist.

CDFA interviewed eight consultants who prepare NMPs. Some of the consultants bundled the cost of the NMP with annual reports and monthly monitoring, particularly for the annual NMP updates; while others treat the preparation of an NMP as a separate service. The cost of NMP varies by the size of the dairy and the number of fields that receive manure applications. Reported costs for the NMP range from $250 to $7,000 for a dairy with 25 fields. The average cost of an NMP is $3,295. In addition to the cost to prepare the NMP are costs for sampling and record keeping associated with the NMP.

NMP updates may trigger additional costs. Because the NMP was required in 2009 and updates are only required if changes are made, there is insufficient data at this time to determine those costs. However some consultants estimate that 20% of the NMPs need an update and will charge on a time and material basis. One consultant reports that they have had 5 or 6 dairies update their plans in mid-2010. The costs for these revisions ranged from approximately $450 on the low side to $1600 on the high side.

As operators become more adept at implementing their NMP, they may experience some economic benefit from improving manure management. Optimizing the use of manure as a fertilized may result in less purchase of synthetic fertilizers or more sale of manure to neighboring farms. This report does not consider the economic benefits that may accrue.

E. Waste Management Plan

The General Order also calls for each dairy to submit a WMP. Initially, the WMP was to be submitted in July 2009; however, RB5 allowed an additional year to meet this deliverable.

The Waste Management Plan is a comprehensive document with many components, including:

a) Facility information summary;
b) Updated maps of structures, milking parlor, other buildings, corrals, ponds settling basins, etc.;
c) Documentation of lagoon capacity (requires Registered Professional signature);
d) Evaluation of flood protection (may require Registered Professional signature);
e) Evaluation of design and construction of the production area;
f) Operation and maintenance plan;
g) Backflow prevention implementation by July 1, 2010 (trained professional signature).

Some engineering firms are partnering with dairy consulting firms for WMP completion. Other engineering firms are contracting directly with operators. Some consultants charge a flat fee for the WMP, while others charge a range. In addition to the costs to prepare the WMP, there will be costs to make any necessary improvements to implement the WMP. For example, if pond capacity is inadequate for storage of process water, there will be design and construction costs for additional storage. Because the General Order requires additional analysis for dairies located in a flood zone, most firms assess an extra fee for such dairies. The costs of implementing the NMP also vary with the amount of information previously collected and with the number of wells that require backflow certification.

Engineering consultants report that the WMP will be highly site-specific and that the herd size of the dairy is not a significant factor in the cost of the WMP, though the size of the production area is. The following factors will affect the cost of WMP development:

- The amount of data needed to be collected (to save money, some operators may conduct that data collection themselves)
- Flood protection evaluations (Depending on the terrain and creeks in the vicinity of the dairy, this can be a significant cost component. No guidance was provided to consultants regarding the information to be included in the evaluation, so costs are difficult to predict.),
- The need to use more sophisticated modeling software.

Reported costs of the WMP vary widely from $2,000 for a smaller dairy not in a flood zone up to $27,000 for a large dairy located in a flood zone.

F. Additional Groundwater Monitoring

The General Order calls for additional groundwater monitoring beyond the monitoring discussed in Section 6(D) above. The purpose of this additional monitoring is to confirm that the facility, including cropland, wastewater retention system and the production area, is in compliance with the groundwater limitations. Operators must install a sufficient number of monitoring wells to characterize:

- Groundwater flow direction and gradient beneath the site;
- Groundwater quality upgradient of the dairy (water that is not affected by the dairy operations, but that may have been affected by upgradient activities);
- Groundwater quality down gradient of the corrals, retention ponds, and land application areas.

This means that a minimum of three wells will be necessary, and perhaps many additional wells will be needed depending on site characteristics. The depth to groundwater is a major factor that can increase costs. If both shallow aquifer and a deeper aquifer must be monitored, costs can increase dramatically.

The General Order calls for phased implementation of additional groundwater monitoring. At this time, based on an evaluation of the dairies' threat to water quality, 100 to 200 dairies per year may be directed by RB5 to submit a monitoring well installation plan, install monitoring wells, and sample those wells.

The first group of dairies ordered to install groundwater monitoring wells were those who did not complete the NMP by 1 July 2009 and had nitrate-nitrogen levels of 10 mg/l or more detected in a well or subsurface drainage system in the vicinity of the dairy.

RB5 will further prioritize groundwater monitoring requirements based on a number of factors including the location of the production area or land application area relative to California Department of Pesticide Groundwater Protection Area; the distance of production area or land application area from an artificial recharge area; the distance from the dairy production area or land application area and the nearest off-property domestic well; the distance from dairy production area or land application area and the nearest off-property municipal well; the number of crops grown per year per field; and Whole Farm Nitrogen Balance.

A registered engineer or geologist must prepare the monitoring well installation plan and submit it for approval by RB5. Initial estimates for the cost of Individual Groundwater Monitoring developed by Dairy CARES (an association of dairy operators and dairy industry representatives) are $42,500 for upfront costs (well plan, drilling of at least 3 wells, annual sampling and analysis), and $5,000 per year for reporting.

Alternative Representative Groundwater Monitoring Program

The General Order also allows for establishing an alternative groundwater monitoring program in lieu of each producer installing monitoring wells and conducting sampling. Representatives of Dairy CARES, Western United Dairymen and other industry associations are actively developing an alternative plan which is subject to approval by the Executive Officer of the RB5.

As of September, 2010, the Alternative Representative Groundwater Monitoring Program has not been approved by RB5. In addition there are some dairies that will not be included in the program.

The current draft of the alternative plan includes establishing a nonprofit organization with a Board of Directors to manage clustered groundwater monitoring program and collect fees from enrolled dairy operators to support the monitoring. This approach would allow operators to enroll in the groundwater monitoring organization and pay a fee. The collected fees will support the installation of groundwater monitoring wells and associated sampling, analyses, and reporting requirements on a select group or groups of dairies.

Table 2 includes estimates for the representative groundwater monitoring network developed by Dairy CARES. The fee estimate is based on the number of dairymen who enroll in the representative monitoring program and this cost range is based on estimates of 60% to 80% of the industry participating. The 5-year total cost for the representative monitoring program could range $3,320 to $4,860 including well installation, sampling, analysis, and reporting). Compared to groundwater monitoring by individual dairies, the representative monitoring plan is considerably less expensive – especially given that the monitoring will continue into the future.

The final cost list (Table 3) includes both the representative groundwater program and the individual monitoring since there is uncertainty regarding the final structure of this requirement. If this program is not approved and implemented then costs for individual dairy operators to develop and install wells will increase significantly.

Table 2. Estimated Costs for Representative Monitoring Program

One time Sign Up Fee	$500
Annual Membership Fee (estimate)	$664 - $972
Total 2010	$1164 - $1472

Dairy CARES - Jan 2010

7. Dairy Operators' Time

One cost factor that must be evaluated is the dairy operators' time dedicated to fulfilling the General Order requirements. CDFA Dairy Marketing Branch collects cost of production information from approximately 10 percent of the dairies located in the Central Valley. CDFA surveyed 62 operators to determine how much time an employee or manager spent on the General Order on a monthly basis to maintain records, taking samples, etc. Estimates of the amount of time operators dedicated to complying with the General Order range from 1 to 28 hours per month. Additional time is needed to attend classes, read reports, and review documents.

The average hourly wage for employees working on a dairy in 2009 was $28.00 (CDFA, 2010). This average wage value and estimates of time spent was used to establish the cost of complying with the General Order. The annual cost ranges from $336 to $9,408 with an average of $3,148.

8. Capital Investment

Capital investment upgrades to dairy facilities and structures are another cost operators have to incur to comply with the General Order. ***At this time we are only noting that these costs are occurring but we have no way of determining a representative cost to apply, so they are not included for this study, however it is likely that these are significant costs.*** Since every dairy facility is designed and operated differently, each facility had a different set of issues they had to deal with for their NMP and WMP. Infrastructure improvements related to NMPs and WMPs in many cases have not yet been implemented and are not required to be completed until 2011. Capital investment for infrastructure may include expanding retention ponds, exporting nutrients offsite, adding equipment to process manure on site for export, installation of irrigation delivery systems and related equipment such as flow meters, and installation of flood/runoff control structures such as berms and tailwater return systems.

Interviews with operators show that some had made no capital improvements while others have invested up to $350,000 in facility improvements. However, in many cases it is difficult to distinguish between general facility improvements and improvements necessary to comply with the General Order. Facility upgrades that were completed include back flow prevention, raising stand pipes, upgrading irrigation pipes, installing concrete silage pads, installing rain gutters, corral grading, adding a new lagoon, and expanding an existing lagoon.

9. Technical and Financial Assistance

Both technical and financial assistance is available to dairy operators to help them understand and implement the General Order. The CA Dairy Quality Assurance Program (CDQAP) is a partnership among California's dairy industry, federal, state and regional government agencies and the University of California Cooperative Extension. CDQAP provides technical assistance to operators and helps them understand and comply with the regulations. A range of services is provided including educational workshops targeted at consultants to provide detailed information and greater understanding of compliance requirements. Producer workshops have focused on providing updated information and immediate deliverable requirements. The curriculum developed has been reviewed by RB5 staff. When possible, example documents and templates have been created to assist operators and their consultants to comply with the General Order. Lastly, CDQAP also provides a voluntary evaluation program with certification available for facilities and managers meeting local, state and federal environmental requirements.

RB5 also provided funding to Merced County to create and maintain on-line forms tailored to meet annual reporting requirements.

Limited financial assistance is also available for dairy operators for planning and implementation on a cost-share basis. The USDA Natural Resources Conservation Service (NRCS) Farm Bill conservation programs are a key funding source.

From 2008 – 2010, NRCS invested $32.5 million for 1,064 contracts with California dairy and other livestock farmers to implement conservation practices that will help them comply with regulations, manage and use the manure from their animals to fertilize their crops, and improve water quality. The key farm bill programs are Environmental Quality Incentives Program (EQIP), Cooperative Conservation Partnership Initiative (CCPI), and the Agricultural Water Enhancement Program (AWEP – a partnership program with Western United Dairymen).

These programs provide funds on a cost-share basis. Most operators must provide 50% of the cost in order to receive funds. Some of the common practices are concrete stacking pads which reduce leaching to groundwater; manure transfer pipelines which increase the ability to evenly distribute liquid manure to land; flow meters and other devices so that manure applications can be precisely measured; mechanical separators which reduce solids getting in to ponds and tail-water return systems which capture drainage water and return it to the field. Waste management plans are also a cost-share practice; in 2009, NRCS was able to fund the development of more than 600 waste management plans.

Dairy trade associations have also been awarded funds through Farm Bill programs mentioned above. In addition, the California Dairy Campaign received $750,000 in NRCS Conservation Innovation Grant funds to provide compliance assistance.

Limited assistance was also available through Proposition 50 grant funds administered by the State Water Resources Control Board. Both Western United Dairymen and the California Dairy Campaign had programs to assist dairy operators obtain grant funding for necessary improvements in manure management.

The amount of financial assistance that an operator receives varies widely. Because funds are limited, screening and ranking criteria for the programs are subject to change each year and not all operators apply for or receive funding; these funds are not included as a potential offset in the total costs table below. However, it is important to know that funds may be available for those who apply, and that funding is critically important.

However even with the significant amount of funds available, supply is insufficient to meet current demand. In 2010, the NRCS EQIP dairy programs were largely over-subscribed with 200 applicants placed on waiting list or placed in the pool for following year's application. From 2008 – 2010 only 50% of funding applications for these programs were approved.

10. Analysis and Conclusions

Table 3 presents a total of all the costs of compliance with the General Order. Again it should be emphasized that these costs are estimates and that they are likely to rise in the 2011 and beyond when groundwater monitoring is fully implemented and dairies invest in capital improvements identified in the WMP's.

The table is divided into one-time costs and annual (reoccurring) costs. One-time costs are those associated with specific deliverables such as the NMP and the WMP. Annual costs occur each year as long as the dairy is in operation and has a permit from RB5.

As discussed above there is uncertainty about the additional groundwater monitoring program. Table 3 below includes estimated for both the representative and individual approaches. If the representative program is approved, we expect a majority of dairy producers to join this program; due to its significantly lower costs.

Not including the costs for additional groundwater monitoring, the average one-time costs for operators range from $2,750 to $35,984 with an average of $12,567. Average annual costs range from $3,006 to $42,440 with an average of $14,136. Groundwater monitoring will add significantly to the cost of the program. Total one-time compliance costs including individual groundwater monitoring will range from $45,250 to $77,984 with an estimated average of $55,067 with annual compliance costs of $8,006 to $47,440 with an average cost of $19,136.

Based on the data in Table 3, and using 2007 as the beginning date when compliance costs began, an "average" dairy of 1,000 cows has spent approximately $55,000 in compliance costs; while a larger dairy with more crop fields may have spent $160,000 or more.

In 2007, estimates of the cost of compliance with the General Order were made by Dairy CARES and RB5 as the General Order was being developed. Dairy CARES estimated that the cost of compliance would be $49,780 for one-time costs and $33,570 for costs that will occur annually for as long as the dairy is producing.

In 2007, RB5 estimated $41,700 for up-front costs and $33,300 reoccurring. While it appears that CDFA's estimates are lower - direct comparisons to Dairy CARES and RB5 are problematic because of differences in study methodology.

While this paper provides compliance costs for water quality concerns, dairy operators are also faced with air quality regulations and associated compliance costs from the San Joaquin Valley Air Polltion Control District. CDFA will examine these regulations and costs in future studies.

Table 3. Range of Cost Estimates for Central Valley Dairy Operators to Comply with WDR.

	ONE-TIME COSTS [1]			ANNUAL COSTS [2]		
	LOW	HIGH	AVERAGE	LOW	HIGH	AVERAGE
Existing Conditions Report & Preliminary Dairy Facility Assessment (2007)	$500	$1,484	$992	n/a	n/a	n/a
Waste Management Plan (2010)	$2,000	$27,000	$8,280	n/a	n/a	n/a
Nutrient Management Plan (2009)	$250	$7,000	$3,295	n/a	n/a	n/a
Monitoring and Reporting Program						
Laboratory Sampling and Analysis	n/a	n/a	n/a	$1,500	$15,000	$3,350
Monthly Inspections	n/a	n/a	n/a	$600	$9,600	$5,148
Annual Report	n/a	n/a	n/a	$150	$3,000	$810
RWQCB Annual Discharge Fee[3]	n/a	n/a	n/a	$420	$5,600	$1,680
Dairy Labor[4]	n/a	n/a	n/a	$336	$9,240	$3,148
SUBTOTAL	**$2,750**	**$35,484**	**$12,567**	**$3,006**	**$42,440**	**$14,136**
Representative Groundwater Monitoring Program[5]	$500	$500	$500	$664	$972	$818
Additional Groundwater Monitoring (individual)[6]	$42,500	$42,500	$42,500	$5,000	$5,000	$5,000
TOTAL COMPLIANCE COSTS - Representative Groundwater Monitoring Program	**$3,250**	**$35,984**	**$13,067**	**$3,670**	**$43,412**	**$14,954**
TOTAL COMPLIANCE COSTS - Individual Groundwater Monitoring	**$45,250**	**$77,984**	**$55,067**	**$8,006**	**$47,440**	**$19,136**

[1] One-time costs meet specific deliverables in the General Order.

[2] Annual costs will re-occur each year.

[3] 2009-2010 RWQCB Waste Discharge Fee; http://www.swrcb.ca.gov/resources/fees/docs/confined_animal_facilities_fees.pdf

[4] Work done on dairy by employee and/or managers taking samples, filling out reports, etc.

[5] Estimated enrollment and annual fees for Representative Program

[6] Estimated cost ($42,500) well plan, drilling of at least 3 wells, annual sampling and analysis, and $5,000 per year for reporting.

Table 4. Total Cost Estimates of General Order by RB5 and CARES, 2007

Requirement	RB5 Upfront (one-time)	RB5 Annual (reoccurring)	CARES Estimate Upfront (one-time)	CARES Estimate Annual (reoccurring)
Existing Conditions Report	$2,100	$0.00	$2,000	$0
Waste Management Plan	$11,400	$0.00	$9,400	$0
Nutrient Management Plan	$800	$3,800	$2,700	$3,500
Monitoring and Reporting	$27,400	$29,500	$35,680	$30,070
Total Costs	**$41,700**	**$33,300**	**$49,780**	**$33,570**
Cost Range	**$12,000 to $56,000**	**$30,000 to $36,000**		

RB5, 2007 and CARES 2007

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James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT "F"

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UCRL-TR-223509

California GAMA Program: Impact of Dairy Operations on Groundwater Quality

Bradley K. Esser,
Harry R. Beller,
Steven F. Carle,
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Roald N. Leif,
Tracy E. LeTain,
Walt M. McNab,
Jean E. Moran

Prepared in cooperation with the
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

August 8, 2006 (Draft)
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Auspices Statement

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LAWRENCE LIVERMORE NATIONAL LABORATORY

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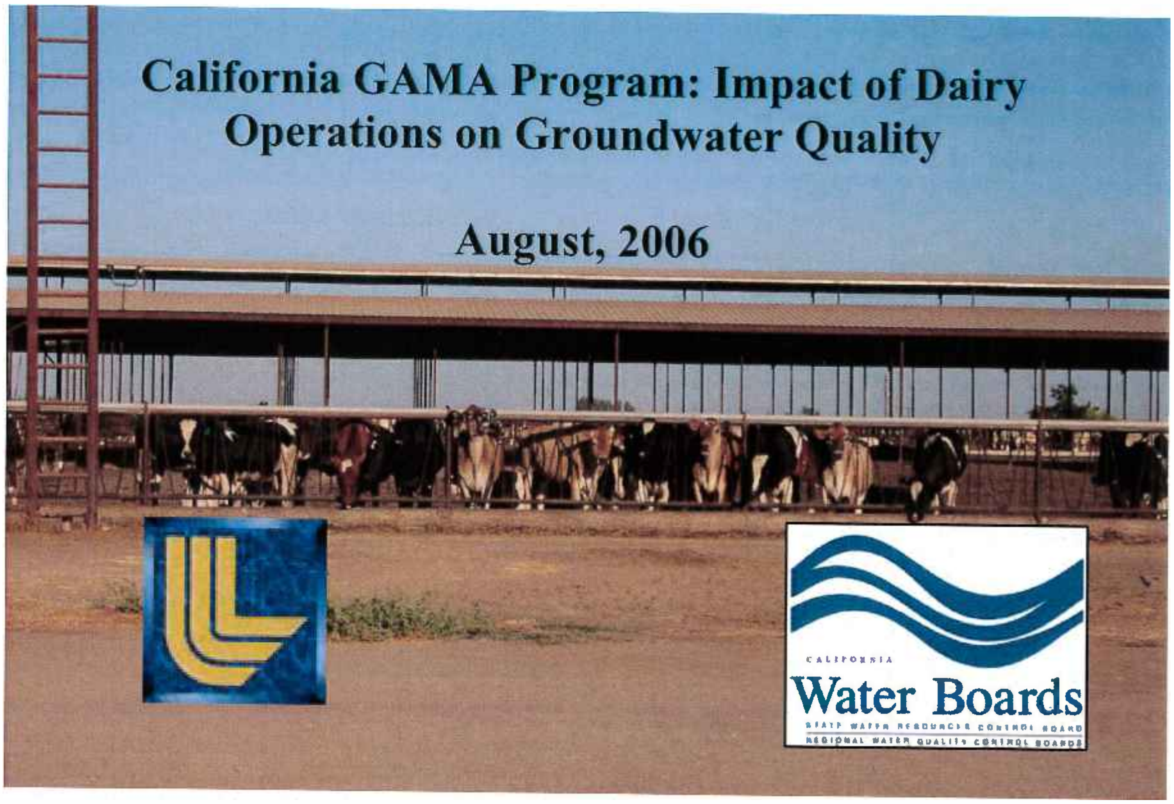
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD



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California GAMA Program: Impact of Dairy Operations on Groundwater Quality

Bradley K. Esser, Harry R. Beller, Steven F. Carle, G. Bryant Hudson, Staci R. Kane, Roald N. Leif, Tracy E. LeTain, Walt M. McNab and Jean E. Moran
Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550

Table of Contents

EXECUTIVE SUMMARY .... **Error! Bookmark not defined.**
STUDY SITES: HYDROGEOLOGIC SETTING 5
  Northern Sites 5
  Southern Sites 7
STUDY SITES: SAMPLING AND INSTRUMENTATION 8
  Kings County Dairy Site 1 (KCD1) 8
  Kings County Dairy Sites 2 and 3 (KCD2 and KCD3) 11
  Merced and Stanislaus Dairy Sites (MCD and SCD) 11
METHODS 11
  Cone Penetrometer (CPT) and Direct Push (DP) Methods 11
  Standard Drilling Methods 12
  Sample Collection and Field Parameters 13
  Chemical Composition Analysis 13
  Stable Isotope Mass Spectrometry 14
  Membrane Inlet Mass Spectrometry (Excess N_2) 14
  Noble Gas Mass Spectrometry ($^3H/^3He$ dating) 15
  Quantitative Real-Time Polymerase Chain Reaction (rt-qPCR) 16
  Wastewater Co-Contaminants 16
DATA 17
  Sediment Data 17
  Bacterial Population Data 17
RESULTS AND DISCUSSION 21
  Saturated-Zone Denitrification at KCD1 and MCD 21
  Spatial Distribution of Saturated-Zone Denitrification at KCD1 21
  Saturated-Zone Denitrification at the Northern Dairy Sites 23
  The Impact of Dairy Manure Lagoons on Groundwater Quality 24
  A New Tracer for Manure Lagoon Seepage 24
  Source, Fate and Transport of Dairy Nitrate at KCD1 26
  The Impact of Lagoon Seepage on Groundwater Quality 28
  The Impact of Dairy Wastewater Irrigation on Groundwater Quality 29
  The Impact of Pumping and Wastewater Irrigation on Groundwater Quality 32
  The Development of Reducing Conditions in Dairy Site Groundwaters 40
CONCLUSIONS 42
PUBLICATIONS AND PRESENTATIONS 43
REFERENCES 45

List of Figures

Figure 1. Dairy Field Sites in the Central Valley ... 6
Figure 2. KCD1 Dairy Field Site. ... 9
Figure 3. KCD1 field site with CPT/DP locations ... 10
Figure 4. KCD Field Site CPT Logs. ... 12
Figure 5. KCD1 Well Cluster 1 sediment composition, texture & groundwater oxidation state . 18
Figure 6. KCD1 depth profiles of sediment and water properties. ... 19
Figure 7. KCD1 depth profiles of nitrogen speciation and bacterial populations. ... 20
Figure 8. KCD1 site saturated-zone denitrification. ... 22
Figure 9. KCD1 and KCD2 manure lagoon dissolved argon content ... 25
Figure 10. Dissolved argon and oxygen at KCD2. ... 26
Figure 11. Simulation of transport of lagoon seepage through groundwater. ... 28
Figure 12. Simulation of dairy wastewater percolation through sediment. ... 30
Figure 13. Simulation of denitrification associated with dairy wastewater percolation. ... 31
Figure 14. Geostatistical representation of the subsurface at KCD1. ... 34
Figure 15. Simulation of groundwater flow at KCD1. ... 36
Figure 16. Simulation of transport at KCD1 ... 37
Figure 17. Simulation of apparent groundwater age at KCD1. ... 38
Figure 18. Comparison of measured and simulated groundwater ages at KCD1. ... 39

List of Tables

Table 1: KCD2, KCD3, & SCD Site Data ... 49
Table 2: KCD1 Site Sediment C, S Data ... 50
Table 3. KCD1 Sediment PCR Data ... 51

Appendices

Appendix A: Singleton, M. J., Esser, B. K., Moran, J. E., Hudson, G. B., McNab, W. W., and Harter, T., 2007. Saturated zone denitrification: Potential for natural attenuation of nitrate contamination in shallow groundwater under dairy operations. *Environmental Science & Technology* **41**, 759-765.

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EXECUTIVE SUMMARY

A critical component of the California State Water Board's Groundwater Ambient Monitoring and Assessment (GAMA) Program is to assess the major threats to groundwater resources that supply drinking water to Californians (BELITZ et al., 2003). Nitrate is the most pervasive and intractable contaminant in California groundwater and is a focus of special studies under the GAMA program.

This report assesses the impact of Central Valley dairy operations on underlying groundwater quality and on groundwater processes using new tools developed during the course of the study. During the investigation, samples were collected and analyzed from a total of five dairies in the San Joaquin-Tulare Basins of California: three in Kings County, one in Stanislaus County, and one in Merced County (Figure 1). The study investigated water samples from production wells, monitor wells, and manure lagoons..

The three primary findings of this research are that dairy operations do impact underlying groundwater quality in California's San Joaquin Valley, that dairy operations also appear to drive denitrification of dairy-derived nitrate in these groundwaters, and that new methods are available for characterization of nitrate source, transport and fate in the saturated zone underlying dairy operations.

This study demonstrated groundwater quality impact at three sites using a multi-disciplinary approach, and developed a new tool for source attribution in dairy groundwater. Negative groundwater quality impacts from dairy-derived nitrate were demonstrated using groundwater chemistry, nitrate isotopic composition, groundwater age, and transport modeling. A significant advance in characterization of groundwaters for nitrate source determination was the use of groundwater dissolved gas content to distinguish dairy wastewater irrigation from dairy wastewater lagoon seepage, both of which contributed to dairy groundwater contamination.

The demonstration of saturated-zone denitrification in dairy groundwaters is important in assessing the net impact of dairy operations on groundwater quality. The extent of denitrification can be characterized by measuring "excess" nitrogen and nitrate isotopic composition while the location of denitrification can be determined using a bioassay for denitrifying bacteria that developed in this research. In both northern and southern San Joaquin Valley sites, saturated-zone denitrification occurs and mitigates the impact of nitrogen loading on groundwater quality.

Other new methods developed during the course of this study include the field determination of denitrification in groundwater (allowing siting of monitor wells and mapping of denitrifying zones) and characterization of aquifer heterogeneity using direct-push drilling and geostatistics (allowing development of more accurate groundwater transport models). Application of these new methods in conjunction with traditional hydrogeologic and agronomic methods will allow a more complete and accurate understanding of the source, transport and fate of dairy-derived nitrogen in the subsurface.

STUDY SITES: HYDROGEOLOGIC SETTING

Two concentrations of dairies exist in the Central Valley of California, which is a low relief structural basin that is from 60 to 100 km wide and 700 km long. Both centers are in the southern two-thirds of the basin - the northern concentration is in Merced and Stanislaus Counties, and the southern concentration is in Kings and Tulare Counties. Both concentrations of dairies occur in the San Joaquin Valley Groundwater Basin, as designated by the California Department of Water Resources (2003). The San Joaquin Valley groundwater basin comprises two of the Central Valley's three large structural sub-basins: the San Joaquin Basin and the Tulare Basin. In this document, we will use "San Joaquin Valley Basin" and "San Joaquin-Tulare Basin" interchangeably.

During the investigation, samples were collected and analyzed from a total of five dairies in the San Joaquin-Tulare Basins of California: three in Kings County, one in Stanislaus County, and one in Merced County (Figure 1). Groundwater samples were collected from production wells on each of the dairies. On three of the dairies, samples were also collected from monitoring wells: one of sites in Kings County was instrumented by LLNL, and the two sites in Stanislaus and Merced Counties were instrumented by UC-Davis. Samples were collected from manure lagoons at four of the sites.

Northern Sites

The two northern sites (SCD and MCD) are part of an extensive shallow groundwater monitoring network on five representative dairies set up by Thomas Harter of UC-Davis and the UC Cooperative Extension. The following description of the study area and the dairies is adapted from Harter et al. (2002).

The northern sites study area is in the central-eastern portion of the northern San Joaquin Valley, an area of low alluvial plains and fans bordered by the San Joaquin River to the west, tertiary upland terraces to the east, the Stanislaus River to the north, and the Merced River to the south. The region has a long history of nitrate and salt problems in groundwater (LOWRY, 1987; PAGE and BALDING, 1973).

The main regional aquifer is in the upper 100-200 m of basin deposits, which consist of Quaternary alluvial and fluvial deposits with some interbedded hardpan and lacustrine deposits. Groundwater generally flows from the ENE to the WSW following the slope of the landscape. The average regional hydraulic gradient ranges from approximately 0.05% to 0.15%. The water table at the selected facilities is between 2 and 5 m below ground surface. Measured K values range from 0.1 to 2 x 10^{-3} m/s, as consistent with the predominant texture of the shallow sediments.

The dominant surface soil texture is sandy loam to sand underlain by silty lenses, some of which are cemented with lime. Water holding capacity is low and water tables are locally high (and maintained by community drainage systems and shallow groundwater pumping). Border flood irrigation of forage crops has historically been the dominant cropping system among dairies in the study area. Low-salinity (0.1–0.2 μS/cm) surface water from the Sierra Nevada is the main source of irrigation water.

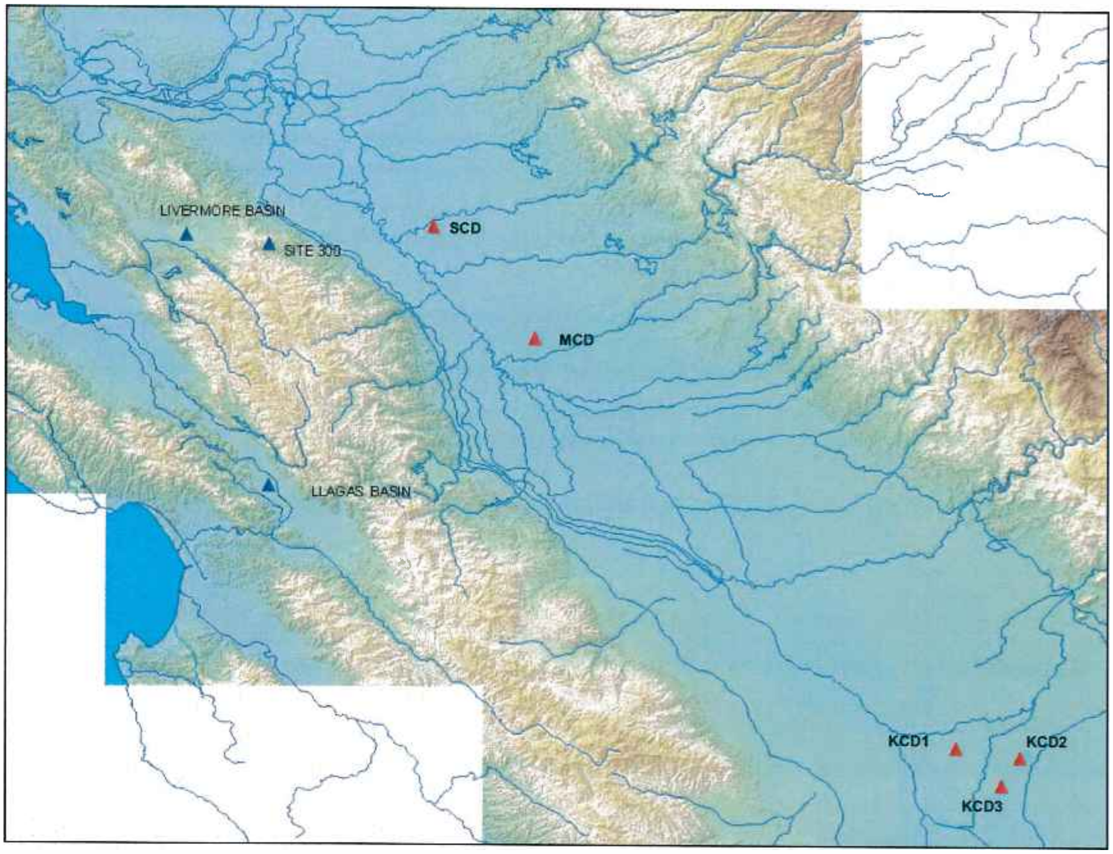

Figure 1. Dairy Field Sites in the Central Valley.

Dairy Field Sites in the Central Valley Dairy study sites in Kings County (KCD1, KCD2, and KCD3), Merced County (MCD) and Stanislaus County (SCD) are shown with red triangles. Other sites where LLNL has conducted groundwater nitrate studies are shown with blue triangles

A number of hydrogeologic criteria make the area suitable as a field laboratory for investigating recharge water quality from dairies: 1) Groundwater in the area is highly vulnerable because of the sandy soils with high infiltration rates and shallow water tables. 2) The shallow groundwater table and small long-term fluctuations in water level (1-2 m) allow sampling from vertically narrow groundwater zones with well-defined recharge source areas. 3) These same two factors also allow installation of a relatively inexpensive fixed-depth monitoring well network that is also inexpensive to sample.

The five dairy facilities in the UC-Davis network are progressive with respect to herd health, product quality, and overall operations. Improvements in manure and pond management have continually occurred since the inception of the project. The dairies are located in a geographic and hydrogeologic environment that is representative of many other dairies on the lowlands of the northern San Joaquin Valley. The manure management practices employed at these dairies over the past 35 years, particularly with respect to corral design, runoff capture, and lagoon management, have been recognized by industry, regulators, and university extension personnel as typical or even progressive relative to other California dairies (see references in HARTER et al., 2002). Over the past 30– 40 years, the herd size on these dairies has continually grown from less than 100 at their inception to over 1000 animal units in the 1990s.

In 1993, UC-Davis installed 6 to 12 monitoring wells on each dairy for a total of 44 wells. Monitoring wells are strategically placed upgradient and downgradient from fields receiving manure water, near wastewater lagoons (ponds), and in corrals, feedlots, and storage areas (henceforth referred to as ''corrals''). Wells are constructed with PVC pipe (3 or 5 cm diameter) and installed to depths of 7–10 m. The wells are screened from a depth of 2–3 m below ground surface to a depth of 10 m. Water samples collected from monitoring wells are representative of only the shallowest "first-encounter" groundwater.

Southern Sites

To augment the UC-Davis dairy monitoring network, LLNL chose to establish sites in the southern San Joaquin Valley groundwater basin. LLNL developed a list a five potential cooperators, sampled three sites, and chose to instrument one site. The cooperators were chosen with the expertise and assistance of the University of California Cooperative Extension (Thomas Harter, Carol Collar and Carol Frate). Sampling sites were chosen from the list of cooperator dairies using regional water quality data, including NAWQA data from the USGS and water quality dairy data from the Central Regional Water Quality Control Board (Fresno office). The site chosen for more extensive instrumentation was chosen with the following criteria: 1) a cooperative operator, 2) a shallow depth to groundwater to allow cost-effective installation of multi-level wells and synoptic soil-groundwater surveys, 3) a dairying operation typical for the region, and 4) regional evidence for nitrate contamination and denitrification.

The three dairies sampled are within the Tulare Lake Groundwater Subbasin of the San Joaquin Valley Groundwater Basin (CALIFORNIA DWR, 2003) (Figure 1). The sites are located south of the Kings River and north-northeast of the Tulare Lake basin, the natural internal drainage for this hydrologically closed system. Groundwater hydraulic gradients are regionally from the Kings River toward Tulare Lake, but are generally low and are locally influenced by recharge from unlined irrigation canals and by agricultural and municipal groundwater extraction. Surface soils at these sites are predominantly Nord series (USDA NATIONAL RESOURCE CONSERVATION SERVICE, 2006), and are developed on distal Kings River alluvial fan deposits (WEISSMANN et al., 2003; WEISSMANN et al., 1999; WEISSMANN and FOGG, 1999; WEISSMANN et al., 2002a), which in general are less sandy and have more fine-grained interbeds than the sediments in the northern UC-Davis monitoring network. Groundwater levels in the area are in general deeper (50-200' below ground surface) and more variable (50' over 2-5 years) than in the north. A deeper depth to groundwater and heavier textured soils indicate that southern groundwaters should be less vulnerable to contamination than northern groundwaters. The regional groundwater is highly impacted by agricultural activities and contains elevated concentrations of nitrate and pesticides (BUROW et al., 1998b; BURROW et al., 1998).

Two of the three dairies sampled (KCD2 and KCD3) have deep water tables typical of the region. The one dairy that LLNL instrumented is located in an area to the west of Hanford characterized by a shallow perched aquifer, with depth to groundwater on the order of 15 feet. California Department of Water Resources (DWR) water level data for wells in the area indicate that this perched aquifer developed in the mid-1960's in response to local groundwater overdrafting (CARLE et al., 2005), and is separated by an unsaturated zone from the deeper regional aquifer (that is sampled by wells on KCD2 and KCD3 to the east and south of Hanford).

The three dairy sites sampled by LLNL in Kings County each have close to the average of 1000 dairy cows, fed in free stalls with flush lanes. The manure management practices employed at these dairies, with respect to corral design, runoff capture, and lagoon management, are typical or progressive relative to other California dairies (see references in HARTER et al., 2002). The most intensively studied dairy, KCD1, operates three clay-lined wastewater lagoons that receive wastewater after solids separation. Wastewater is used for irrigation of 500 acres of forage crops (corn and alfalfa) on the dairy and on neighboring farms; dry manure is exported to neighboring farms. This dairy is also immediately adjacent to another dairy operation, and many of the conclusions regarding nitrate impact apply to dairy practices shared by both operations.

STUDY SITES: SAMPLING AND INSTRUMENTATION

Kings County Dairy Site 1 (KCD1)

Kings County Dairy #1 (KCD1; see Figure 1, Appendix A-Figure 1, and Appendix B-Figure 1), was the primary site in Kings County, and was sampled on multiple occasions, from existing production wells, from LLNL-installed monitor wells, from manure lagoons and irrigation canals, and with direct push soil and water sampling methods. A total of 31 days were devoted to collecting 139 water samples at the site, including 29 direct push samples, 17 surface water samples from 3 manure lagoons and a nearby irrigation canal, 16 groundwater samples from 9 production wells, and 60 groundwater samples from 17 monitor wells. A large number of subsurface soil samples were also collected, both as continuous drill core and as depth-discrete grab samples. Production and monitor wells were sampled on semi-regular intervals between August 2003 and August 2005.

KCD1 was instrumented with five sets of multi-level monitoring wells and one "up-gradient" well near an irrigation canal (Figure 2). The multi-level well "clusters" consisted of wells installed in separate boreholes approximately 5' apart. A first set of three nested 2" wells in one cluster was installed in September 2003. In August 2004, three new well clusters were installed, each with four 2" wells. Also at that time, an upgradient 2" well was installed, and a small cluster of three 1.25" wells were installed. Two aquifers underlie the KCD1 dairy site, a shallow perched aquifer and a more regionally extensive deep aquifer. The deep aquifer is instrumented with one 2" well screened at 178-180' below ground surface (bgs) that was installed in September 2003. The remaining monitor wells are all in the shallow perched aquifer and are screened between 18' and 65' bgs.

In August 2004, shortly before the second sets of well clusters were installed, a CPT/DP survey (see methods section) was conducted across the site (Figure 3). Depth discrete water and soils samples were collected at this time, after which the holes were grouted and abandoned. With the exception of the upgradient monitor well near the canal, CPT/DP sites included locations near all of the multi-level monitor well clusters.

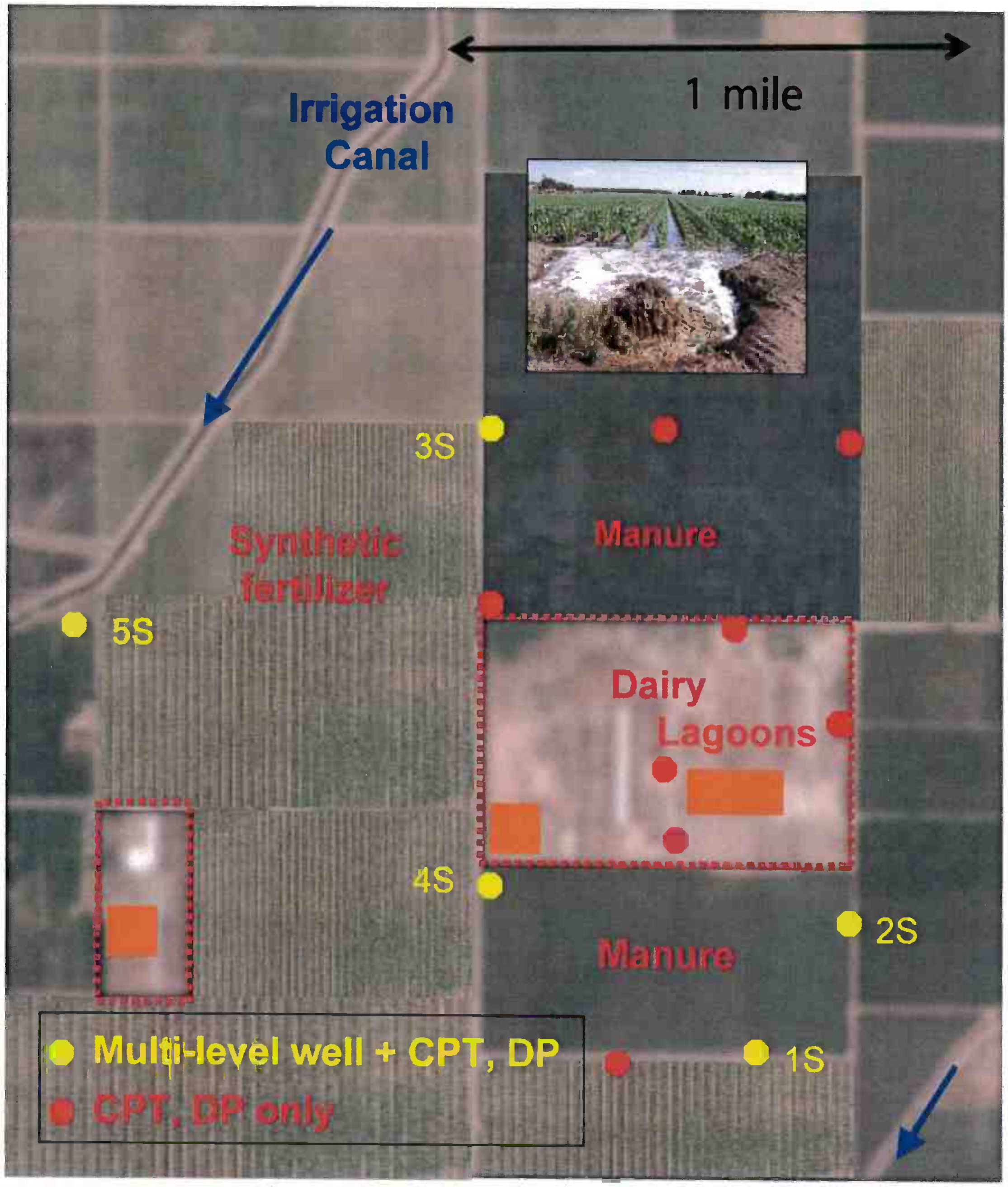

Figure 2. KCD1 Dairy Field Site.

KCD1 site, showing monitor wells and direct-push locations. Sites 1, 2, 3, and 4 (S1 through S4) are all multi-level two-inch monitor well clusters; site 5 (S5) is a single two-inch first-encounter well. The Site 1 cluster (S1) also includes a well in the deep aquifer. Direct-push (DP) and cone penetrometer (CPT) holes are also shown. CPT/DP was done at all multi-level well sites; it was not done at the single-level 5S site. Inset shows application of manure lagoon wastewater for furrow irrigation of silage corn crops at the site.

The production wells are screened in both the shallow and deep aquifer, and have 20-30' long screens. Domestic supply wells, one of which was sampled, are screened in the deep aquifer, and typically have 20' long screens. Agricultural supply wells, eight of which were sampled, typically have 30' long screens, with the top of the screen at 30' bgs. Information on screen length and depth is from conversations with the water well company which installed the more recent wells and has extensive experience in the region.

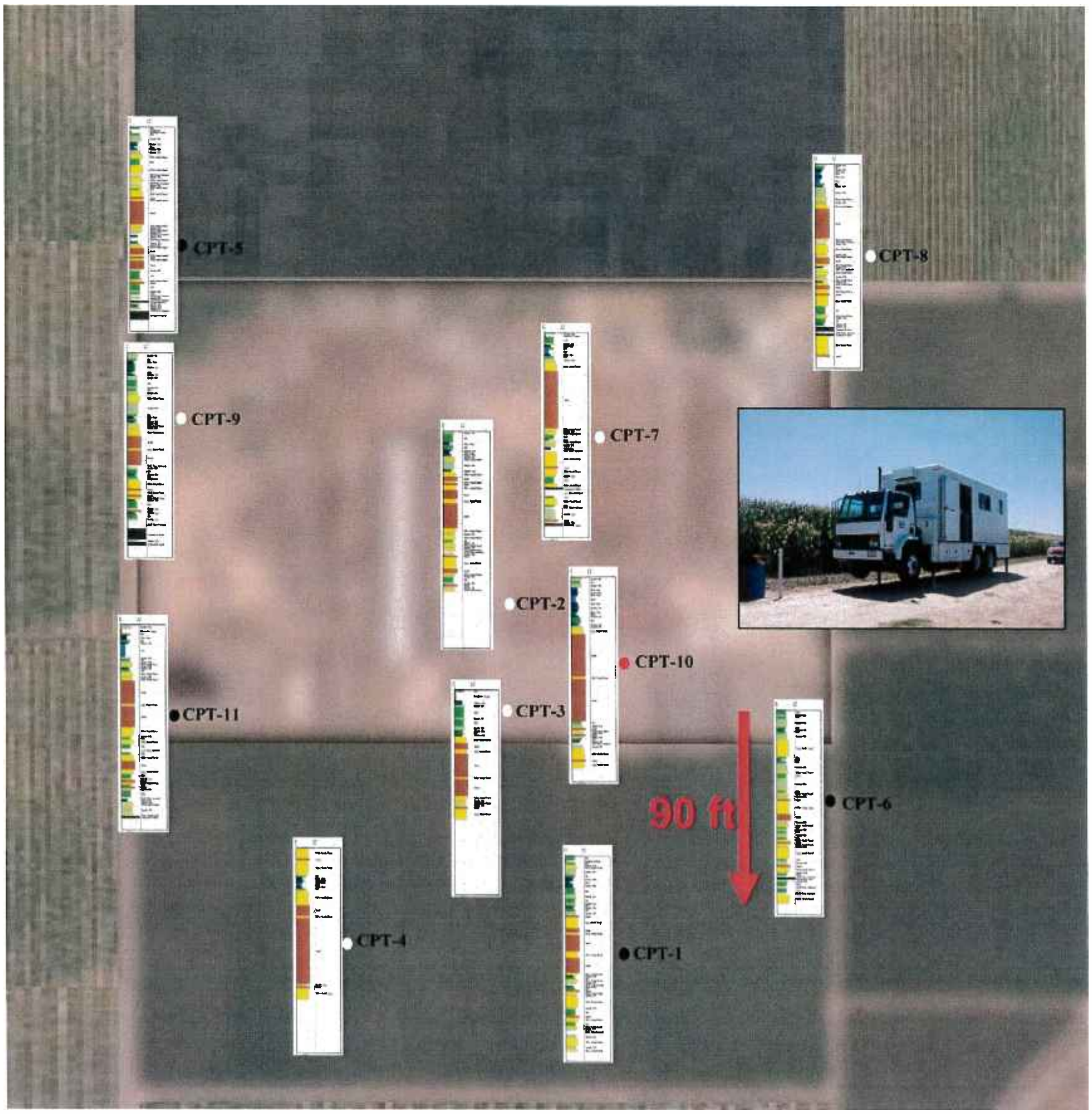

Figure 3. KCD1 field site with CPT/DP locations.

Soil Behavior Type (SBT) profiles from Direct-Push Cone Penetrometer Testing on the KCD1 dairy field site. Large inset shows direct-push rig.

Kings County Dairy Sites 2 and 3 (KCD2 and KCD3)

The second and third Kings County dairy sites (Figure 1) were sampled during initial screening of Kings County sites in August 2003. At each site, groundwater pumped from a domestic supply well was analyzed for inorganic cations and anions (including nitrate, nitrite and ammonia), dissolved gases by membrane-inlet mass spectrometry, and tritium/helium-3 mean groundwater age by noble gas mass spectrometry. Groundwater in the area is 120-150 feet below ground surface, and the Corcoran Clay is generally 400-450' below ground surface and 90-100' thick. At each site, groundwater was sampled from wells screened between 200 and 300 feet below ground surface.

The second dairy was sampled again in April 2005. On this occasion, groundwater from the same domestic supply well sampled in 2003 was re-sampled, and manure lagoon and field water from six sampling locations was sampled. The groundwater was analyzed as before; while the lagoon water samples were analyzed for inorganic cations and anions (including nitrate, nitrite and ammonia), and dissolved gases by membrane-inlet mass spectrometry.

Merced and Stanislaus Dairy Sites (MCD and SCD)

MCD and SCD (Figure 1, Appendix A-Figure 1: The Merced County and Stanislaus County Dairies (MCD and SCD) were sampled on three occasions: August 2003, April 2005 and June 2005. Almost 40 samples were taken broken down as follows: 30 MCD samples and 9 SCD samples; 28 groundwater samples from 22 wells, 1 lagoon water sample, and 1 tile drain sample. Groundwater samples were analyzed for field parameters (temperature, conductivity, dissolved oxygen and ORP); inorganic cations and anions (including nitrate, nitrite and ammonia), dissolved gases by membrane-inlet mass spectrometry, tritium/helium-3 mean groundwater age by noble gas mass spectrometry, stable isotopic composition of nitrate and water, and organic co-contaminants. Tritium/helium-3 samples were not taken from the surface water sampling sites. These sites and data from these sites are described in Harter et al. (2002)

METHODS

Cone Penetrometer (CPT) and Direct Push (DP) Methods

Standard cone penetrometer/direct push methods were used to characterize the shallow hydrostratigraphy at the site. The survey was accomplished using a 20-25 ton CPT rig and accompanying support rig. The dead weight of the CPT rig was used to push the cone penetrometer to depths up to 90 feet using a hydraulic ram located at the center of the truck. Soil parameters such as cone bearing, sleeve friction, friction ratio and pore water pressure were measured as the cone penetrometer was advanced. These measurements were sent through the cone rods to the CPT rig's on-board data acquisition system. All data was processed in real time in the field, and CPT plots of tip resistance, sleeve friction; friction ratio and pore pressure were provided in the field along with a table of interpreted soil parameters. For development of geostatistical models of subsurface hydraulic properties, soil behavior types determined by CPT (ROBERTSON et al., 1983) were calibrated and validated against a 200-foot continuous core log recovered from the first site (Figure 4.)

After CPT logging, a second hole was developed for collecting depth-discrete groundwater and soil samples using direct push methods. For water, a Hydropunch groundwater sample was taken at specified depth intervals. The Hydropunch operates by pushing 1.75-inch diameter hollow rods with a steel tip. A filter screen is attached to the tip. At the desired sampling depth, the rods are retracted, exposing the filter screen and allowing for groundwater infiltration. A small diameter bailer is then used to collect groundwater samples through the hollow rod. Typically, 4 or more 40 ml VOA vials were collected. For soil, a piston-type soil sampler was used to collect undisturbed soil samples (12" long x 1" diameter) that were stored on ice or dry ice immediately upon retrieval. After completion of logging and sampling, CPT/DP sampling holes were grouted under pressure with bentonite using the support rig.

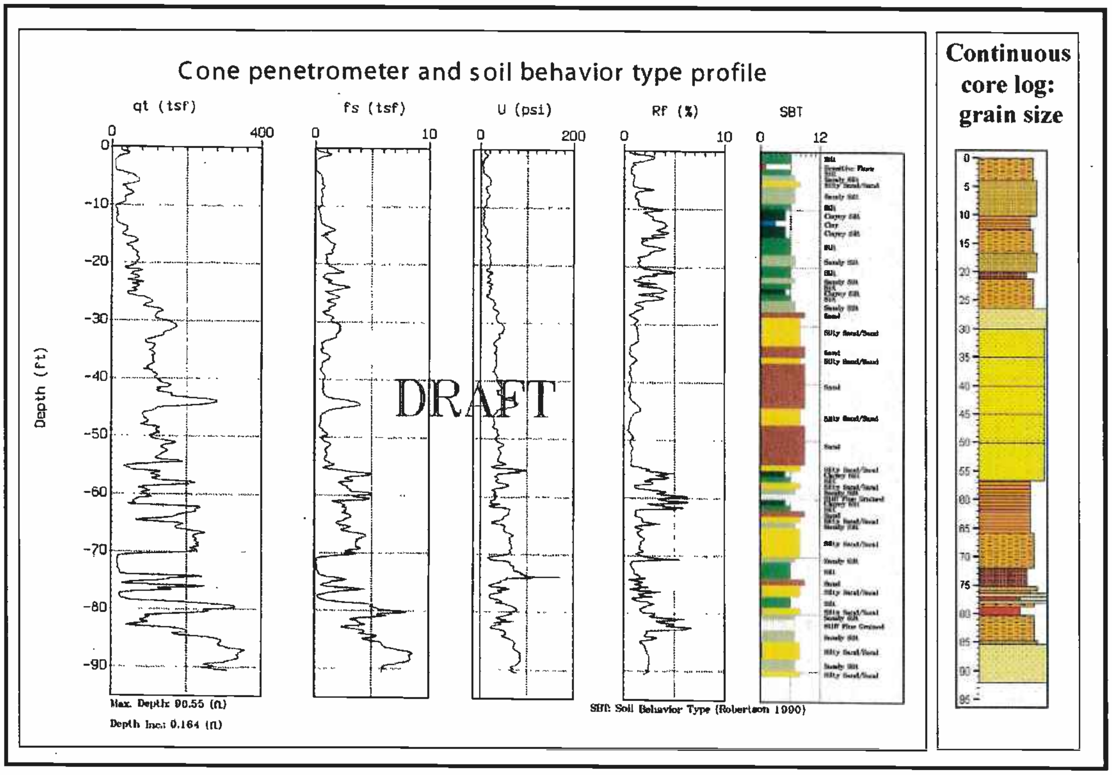

Figure 4. KCD Field Site CPT Logs.

Comparison of soil behavior type (SBT) profile derived from CPT data to sediment texture profile as logged by a State of California certified drilling geologist at the KCD1 Site 1. Depth is shown in feet below ground surface. The thick sequence of sand between 25 and 55 feet shows up in both profiles, as does the confining unit at about 80 feet.

Standard Drilling Methods

Monitor wells were emplaced using standard methods. The first and deepest 200-foot bore-hole was drilled with a mud-rotary rig; subsequent wells were drilled using hollow-stem auger. In the deep 200-foot hole, continuous log core was recovered and logged by a State-certified geologist (Figure 4) and down-hole geophysical data were obtained, including caliper, gamma ray, electro-magnetic induction, and spontaneous potential and resistivity logs. Wells were cased with either 2" or 1.25" PVC pipe with short (generally 2') slotted screens and sand packs, and completed with a sanitary seal. Early wells (installed in 2003) were completed with stovepipe installation, which were subsequently converted to ground-level flush-mount installations in 2004 to accommodate farm activities. All wells installed in 2004 were completed with a flush-mount installation. The 2"-diameter wells were developed using standard bail, surge and pump methods.

Sample Collection and Field Parameters

Groundwater samples were collected after purging the well by either pumping or bailing, after determining water level against a marked datum. Groundwater from production wells was sampled, whenever possible, from upstream of any storage or pressure tank. A variety of methods were used to draw samples from monitor wells, depending on their diameter. Two-inch diameter monitor wells were sampled with a Grundfoss MP-1 submersible pump and Teflon-lined sample line. Smaller 1.25"-diameter monitor wells were sampled with small-diameter Teflon bailers or with a bladder pump and Teflon sample line.

When practical, field measurements of temperature (°C), conductivity (μS/cm), pH, dissolved oxygen (mg/L) and oxidation reduction potential (mV using Ag/AgCl with 3.33 mol/L KCl as the reference electrode) were carried out using a Horiba U-22 ® water quality analyzer. Sampling protocols were specific for different sets of analytes (see sampling sheet in Appendix C), and differed with regard to filtration, sample volume and container, the presence of headspace, and the use of gloves.

Chemical Composition Analysis

Samples for anions and cations were filtered in the field to 0.45 μm, and stored cold and dark until analysis. Anion (NO_3^-, SO_4^{2-}, Cl^-, F^-, Br^-, PO_4^{3-}, NO_2^-) and cation (Ca^{2+}, Mg^{2+}, Na^+, K^+, Li^+, NH_4^+) concentrations were determined by ion chromatography using a Dionex DX-600. Total inorganic and organic carbon (TIC/TOC) was determined on unfiltered samples poisoned with mercuric chloride using a carbon analyzer (OI Analytical TOC Analyzer 1010). Dissolved inorganic carbon (DIC) concentrations were estimated in the water samples by employing the PHREEQC geochemical model (PARKHURST and APPELO, 2002) to achieve charge balance in the samples by adjusting and speciating DIC at the measured pH values. Dissolved organic carbon was also measured in a subset of samples as CO_2 gas pressure after acidification with orthophosphoric acid.

Sediment sulfur and carbon content was determined by elemental analysis by Actlabs (Ancaster, Ontario, Canada). Total C and S were determined on an ELTRA CS 2000 carbon sulfur analyzer. A weighed sample is mixed with iron chips and a tungsten accelerator and is then combusted in an oxygen atmosphere at 1370C. The moisture and dust are removed and the CO_2 gas and SO_2

gas are measured by a solid-state infrared detector. Sulphate S was determined by elemental analysis of the residue from roasting at 850° C. Reduced S was determined by difference. Carbonate C was determined by digestion of the sample in 2 N perchloric acid followed by coulometric titration. Graphitic C was determined by elemental analysis of the residue from roasting at 600° C. Organic C was determined by difference.

Stable Isotope Mass Spectrometry

Samples for nitrate N and O isotopic compositions are filtered in the field to 0.45 μm, and stored cold and dark until analysis. Anion and cation concentrations are determined by ion chromatography using a Dionex DX-600. The nitrogen and oxygen isotopic compositions ($\delta^{15}N$ and $\delta^{18}O$) of nitrate in 26 groundwater samples from KCD1 and MCD were measured at Lawrence Berkeley National Laboratory's Center for Isotope Geochemistry using a version of the denitrifying bacteria procedure (CASCIOTTI et al., 2002) as described in Singleton et al. (SINGLETON et al., 2005). In addition, the nitrate from 34 samples were extracted by ion exchange procedure of (SILVA et al., 2000) and analyzed for $\delta^{15}N$ at the University of Waterloo. Analytical uncertainty is 0.3 ‰ for $\delta^{15}N$ of nitrate and 0.5‰ for $\delta^{18}O$ of nitrate.

Isotopic compositions of hydrogen and oxygen in water ($\delta^{2}H$ and $\delta^{18}O$) were determined at LLNL using a VG Prism II ® isotope ratio mass spectrometer, and are reported in per mil values relative to the Vienna Standard Mean Ocean Water (VSMOW). Isotopic composition of oxygen in water using the CO_2 equilibration method (EPSTEIN and MAYEDA, 1953), and have an analytical uncertainty of 0.1‰. Hydrogen isotope compositions were determined using the Zn reduction method (COLEMAN et al., 1982)

Membrane Inlet Mass Spectrometry (Excess N_2)

Previous studies have used gas chromatography and/or mass spectrometry to measure dissolved N_2 gas (BOHLKE and DENVER, 1995; MCMAHON and BOHLKE, 1996; VOGEL et al., 1981; WILSON et al., 1990; WILSON et al., 1994). Both methods require extraction of a gas sample, which adds time and can limit precision. Membrane inlet mass spectrometry (MIMS) allows precise and fast determination of the concentrations of nitrogen, oxygen and argon dissolved in groundwater samples without a separate extraction step. This method has been used to document denitrification in estuarine and ocean settings (AN et al., 2001; KANA et al., 1994), as well as for detection of volatile organic compounds in water (KETOLA et al., 2002). The MIMS technique has also proven useful for determining excess N_2 from denitrification in groundwater systems (BELLER et al., 2004).

Samples for N_2, O_2, Ar, CO_2 and CH_4 concentration were analyzed by MIMS. A water sample at atmospheric pressure is drawn into the MIMS through a thin silicone rubber tube inside a vacuum manifold. Dissolved gases readily permeate through the tubing into the analysis manifold, and are analyzed using a quadrupole mass spectrometer. Water vapor that permeates through the membrane is frozen in a dry ice cold trap before reaching the quadrupole. The gas abundances are calibrated using water equilibrated with air under known conditions of temperature, altitude and humidity (typically 18 °C, 183 m, and 100% relative humidity). A small isobaric interference from CO_2 at mass 28 (N_2) is corrected based on calibration with CO_2-rich waters with known dissolved N_2, but is negligible for most samples. Typical sample size is 5 mL, and each analysis takes approximately 3 minutes. Dissolved oxygen, methane, carbon dioxide and argon content are measured at the same time as nitrogen. Samples are collected for MIMS analysis in 40 mL amber glass VOA vials, with no headspace, and kept cold during transport. Samples are analyzed within 24 hours to minimize the risk of gas loss or biological fractionation of gas in the sample container. The MIMS is field portable, and can be used on site when fieldwork requires extended time away from the laboratory, or when samples cannot be readily transported to the laboratory.

Noble Gas Mass Spectrometry ($^3H/^3He$ dating)

Dissolved noble gas samples are collected in copper tubes, which are filled without bubbles and sealed with a cold weld in the field. Dissolved noble gas concentrations were measured at LLNL after gas extraction on a vacuum manifold and cryogenic separation of the noble gases. Concentrations of He, Ne, Ar and Xe were measured on a quadrupole mass spectrometer. Calculations of excess air and recharge temperature from Ne and Xe measurements are described in detail in Ekwurzel (2004), using an approach similar to that of Aeschbach-Hertig et al. (2000). The ratio of ^3He to ^4He was measured on a VG5400 mass spectrometer.

Tritium samples are collected in 1 L glass bottles. Tritium was determined by measuring ^3He accumulation after vacuum degassing each sample and allowing three to four weeks accumulation time. After correcting for sources of ^3He not related to ^3H decay (AESCHBACH-HERTIG et al., 1999; EKWURZEL et al., 1994), the measurement of both tritium and its daughter product ^3He allows calculation of the initial tritium present at the time of recharge, and apparent ages can be determined from the following relationship based on the production of tritiogenic helium ($^3He_{trit}$):

$$\text{Groundwater Apparent Age (years)} = -17.8 \times \ln\left(1 + {}^3He_{trit}/{}^3H\right)$$

The reported groundwater age is the mean age of the mixed sample, and furthermore, is only the age of the portion of the water that contains measurable tritium. Average analytical error for the age determinations is ±1 year, and samples with ^3H that is too low for accurate age determination (<1 pCi/L) are reported as >50 years. Loss of ^3He from groundwater is not likely in this setting given the relatively short residence times, lack of water table fluctuations, and high infiltration rates from irrigation. Groundwater age dating has been applied in several studies of basin-wide flow and transport (EKWURZEL et al., 1994; POREDA et al., 1988; SCHLOSSER et al., 1988; SOLOMON et al., 1992). Mean ^3H-^3He apparent ages are determined for water produced from 20 KCD monitor wells at depths of 6 m to 54 m, and from 14 sites at MCD. The apparent ages give a measure of the time elapsed since water entered the saturated zone, but only of tritium-containing portion of the groundwater sample. Apparent ages therefore give the mean residence time of the fraction of recently recharged water in a sample, and are especially useful for comparing relative ages of water from different locations at each site. The absolute mean age of groundwater may be obscured by mixing along flow paths due to heterogeneity in the sediments (WEISSMANN et al., 2002b).

Quantitative Real-Time Polymerase Chain Reaction (rt-qPCR)

We have developed a simple bioassay to quantify populations of denitrifying bacteria in moderate amounts of aquifer material (on the order for a few grams of sediment or filtrate). The method detects the presence of bacterial genes that encode nitrite reductase, a central enzyme involved in denitrification. The assay is not species-specific, but rather a functional test for the presence of bacterial populations capable of nitrite reduction. Nitrite reduction is considered to be the "committed" step in denitrification, and bacteria capable of nitrite reduction are generally also capable of nitric and nitrous oxide reduction to nitrogen gas (TIEDJE, 1988). Currently, the assay provides valuable information on the distribution of denitrifying bacteria populations in aquifers. Ultimately, data on denitrifier populations (i.e., biomass) can be used in combination with specific (i.e., biomass-normalized) denitrification rate constants to determine subsurface denitrification rates.

Real-time, quantitative Polymerase Chain Reaction (rt-qPCR) analysis (Gibson et al., 1996; Heid et al., 1996; Holland et al., 1991), specifically the 5'-nuclease or TaqMan® assay, was chosen for this assay because it offers many advantages over traditional methods used to detect specific bacterial populations in environmental samples, such as DNA: DNA hybridization (Beller et al. 2002). Although most real-time PCR applications to date have involved the detection and quantification of pathogenic bacteria in food or animal tissue, the technique has recently been used to quantify specific bacteria in environmental samples (Hristova et al., 2001; Suzuki et al., 2000; Takai and Horikoshi, 2000).

Real-time qPCR is a rapid, sensitive, and highly specific method. The rt-qPCR assay developed targets two variants of the nitrite reductase gene: *nirS* (Fe-containing nitrite reductase) and *nirK* (Cu-containing nitrite reductase). Homologous gene sequences were used to develop a primer/probe set that encompasses functional *nir* genes of known denitrifying soil bacteria (including heterotrophic and autotrophic species) and that does not result in false positive detection of genes that are not associated with denitrification. The rt-qPCR primers and probes were designed based on multiple alignments of 14 *nirS* and 20 *nirK* gene sequences available in GenBank. During development of the assay, the first nitrite reductase gene (*nirS*) reported in an autotrophic denitrifying bacterium (*T. denitrificans*) was sequenced and amplified, and demonstrated to have high homology to *nirS* in a phylogenetically diverse set of heterotrophic denitrifying bacteria.

Real-time PCR was also be used to quantify total eubacterial population, based on detection of the sequence encoding the eubacterial 16S rRNA subunit, which is specific for bacteria.

Wastewater Co-Contaminants

A number of co-contaminants expected to occur on a dairy farm from the dairy operation proper or from associated field crop production were determined using GC-MS or LC-MS. Co-contaminants targeted included herbicides, pesticides, VOCs, fecal sterols, caffeine and nonylphenol. The analysis of these compounds and a discussion of their distribution at the dairy sites is in Moran et al. (2006).

DATA

Chemical, isotopic, dissolved gas, and groundwater age data for the KCD1 and MCD sites are discussed in Appendix A and Appendix B, and are tabulated in Table 1 of Appendix A and Table 1 of Appendix B. Chemical composition, stable isotope, and groundwater age data for KCD2, KCD3 and SCD2 are tabulated in Table 1 of the main report. In addition, membrane inlet mass spectrometry data for KCD2 is presented graphically in Figures 8 and 9. Neither Appendix A nor Appendix B contains sediment C and S data or bacterial population data, which are discussed below.

Sediment Data

In zones sampled for groundwater at the KCD1 site, sediment texture as determined from well logging, CPT and laser diffraction particle size analysis ranges from sand to clayey silt (with trace to >95% fines). Sedimentary carbonate C is extremely low (generally < 0.003 wt %); organic C is low but generally detectable (0.05-0.10 wt %), although occasional beds have 0.1-1.3% organic C; sulfate S ranges from nondetectable (<0.017) to 0.08 wt%; and reduced S is only detectable in a few wells (<0.01 to 0.15 wt %). For organic C and total S, no strong vertical gradients exist, and no significant difference exists between sediment in the oxic groundwater column, sediment in the anoxic water column, and sediment at the interface. Sediment data are summarized in Table 2, and represented graphically in Figures 5 and 6.

Bacterial Population Data

In this study we use the abundance of the *nir* gene, as determined by rt-qPCR, to map the vertical distribution of denitrifying bacterial populations in the saturated zone. We use the abundance of the eubacterial 16S rRNA gene, as determined by rt-PCR, to map the vertical distribution of total eubacteria in the subsurface. The analyses were performed on soil returned from four locations at the KCD1 dairy during the course of the DP sampling survey in August 2003. Soil samples were placed on ice upon recovery, and subsequently stored frozen until analysis. Total *nir* data are reported as gene copies per 5 g of sediment, and comprise both *nirS* and *nirK* assay results. Total eubacteria data are reported as cells per 5 g sediment. The data are tabulated in Table 3 and in Figure 7.

Relative abundances of *nirS*, *nirK* and eubacteria are consistent with previous studies in non-groundwater systems: *nirS* and *nirK* gene copies typically constitute ~5% and ~0.1% of total bacteria, respectively. Total *nir* abundance varies by almost four orders of magnitude and is not well-correlated with total eubacteria ($R^2 \sim 0.19$ for 5 locations with multiple depths). Peak populations occur either at or below the redoxicline where strong vertical gradients exist in ORP, nitrate and excess nitrogen. Where *nir* abundance is high, total *nir* gene copies tend to constitute a larger fraction of total bacteria (up to 18%).

The presence of high and localized *nir* populations near the interface between oxic high-nitrate groundwater and suboxic low-nitrate groundwater indicates active denitrification is occurring near that interface.

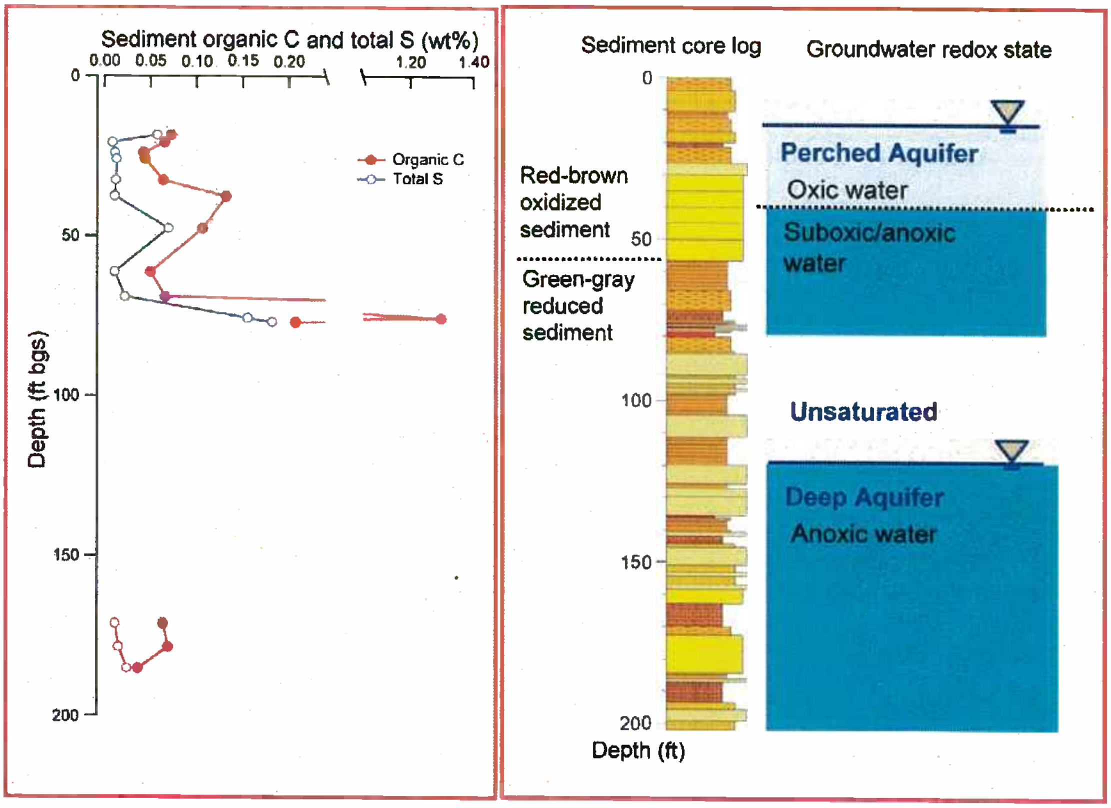

Figure 5. KCD1 Well Cluster 1 sediment composition, texture & groundwater oxidation state
Sediment composition and texture and groundwater oxidation state at KCD1 Site 1. From left to right are shown profiles of sediment organic carbon and total sulfur, sediment iron oxidation state as indicated by sediment color, a continuous core log of sediment texture (yellow sands, brown silty sands, and red silts), the location of the perched and deep aquifer along with groundwater oxidation state (as determined by dissolved oxygen and oxidation-reduction potential probes and the presence of hydrogen sulfide gas).

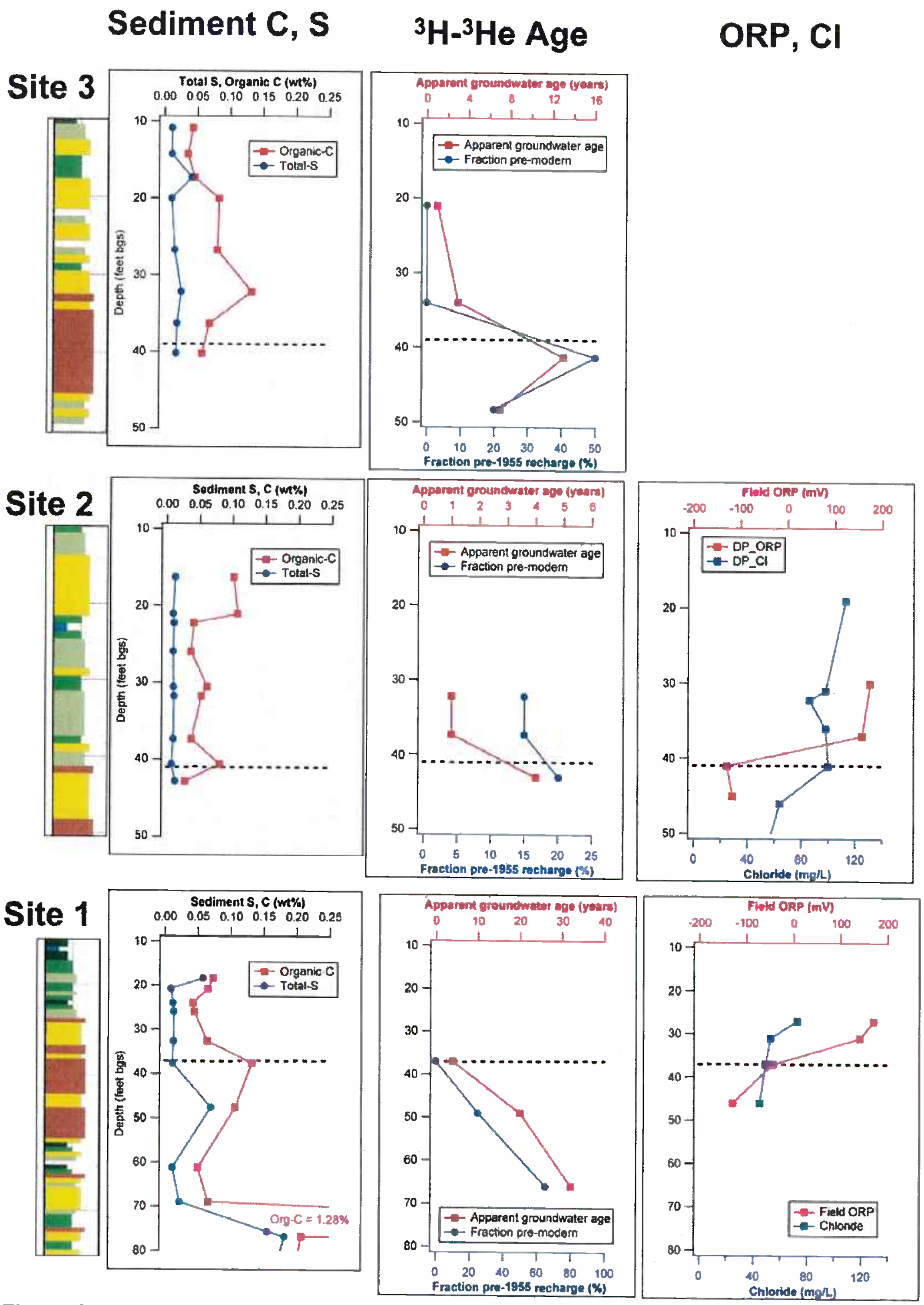

Figure 6. KCD1 depth profiles of sediment and water properties.

KCD1 soil behavior type, sediment organic carbon and total sulfur, ^{3}H-^{3}He groundwater age and fraction pre-modern water, field oxidation-reduction potential (ORP) and dissolved chloride content. The dashed line indicates the transition from nitrate to dissolved nitrogen from denitrification.

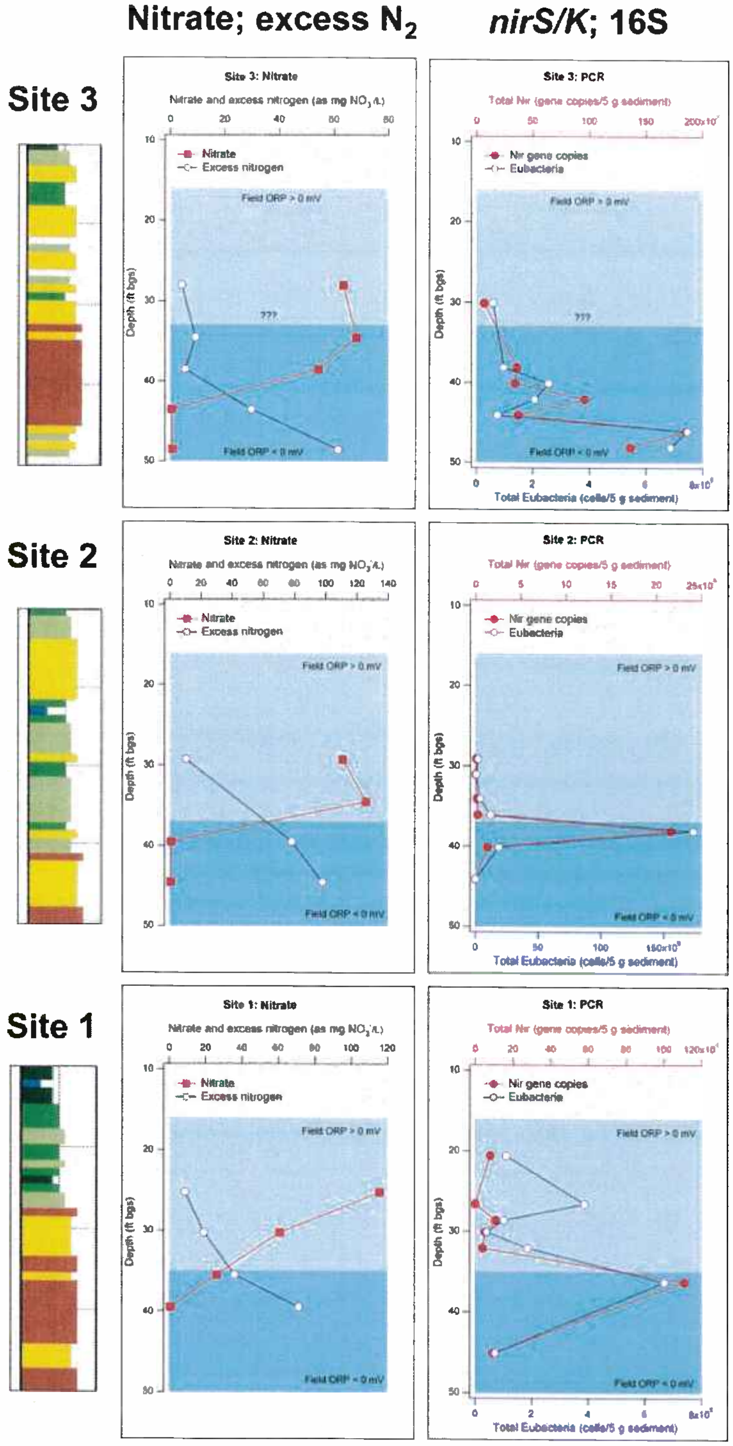

Figure 7. KCD1 depth profiles of nitrogen speciation and bacterial populations.
KCD1 depth profiles of soil behavior type, nitrate, excess nitrogen, total nir gene copies, and total eubacteria. The colored fields indicated water oxidation state based on field ORP.

RESULTS AND DISCUSSION

Saturated-Zone Denitrification at KCD1 and MCD

Appendix A is a manuscript prepared for submittal to a peer-review journal. The manuscript addresses evidence for saturated-zone denitrification in groundwaters impacted by dairy operations. The manuscript abstract follows.

Results from field studies at two central California dairies (KCD1 and MCD) demonstrate the prevalence of saturated-zone denitrification in shallow groundwater with $^3H/^3He$ apparent ages of 30 years or younger. Confined animal feeding operations are suspected to be major contributors of nitrate to groundwater but saturated zone denitrification could effectively mitigate their impact to groundwater quality. Denitrification is identified and quantified using stable isotope compositions of nitrate coupled with measurements of excess N_2 and residual NO_3^-. Nitrate in dairy groundwater from this study has $\delta^{15}N$ values (4.3–61 ‰), and $\delta^{18}O$ values (-4.5–24.5 ‰) that plot with a $\delta^{18}O/\delta^{15}N$ slope of 0.5, consistent with denitrification. Dissolved gas compositions, determined by noble gas mass spectrometry and membrane inlet mass spectrometry, are combined to document denitrification and to determine recharge temperature and excess air content. Dissolved N_2 is found at concentrations well above those expected for equilibrium with air or incorporation of excess air, consistent with reduction of nitrate to N_2. Fractionation factors for oxygen and nitrogen isotopes appear to be smaller ($\varepsilon_N \approx$ -10‰; $\varepsilon_O \approx$ -5‰) at a location where denitrification is found in a laterally extensive anoxic zone 5 m below the water table, compared with a site where denitrification occurs near the water table and is strongly influenced by localized lagoon seepage ($\varepsilon_N \approx$ -50‰; $\varepsilon_O \approx$ -25‰).

Spatial Distribution of Saturated-Zone Denitrification at KCD1

At the KCD1 site, multiple lines of evidence indicate saturated-zone denitrification. These include the presence of excess nitrogen from denitrification at depth, the correlation between nitrate-$\delta^{15}N$ and –$\delta^{18}O$ (which has a slope characteristic of denitrification), and the presence of denitrifying bacteria (which occur at above background levels only where excess nitrogen is present). The lateral extent of denitrification at the site and the excess nitrogen and isotopic evidence for denitrification at the site are discussed in Appendix B. Bacterial distributions give valuable evidence for the localization of denitrification.

Denitrifying bacteria populations at the KCD1 site have a high dynamic range, with peak populations occurring at the oxic-anoxic interface in the perched aquifer where strong gradients in oxidation-reduction potential, nitrate and excess nitrogen exist. Denitrifying bacteria populations are not well correlated with total bacteria (R^2 ~ 0.19 for 5 locations with multiple depths). The relative population abundances of *Nir* gene copies, however, are consistent with previous studies in non-groundwater systems: *nirS* and *nirK* gene copies typically constitute ~5% and ~0.1% of total bacteria.

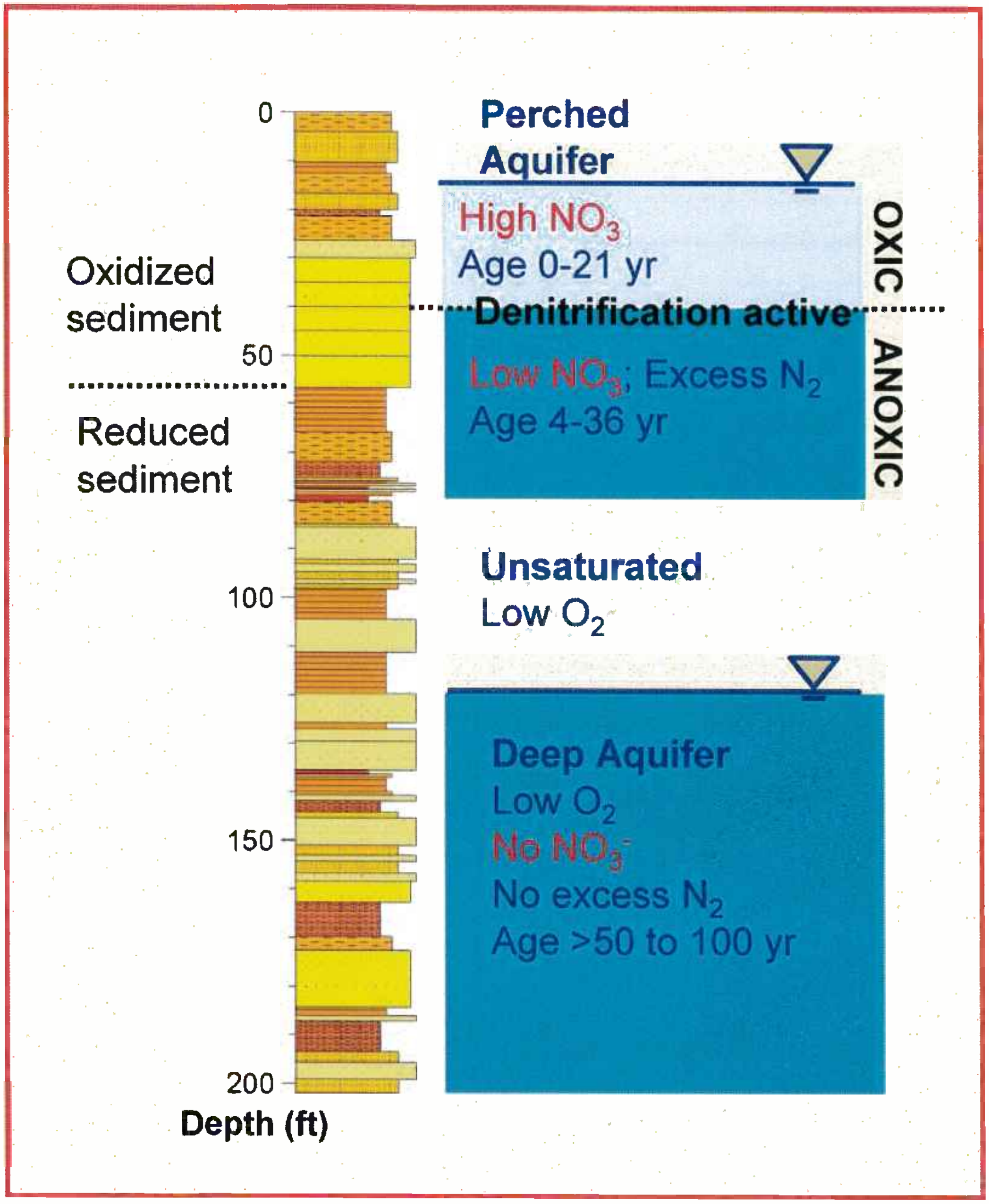

Figure 8. KCD1 site saturated-zone denitrification.

The depth of oxic-anoxic interface is remarkably constant at 37-41 feet below ground surface (Figure 7). This transition is not strongly correlated with lithology or sediment composition (organic-C or total-S content), although it generally occurs in sand. At the irrigated field monitoring sites, the redox interface corresponds to the interface between shallower "young" groundwater (having young apparent ^3H-^3He ages and low mixing ratios of pre-1955 water) and deeper "old" groundwater (with higher fractions of pre-modern water) (Figure 8). The depth of the zone corresponds to the top of several agricultural production pump screens in the area, suggesting that pumping may be a factor.

Saturated-Zone Denitrification at the Northern Dairy Sites

Both of the northern San Joaquin Valley dairy sites (MCD and SCD) are a part of the northern San Joaquin Valley monitoring network described in Harter et al. (2002). Chemical data from these sites have been used to calibrate and validate regional models for nitrogen loading to the shallow groundwater system (VAN DER SCHANS, 2001). The wells sampled are all shallow piezometers that draw first-encounter water, with the exception of one deeper domestic supply well (W-98, Table 1 of Appendix A). A significant finding of the current study is that evidence for saturated-zone denitrification at MCD and SCD only exists in first-encounter wells that are predicted by other criteria (groundwater gradient, the presence of ammonia, total dissolved solids, etc) to be impacted by recharge from lagoons or corrals, i.e. from the dairy operation proper. Wells so impacted include W02, W03, W16, W17, V01, and V21 on the MCD site (Table 1 of Appendix A), and Y03 and Y10 on the SCD site (Table 1). No evidence for denitrification exists in first-encounter wells that are impacted only by wastewater irrigation of either field crops (MCD) or of orchards (SCD). This finding is significant in two respects:

- The UC-Davis nitrate loading model for the region is in agreement with available spatial and time-series groundwater nitrate concentration data. The model does not explicitly consider denitrification of nitrogen fluxes from lagoons and corrals. The absence of evidence for denitrification in first encounter groundwater impacted by wastewater irrigation validates the model assumption that denitrification is not occurring and strengthens confidence in the model as a predictive tool.

- The deep domestic well W-98 is predicted by the UC-Davis model to have approximately 50 mg/L nitrate (T. Harter, personal communication). Groundwater from this well actually has very low nitrate (0.4 mg/L), but does have 45 mg/L nitrate-equivalent of excess N_2 indicating that the mass fluxes and transport in the model are accurate. The mean $^3He/^3H$ groundwater age also matches well with model travel time predictions. The good agreement between predicted nitrate and excess nitrogen in W-98 is consistent with a groundwater impacted by wastewater irrigation in which denitrification is occurring at some depth below the water table, as is the case at KCD1 in Kings County.

- The association of denitrification with groundwater impacted by manure lagoon seepage is consistent with the findings from the KCD1 study (see Appendix B)

To the extent that saturated-zone denitrification is significant and is associated with nitrogen loading from wastewater irrigation from dairy operations (as has been shown on one site, and indicated on another), the process needs to considered when assessing total impact of dairy operations on the groundwater resource. The most effective way to characterize saturated-zone denitrification is the installation of multi-level monitor wells in conjunction with the determination of nitrate stable isotope composition and excess nitrogen content.

The Impact of Dairy Manure Lagoons on Groundwater Quality

Appendix B is a manuscript prepared for submittal to a peer-review journal. The manuscript addresses the impact of dairy manure lagoon seepage on groundwater quality, and discusses a new tracer for manure lagoon seepage. The manuscript abstract follows.

Dairy facilities and similar confined animal operation settings pose a significant nitrate contamination threat to groundwater via oxidation of animal wastes and subsequent transport through the subsurface. While nitrate contamination resulting from application of animal manure as fertilizer to fields is well recognized, the impact of manure lagoon leakage on groundwater quality is less well characterized. For this study, a dairy facility located in the southern San Joaquin Valley of California (KCD1) has been instrumented with monitoring wells as part of a two-year multidisciplinary study to evaluate nitrate loading and denitrification associated with facility operations. Among the multiple types of data collected from the site, groundwater and surface water samples have been analyzed for major cations, anions, pH, oxidation-reduction potential, dissolved organic carbon, and selected dissolved gases (CO_2, CH_4, N_2, Ar, Ne). Modeling of geochemical processes occurring within the dairy site manure lagoons suggests substantial off-gassing of CO_2 and CH_4 in response to mineralization of organic matter. Evidence for gas ebullition is evident in low Ar and Ne concentrations in lagoon waters and in groundwaters downgradient of the lagoon, presumably as a result of gas "stripping". Shallow groundwaters with Ar and Ne contents less than saturation with respect to atmosphere are extremely rare, making the fractionated dissolved gas signature an effective tracer for lagoon water in underlying shallow groundwater. Preliminary evidence suggests that lagoon water rapidly re-equilibrates with the atmosphere during furrow irrigation, allowing this tracer to also distinguish between seepage and irrigation as the source of lagoon water in underlying groundwater. Together with ion exchange and mineral equilibration reactions, identification of lagoon seepage helps to constrain key attributes of the local groundwater chemistry, including input and cycling of nitrogen, across the site.

A New Tracer for Manure Lagoon Seepage

The manuscript in Appendix B uses only data collected from the KCD1 site. We also see evidence for gas stripping in lagoon waters from the KCD2 site (Figure 9). To further test the hypothesis that gas stripping in biologically active manure lagoons, we sampled manure lagoon water from several locations at KCD2 site. At this site, manure-laden water flows from free stall flush lanes to a settling lagoon (Lagoon 1) through an intake near the bottom of the lagoon to a larger holding lagoon (Lagoon 2) to a distribution standpipe to furrows in nearby fields. Samples were collected from the surface of Lagoon 1 near the outtake from the flush lanes, from the outlet of Lagoon 1 into Lagoon 2, from the surface of Lagoon 2 near the intake to the field distribution system, from a distribution standpipe, and from a field furrow about halfway down the length of the furrow. At the time of sample collection in April 2005, water in the distribution standpipe and in the field furrows was entirely from the manure lagoon, and was not mixed with well water or canal water. The results are shown in Figure 10.

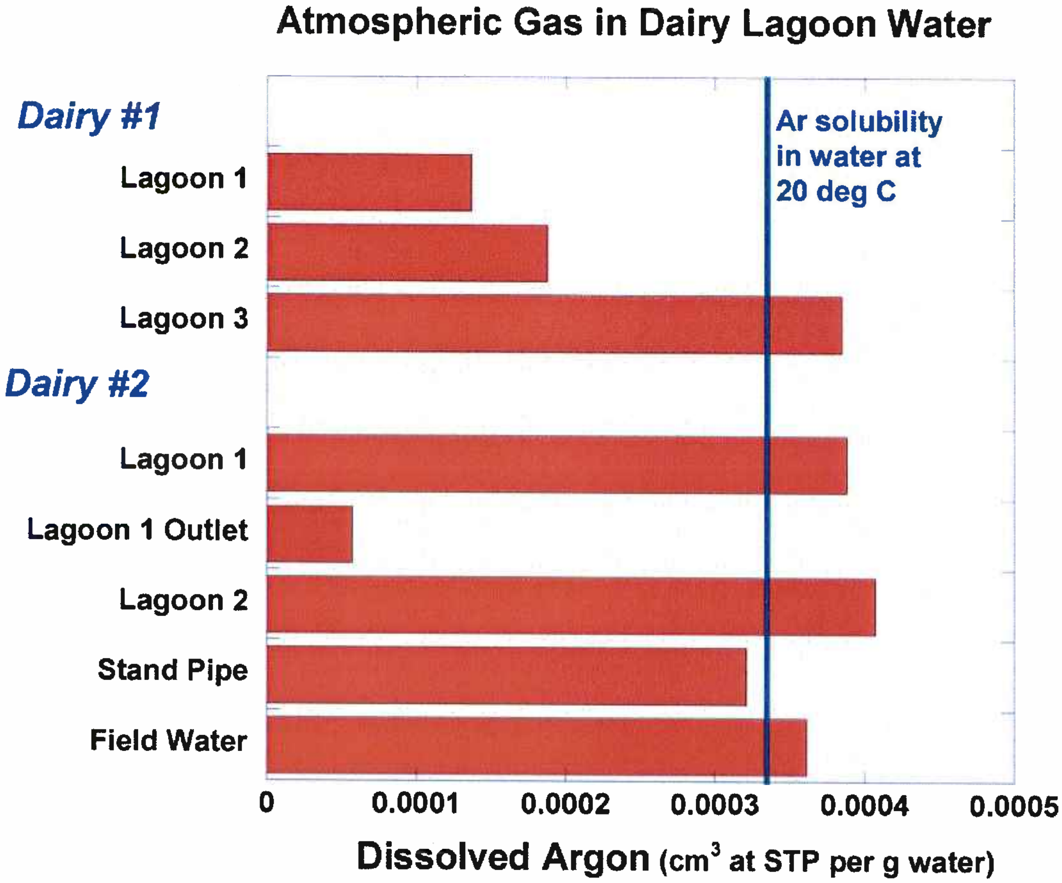

Figure 9. KCD1 and KCD2 manure lagoon dissolved argon content.

As discussed in Appendix B, biological activity in the lagoon consumes oxygen and strips atmospheric gases from the lagoon water through ebullition of carbon dioxide and methane. This effect of this activity is evident in the absence of detectable oxygen in any of the lagoon samples, and in lagoon water argon partial pressures that are close to or far below saturation argon partial pressures. For non-reactive gases such as argon, the "gas-stripping" effect is most evident in the sample drawn from the outlet of Lagoon 1 into Lagoon 2, which presumably represents water from near the bottom of Lagoon 1. This sample has extremely low argon, and may be representative of lagoon seepage through the bottom or sides of the lagoon. Atmospheric re-equilibration does not take place until the water is delivered to the field – the water sample drawn from the distribution standpipe has no detectable oxygen, while surface water from half-down a furrow is at about 40% saturation. We suspect that percolation through the soil zone and through an oxic vadose zone, which is characterized by incorporation of excess air, will result in complete re-equilibration or over-equilibration with soil gases.

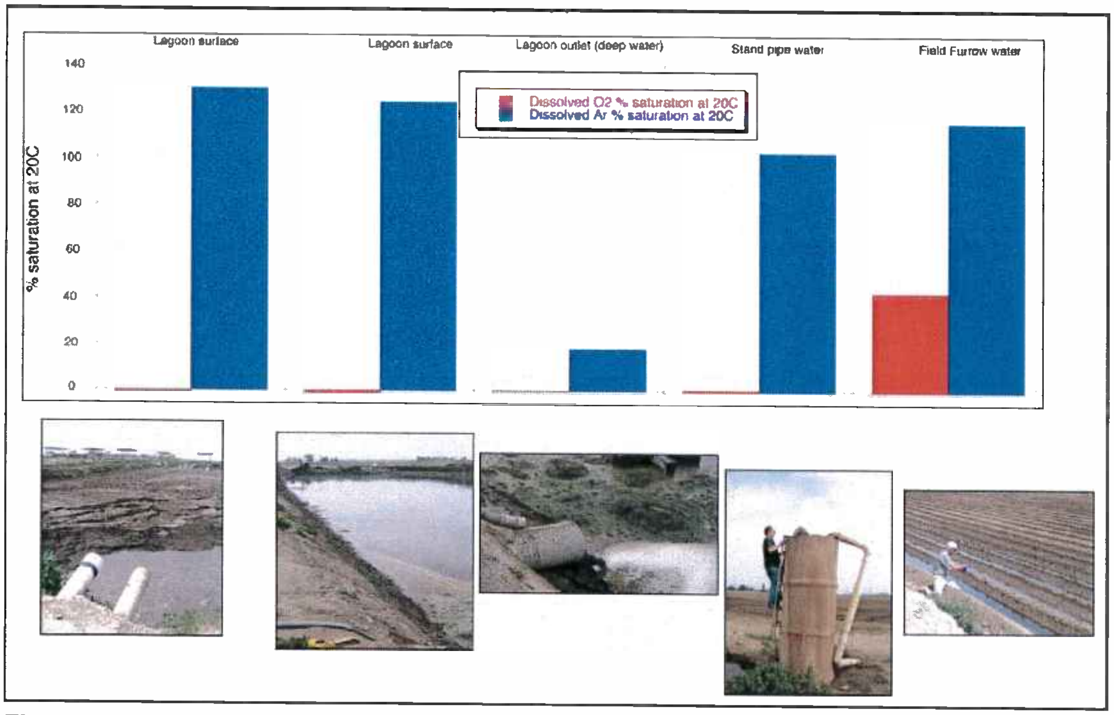

Figure 10. Dissolved argon and oxygen at KCD2.

The evolution of dissolved argon and dissolved oxygen along a "flow path" at KCD2. From left to right in figure: Lagoon 1 surface water , Lagoon 2 surface water, Lagoon 1 outlet into Lagoon 2, an irrigation standpipe, and a field furrow. Note that the Lagoon 1 outlet precedes the Lagoon 2 surface water in the "flow path". See text for explanation.

Dissolved gas samples from a number of manure lagoons on five dairy sites (KCD1, KCD2, MCD, and SCD) are characterized in general by deficiency in reactive and non-reactive atmospheric gases, and in detail by a wide range in non-reactive gas pressures from near equilibrium to far below equilibrium. The only other mechanism known to produce such signals is methane production either in marine sediments or in the deep subsurface in association with natural gas formation (see references in Appendix B). Currently the presence of an air "deficit" (i.e. atmospheric noble gases below saturation values) in shallow groundwater samples associated with dairy operations can be considered as indicative of the presence of a manure lagoon seepage component. To determine the mixing ratio of lagoon seepage with other water sources, however, will require a more quantitative understanding on the dissolved gas content in manure lagoons and manure lagoon seepage.

Source, Fate and Transport of Dairy Nitrate at KCD1

Harter et al. (2002) have demonstrated that dairy operations in the northern San Joaquin Valley strongly impact groundwater quality, resulting in first-encounter water that is high in salinity and inorganic nitrogen. On the KCD1 site in the southern San Joaquin Valley, a number of observations indicate that the dairy operation and associated wastewater irrigation are the source of high nitrate in first encounter groundwaters at the site:

- The isotopic composition of nitrate-N and –O is consistent with a manure or septic nitrogen source (see Appendix A).

- The young age of the first encounter waters (Figure 6 and 8), which we have accurately simulated using an irrigation recharge model (see groundwater transport discussion below) are inconsistent with transport from offsite locations.

- Nitrate co-contaminants can be traced to a specific application event on the site (see MORAN, 2006). In a subset of wells on the site, norflurazon and its degradation product, desmethylnorflurazon, were detected. Norflurazon was applied to a corn field in excess of the intended amount approximately two years prior to sampling. The well closest to the field contains norflurazon; a more distal well contains the degradation product, desmethylnorflurazon.

The unconfined aquifer at KCD1 is strongly stratified with respect to electron donor concentration (oxygen and nitrate), redox state (ORP), and excess nitrogen (Figures 5 and 6). The transition zone is sharp: nitrate levels can drop from significantly above maximum contaminant levels to nondetectable over a depth range of five feet. Our data indicate that the water immediately below the transition zone also has a significant wastewater component:

- Low-nitrate groundwaters nitrate isotopic compositions that are consistent with denitrification of manure or septic source nitrate.

- Some low-nitrate waters have below-saturation dissolved gas pressures that indicate a component of manure lagoon seepage (see Appendix B and discussion below.)

- Groundwater transport modeling (see discussion below) that assumes recharge dominated by wastewater irrigation accurately simulates the mean age and pre-modern mixing rations for low-nitrate groundwaters below the transition zone.

The strong spatial association of high denitrifier bacterial populations (Figure 6) with the transition zone is consistent with active denitrification occurring in this zone and being at least one source of denitrified groundwater seen below the zone. We cannot currently convert *nir* gene copy populations into denitrification rates, and so cannot estimate what fraction of denitrification occurs in the transition zone and what fraction occurs upgradient (proximal to a manure lagoon seepage plume, for example). What is clear, however, is that active denitrification is currently occurring on the dairy site in localized subsurface zones.

The relationship of the dairy operation (including wastewater irrigation and manure lagoon seepage) to nitrate mitigation through the establishment of redox stratification and the enhancement of saturated-zone denitrification is more complex. Any model of the evolution of redox stratification and denitrification must first provide an electron donor and then produce a sharp transition zone (~5 feet in vertical extent) at a remarkably uniform depth across the site (~35-40 feet bgs). A number of hypotheses can be put forward:

- Lateral transport of manure lagoon seepage.

- Field irrigation with dairy wastewater (assuming vertical percolation through a homogeneous soil column that contains a solid-phase electron donor).
- Agricultural pumping and nitrogen loading from dairy operations (assuming strong lateral transport of nitrate through a heterogeneous aquifer).

The Impact of Lagoon Seepage on Groundwater Quality

The first hypothesis is discussed in McNab et al. (Appendix B and Figure 11).

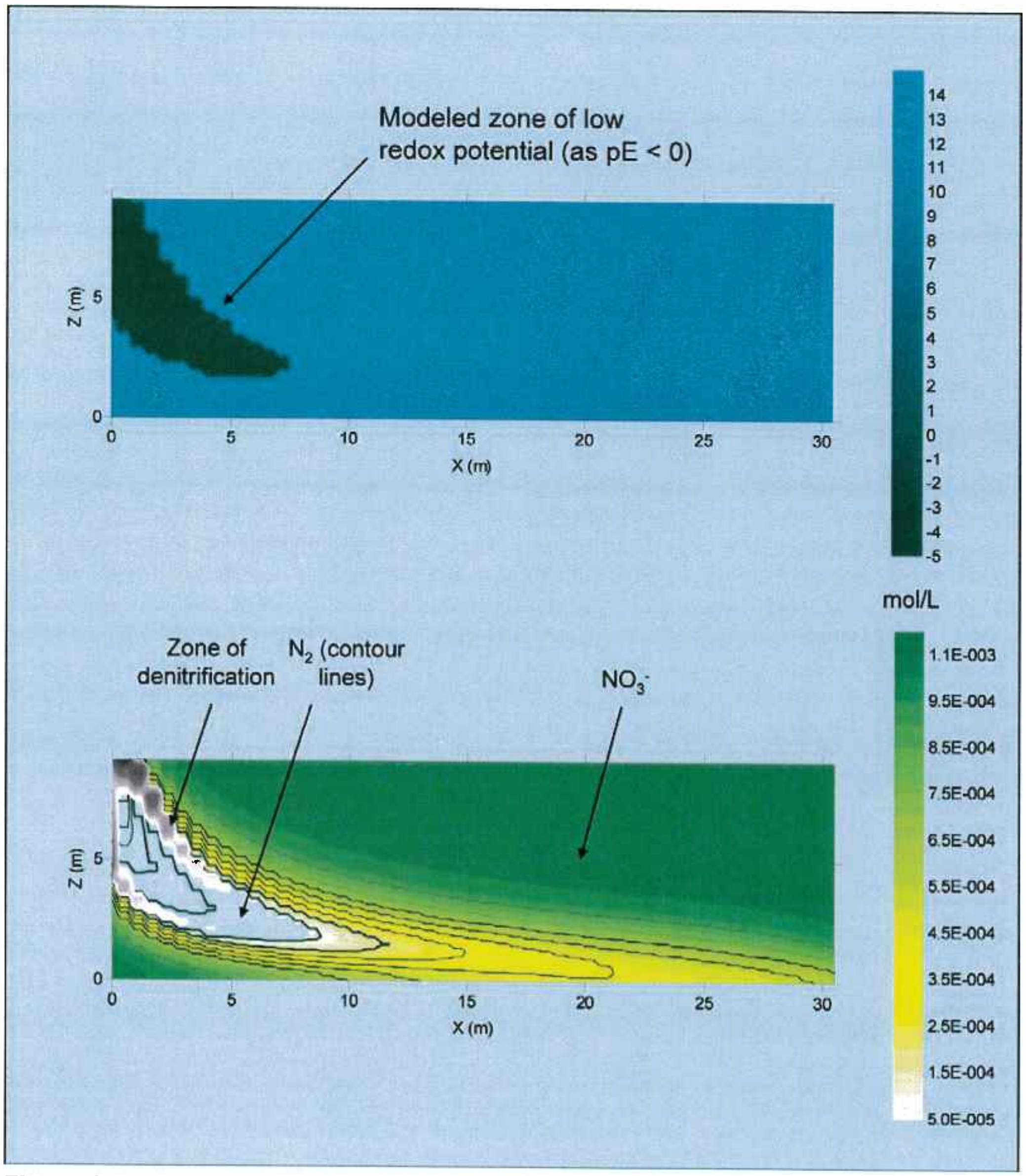

Figure 11. Simulation of transport of lagoon seepage through groundwater.
Simulation of the influence of seepage from a dairy wastewater lagoon on groundwater chemistry. See Appendix B for details on modeling.

McNab et al. assume that oxidation of organic carbon derived from manure creates the reducing conditions and provides the electron donor necessary for denitrification. While manure lagoon seepage is associated with excess nitrogen and does appears to drive denitrification locally, reactive transport modeling of lagoon seepage shows that the modeled zone of denitrification does not extend far from the lagoon, and that the modeled zone of low redox potential (where pE < 0) is localized (Figure 11). These model results are driven by the relative magnitudes of lagoon seepage and wastewater irrigation percolation rates, and are consistent with dissolved gas evidence indicating that lagoon seepage is not a major component in most site groundwaters. We conclude that manure lagoon seepage is not the cause of the laterally extensive reduced zone observed at the KCD1 site.

The Impact of Dairy Wastewater Irrigation on Groundwater Quality

Reactive transport modeling of vertical flow under an irrigated field indicates that vertical redox stratification can be created without a lagoon influence when dairy wastewater percolates through a soil column containing organic carbon in low permeability micro-environments. Attempts to simulate the development of redox stratification in the absence of a sedimentary electron donor were not successful.

We employed a reactive modeling approach using PHREEQC that addresses multispecies solute transport, soil-water reactions (mineral phase equilibria and ion exchange), and reaction kinetics for redox reactions involving nitrogen species as means for identifying the potential roles of different electron donors in the denitrification process at the site. The model parameters are shown below:

Parameters

- 10-m column
  - 10 volume elements (mobile pore water)
  - 10 volume elements (immobile pore water)
- Initial sediment composition:
  - 25% Quartz
  - 15% Na-montmorillonite (ion exchanger)
  - 15% K-mica ("C" model; no K-mica = "X" model)
  - 1% Goethite (HFO surface)
  - 0.02 mol/kg organic carbon

Step 1: Set up initial conditions

- Flush column with 300 pore volumes:
  - 1 mM NaCl
  - mM KCl
- After flushing
  - Equilibrium with CO_2(g) and O_2(g), calcite, and dolomite
  - Undersaturated with gypsum

Step 2: Simulate irrigation

- Flush column with 2 pore volumes with a mixture of agricultural well water and lagoon water (~0.02 M NH4+; ~0.01 M K+) – agricultural well water.
- Allow equilibration with calcite, ion exchanger, and HFO surface.

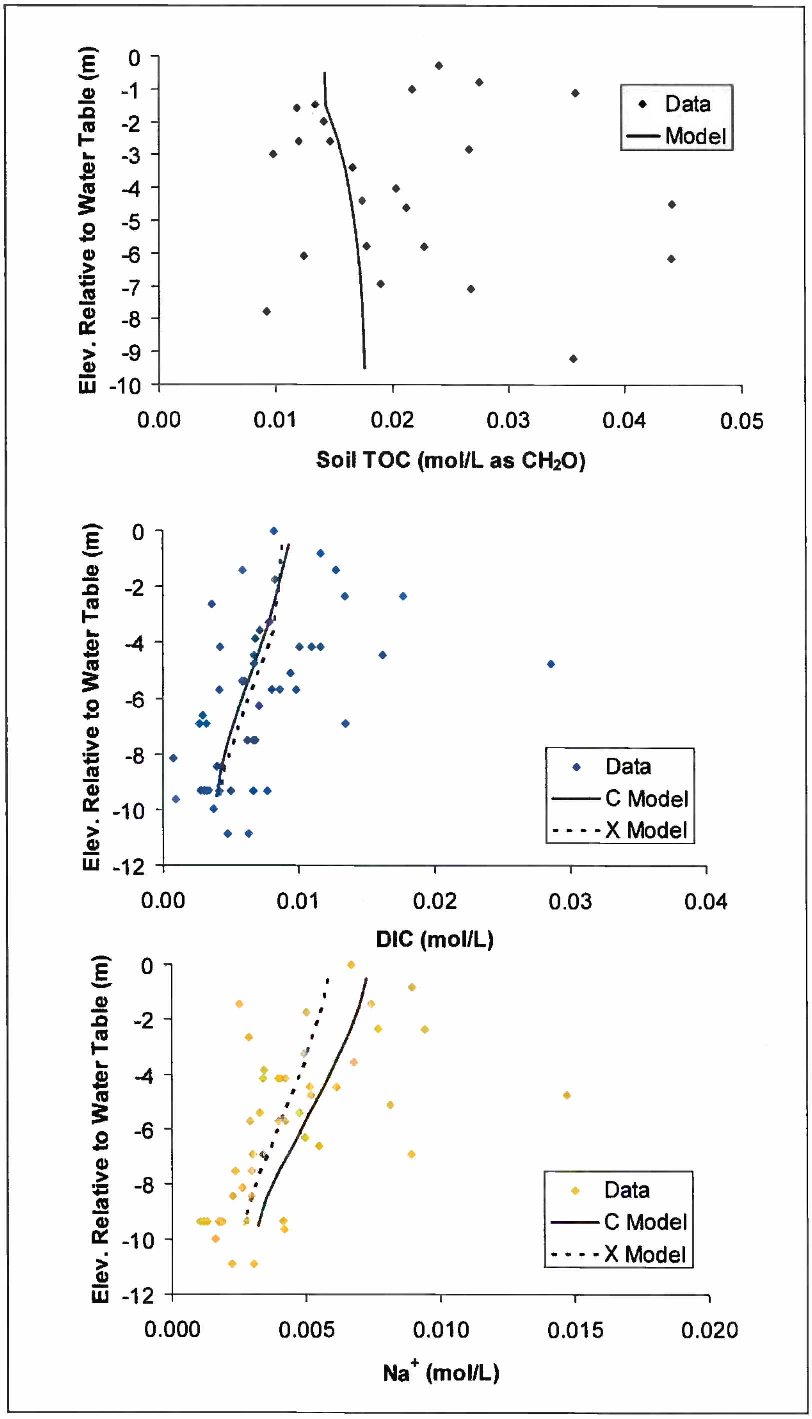

Figure 12. Simulation of dairy wastewater percolation through sediment.

Model results from simulation of vertical percolation of dairy wastewater through a sediment column containing organic carbon in low-permeability environments. See text for explanation.

Results from the reactive transport simulations results generally match most major cation and anion distributions with depth (Figure 12 and Figure 13). Moreover, the quantities of organic carbon required to produce a redox front (via diffusion-limited transport through low-permeability lenses) are consistent with measurements from soil samples (which are low). These results do not depend on any lagoon influence. Reactive transport modeling of vertical flow under the irrigated field demonstrates that general geochemistry in wells distal from the manure lagoons can be explained *without* postulating a lagoon influence, if the aquifer has reducing capacity.

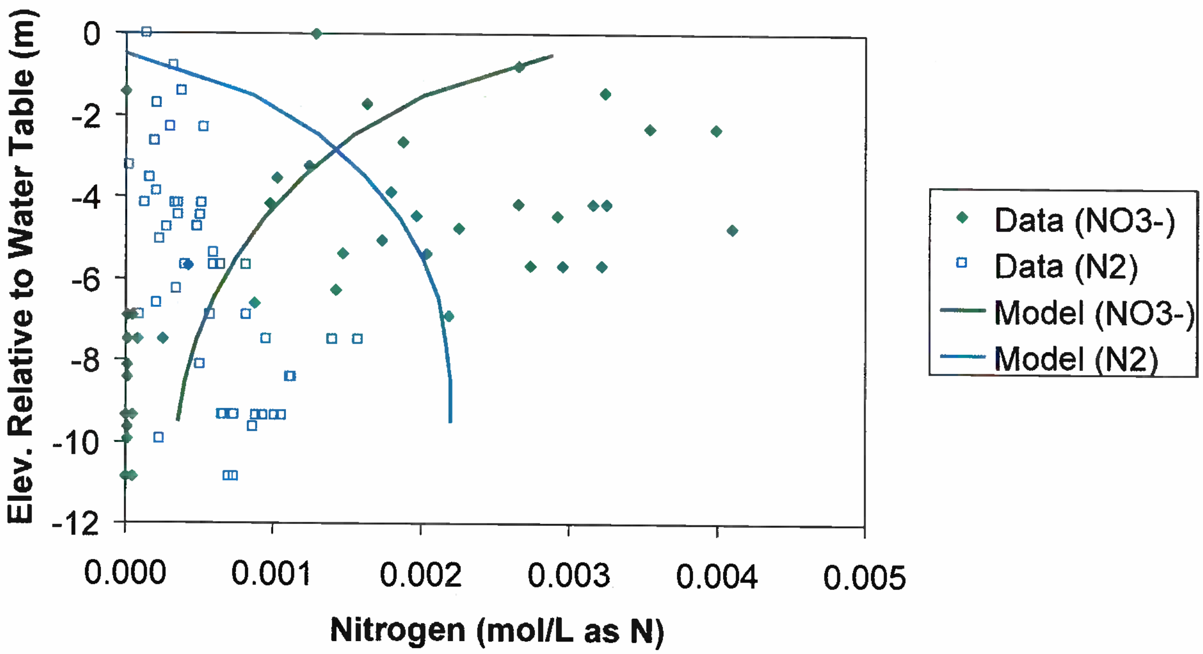

Figure 13. Simulation of denitrification associated with dairy wastewater percolation. Saturated-zone denitrification in a simulation of vertical percolation of dairy wastewater through a sediment column containing organic carbon in low-permeability environments. See text for explanation.

A number of lines of evidence exist that indicate that reducing groundwater conditions are common in the region surrounding the KCD1 site. At a number of NAWQA sites in the region that are not believed to be impacted by dairy wastewater, nitrate in deeper waters is nondetectable and iron and manganese concentrations are high, an association consistent with suboxic or anoxic conditions (BUROW et al., 1998a; BUROW et al., 1998b). The most convincing evidence comes from the deep well at the KCD1 site (KCD1-1D, Table 1 in Appendix A). Groundwater in the lower aquifer sampled by this well is tritium dead with a mean groundwater age in excess of 50 years. Radiogenic ^{4}He content indicates an age on the order of 100 years or more. Neither nitrate nor excess nitrogen is present, indicating that source waters were low in inorganic nitrogen species. This groundwater has extremely low chloride and has isotopically lighter water than water sampled in the perched aquifer. Finally, this groundwater is reduced as indicated by both field ORP and DO measurements, and measurements of volatile sulfide compounds in the water. These observations are consistent with recharge by source waters unimpacted by agriculture and the occurrence of naturally reducing conditions along the flow path. The electron donor driving the evolution of the natural reducing system is unclear. The water is low in TOC (0.8 mg/L). Sediment organic C and reduced S contents are generally low (< 0.1 wt %), but are sufficient to produce reducing conditions, particularly since sediments with organic carbon contents of over 1 wt% have been characterized (Figures 5 and 6). Reducing conditions may have also been created during recharge (in the hyporheic zone during riverbank infiltration).

The existence of regionally reducing conditions is also evident in the redox state of sedimentary iron in site sediments. Above approximately 60' bgs, sediment core is stained with orange, red and brown ferric iron oxides; below 60', this stain is not present (Figures 5 and 8). The existence of a denitrification zone approximately 20-25' above the iron reduction zone is consistent with the energetics of these reactions.

Given the presence of reducing conditions within the aquifer, one-dimensional transport through homogeneous media can drive the development of redox stratification and saturated-zone denitrification within the shallow aquifer. This process, however, can only reproduce the sharpness and uniform depth of the observed groundwater redox stratification 1) if a layer of laterally extensive reducing sediment exists at the groundwater redox boundary or 2) if a sharp transition in sediment reducing capacity exists at or near the depth of the water redox transition. Neither of these conditions is observed at the KCD1 site. The redox boundary is not correlated with sediment texture, nor do any gradients exist in sedimentary organic C, total S, or reduced S that correlate with the depth of the redox boundary.

The Impact of Pumping and Wastewater Irrigation on Groundwater Quality

A number of processes that may contribute to strong vertical stratification of groundwater flow and chemistry are not adequately simulated in a one-dimensional homogeneous model. To explore the effect of aquifer heterogeneity and lateral transport on groundwater flow and transport at the KCD1 site, we used the numerical flow and transport model NUFT to simultaneously simulate three-dimensional variably-saturated groundwater flow processes including canal recharge, agricultural pumping, and irrigation (CARLE et al., 2005). Heterogeneity of sandy, silty, and clayey zones in the system was characterized stochastically by applying transition probability geostatistics to data from 12 CPT logs that vertically transect the perched aquifer. In the first iteration of this model, nitrate in surface irrigation was simulated as a tracer rather than as a reactive species.

Groundwater Hydrology. In the distal reaches of the Kings River within the Tulare Lake Basin, groundwater is extracted from both a perched zone (less than ~ 25 m deep) and a deep zone. Before the 1950's, water levels were nearly equal in both zones (DWR data). Overdraft in the deep zone has caused water level declines of over 100 feet (30 m). Perched zone water level elevations, where they exist, persist well above the deep zone, as evident from DWR water level elevation maps for 2001-2002. The Kings River, unlined ditches and canals, and irrigation appear to provide recharge to sustain the perched aquifer. Crop irrigation uses canal diversions and both shallow and deep groundwater.

At and near the KCD1 site, groundwater level elevations in different wells screened in the perched aquifer are remarkably similar over time and correlate to canal diversions. This suggests canal leakage and irrigation from canal diversions provides substantial recharge to the perched aquifer. Leakage from the canal is estimated at 10% by the irrigation district.

Several dairies are located within the area of the perched aquifer. KCD1 is located about one mile east of the canal. The dairy grows much of its own feed – corn and alfalfa. The crops are irrigated primarily with water pumped from the shallow aquifer. Crops are fertilized largely by mixing in effluent from the dairy operation that is collected in a lagoon. The lagoon water and other fertilizers provide sources of nitrate that appear to impact upper portions of the perched aquifer, but not lower portions of the perched aquifer or the deep aquifer. Other nearby farms also irrigate with canal diversions or groundwater pumped from the deep aquifer. Thus, overdraft from the deep aquifer helps, in part, to sustain the perched aquifer.

The modeling approach was designed to include consideration of the major factors and processes affecting groundwater flow, nitrate transport, and groundwater age dating:

- *Heterogeneity*: Use hydrofacies-based geostatistics.
- *Variably Saturated Flow:* Couple vadose zone and saturated zone using LLNL's NUFT code.
- *Boundary Head Conditions:* Use time-series DWR water levels in perched and deep zone.
- *Perched and Deep Zone:* Use modeling to determine leakage that maintains perched condition.
- *Canal Leakage and Irrigation:* Distinguish different sources with different tracer simulations.
- *Tritium/Helium-3 Age Dating:* Add decay to tracer simulations, simulate apparent age estimate.
- *Groundwater Mixing:* Keep track of proportions of groundwater from different sources.

Heterogeneity. Based on our interpretation of lithologic and CPT logs, we defined three hydrofacies: "sand", "silt", and "clayey" categories. We quantified vertical and horizontal spatial variability with a transition probability matrix using the CPT data categorized as hydrofacies. The solid lines in the probability matrices (Figure 14) represent 1-D Markov chain models used to develop stochastic simulations of hydrofacies architecture at the site.

The hydraulic properties of the hydrofacies categories were estimated from a combination of pump test analysis, soil core measurements, and model calibration.

HYDROFACIES	K (m/d)	POROSITY
Sand	30	0.40
Silt	0.24	0.43
Clayey	0.014	0.45
Sandy Loam Soil	3.0	0.41
Aquitard	1.4e-6	0.45
Canal (sandy)	10.0	0.41

A Van Genuchten model was used to predict unsaturated hydraulic conductivity and capillary pressure. A continuous 1-m thick aquitard layer at 46-47 m elevation sustains the perched aquifer conditions. This aquitard layer correlates to a distinctive clay layer identified in our initial characterization lithologic log.

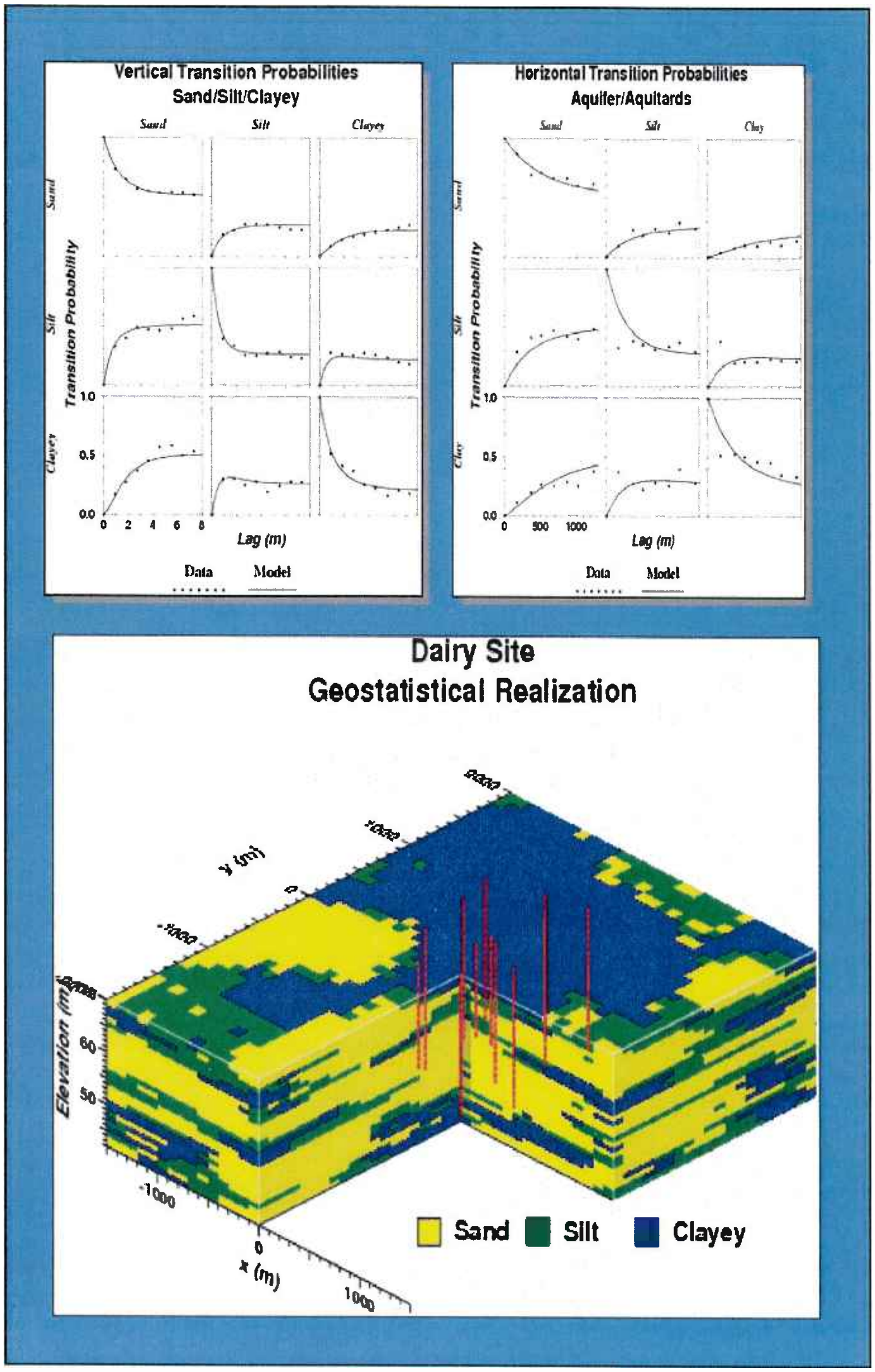

Figure 14. Geostatistical representation of the subsurface at KCD1.

Transition probability matrices and geostatistical representation of hydrofacies architecture for the KCD1 site. See text for explanation.

Flow and transport simulation (Figure 15 and 16). We used LLNL's NUFT code to simulate variably saturated **flow** according to the Richards equation (Figure 15). The simulation runs from late 1949 through 2001. Initial conditions are equilibrated to local head measurements and rainfall recharge of 1 cm/year. For boundary conditions, x-direction and bottom boundaries were conditioned to observed piezometric heads. A fully saturated initial condition is applied to the canal when canal diversions occur (between early April and early October). In the simulation, the six site production wells were pumped during irrigation season a rate greater and proportionate to crop evapotranspiration (ET). Recharge from irrigation was distributed proportionately to crop (ET), with about 25 cm/yr within the dairy crop fields and 10 cm/yr in surrounding areas.

In the simulation, piezometric head in the perched aquifer remains relatively steady, although in fall 1992 (during a drought) head is noticeably lower. However, head in the deep aquifer drops considerably since the 1950s, to the extent that the top of the deep zone begins to desaturate in the 1960s. In effect, the aquifer system near the dairy field site now functions like two unconfined aquifers stacked on top of each other. This is consistent with the observed separation of the DWR water levels between shallow and deep wells in the 1960s.

We used LLNL's NUFT code to simulate tracer **transport** from different recharge sources (Figure 16). The three primary recharge sources near the dairy site are canal, dairy crop irrigation, and irrigation from surrounding areas. The transport simulation results indicate that nitrate entering the saturated zone from dairy crop irrigation is contained in the upper parts of the aquifer. Nitrate containment occurs within the high permeability sand-dominated perched aquifer because the dairy irrigation wells screened in the perched aquifer effectively capture nearly all recharge from dairy crop irrigation. The dairy irrigation wells pump groundwater at rates far higher than the recharge from dairy crop irrigation. The dairy irrigation wells also extract groundwater originating from irrigation of surrounding areas, canal leakage, and older groundwater

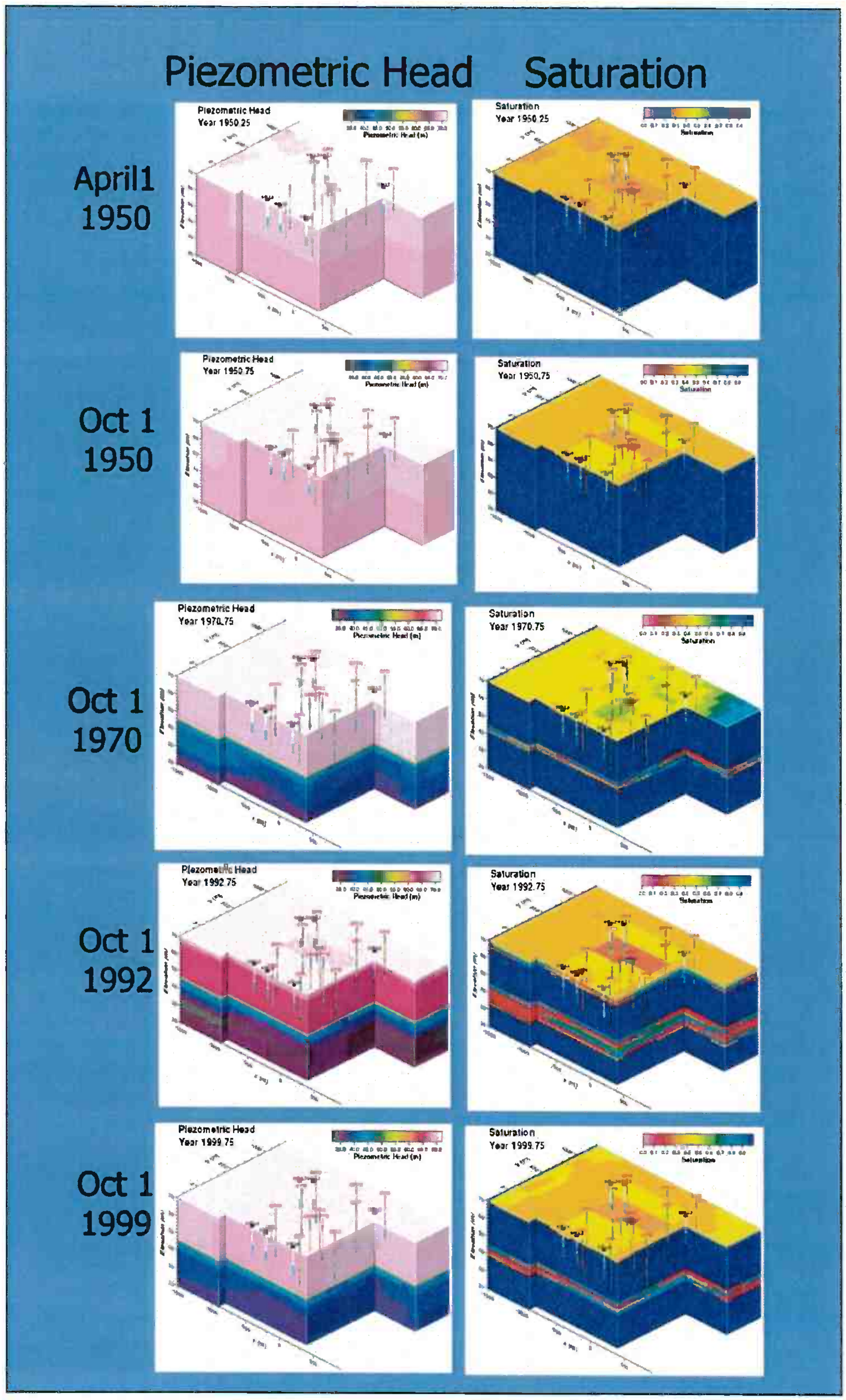

Figure 15. Simulation of groundwater flow at KCD1.

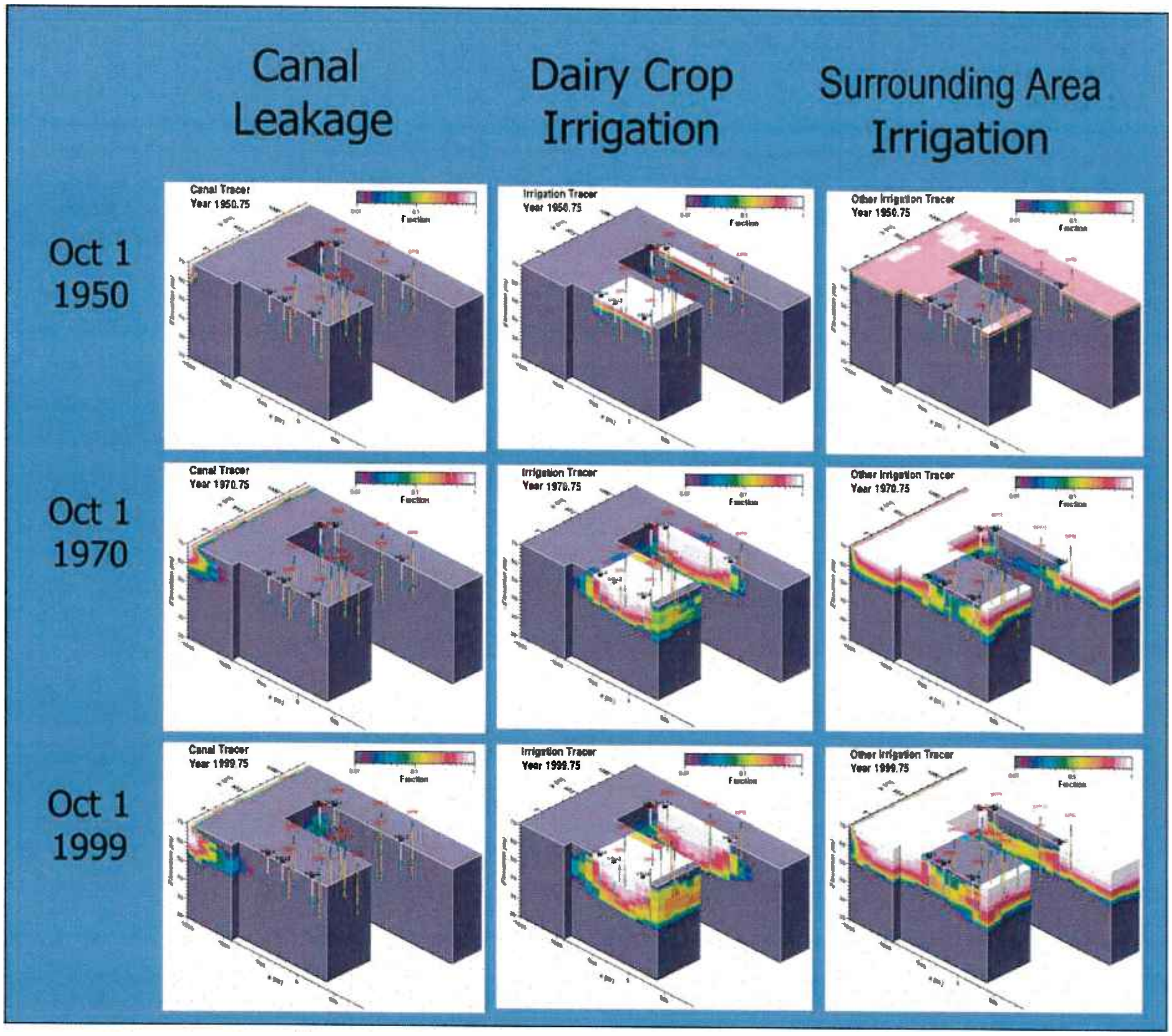

Figure 16. Simulation of transport at KCD1.

Model validation. To validate the groundwater flow and transport model, we used the model to simulate ^3H-^3He groundwater ages in the aquifer and compared the results of the simulation to measured values. Groundwater ages determined using the ^3H-^3He method are apparent age estimates of the average age of a mixed groundwater. Such ages are affected by mixing of groundwater through diffusion and dispersion, transient flow, and sampling, and by the decay of atmospheric tritium activities since 1963 bomb pulse.

To simulate apparent age of groundwater, we used NUFT to tag all surface recharge sources. We then simulated apparent groundwater age for two scenarios: (1) for an "ideal source" that assumes constant tritium concentration over time and (2) for a "bomb source" where tritium concentration varies as measured. The simulated tritium/helium-3 ratios are backed out of the differences in simulated concentration.

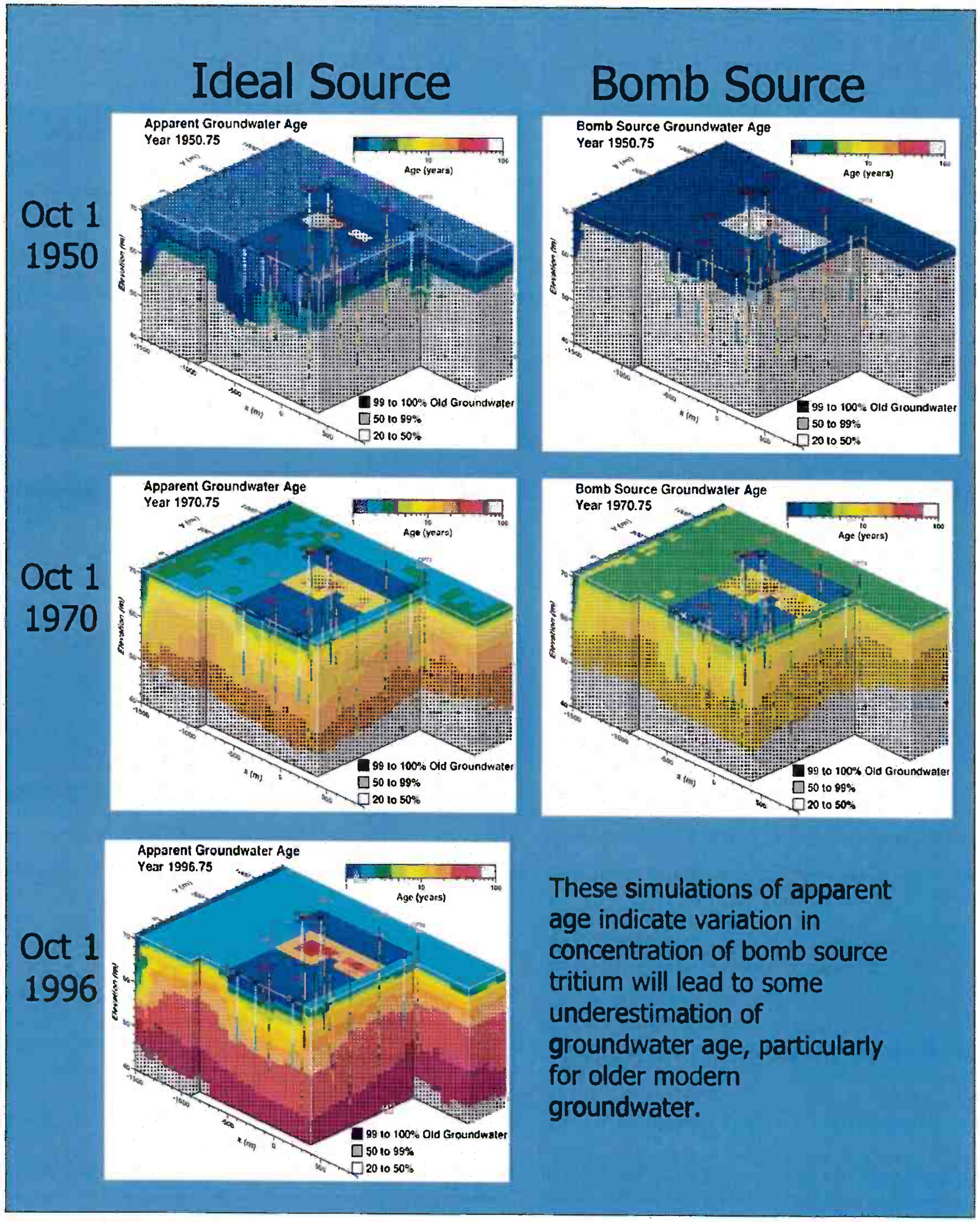

Figure 17. Simulation of apparent groundwater age at KCD1.

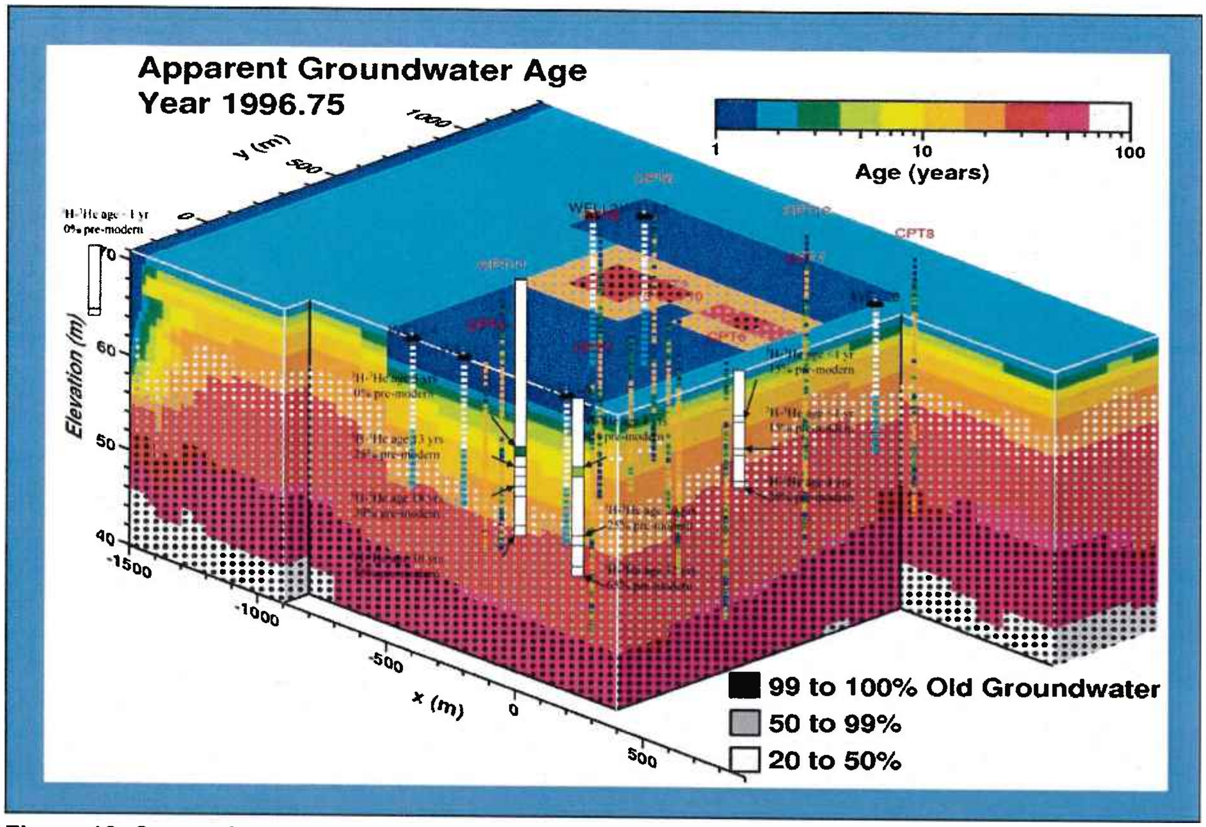

Figure 18. Comparison of measured and simulated groundwater ages at KCD1.
Agreement between measured and simulated apparent groundwater age at KCD1. See text for explanation.

The simulation of apparent age show excellent agreement for the southern Site 1 and Site 4 wells south of the dairy operation (Figure 18). At these well cluster locations, simulated ages are less than measured tritium/helium-3 ages in shallow groundwater at these sites because the simulations assumed that ^{3}He begins accumulating at the ground surface and not the water table. Current modeling efforts address this effort and produce better agreement for shallow groundwater. At Site 2 to the southeast of the dairy operation, measured groundwater ages are younger than simulated ages. This difference may indicate the absence of a shallow clayey zone at this location. These simulations of apparent age indicate variation in concentration of bomb source tritium will lead to some underestimation of groundwater age, particularly for older modern groundwater.

Conclusions. Coupling flow and transport simulations with groundwater age data and geostatistical simulations of hydraulic properties provides invaluable insights. Heterogeneity plays a large role in creating the perched aquifer and in causing vertical compartmentalization of flow patterns. The hydrofacies architecture consists of laterally continuous sand with interbeds of silt and clayey zones. Maintaining head and saturation in perched zone requires a continuous ~3 foot-thick clay layer at ~ 85 feet bgs. Flow simulation desaturates upper portions of the deep zone below the confining layer, and is consistent with observation of de-saturated zone below ~ 80 feet bgs.

The perched zone draws older water and recharge mostly from irrigation and less so from canal leakage. The dairy site pumps more groundwater from the perched aquifer than is recharged by crop irrigation, and thus physically contains lateral and vertical migration of nitrate contamination. High nitrate irrigation water penetrates to depths below the sharp redox gradient. Without denitrification, nitrate concentrations would be greater below the redox gradient, as is consistent with the presence of excess nitrogen in this zone.

The NUFT model presented here does not simulate transport of reactive constituents such as oxygen, nitrate, sulfate and organic carbon, and does not directly address the sharpness and uniform depth of the redox gradient in the shallow groundwater system. The strong vertical compartmentalization of the groundwater flow created by agricultural pumping and the location of the redox gradient close to the top of the production well screens, however, suggest that agricultural pumping and lateral groundwater flow may be important controls on the development of redox stratification in the shallow aquifer.

The Development of Reducing Conditions in Dairy Site Groundwaters

At three sites in this study (KCD, SCD, and MCD), dairy operations have been demonstrated to impact groundwater quality. At all three sites, nitrogen mitigation (either through denitrification or denitrification) has been demonstrated in groundwater impacted by manure lagoon seepage, a finding consistent with geochemical reactive transport modeling. At two of the sites (KCD and MCD), denitrification has also been demonstrated to occur in deeper waters impacted by irrigation with dairy wastewater. For denitrification to occur in the saturated zone, dissolved oxygen must be absent or present in very low concentrations. A key question, then, in assessing the ability of a groundwater to assimilate nitrate loading is what mechanism drives the development of reducing conditions necessary for denitrification to occur.

At the best studied site, KCD1, evidence exists for both natural and anthropogenic influence on the development of suboxic and anoxic groundwater. The deep aquifer at the KCD1 site consists of old water un-impacted by agricultural inputs. The water is tritium-dead and has a radiogenic ^{4}He age of approximately 100 years. In addition to having a mean age that pre-dates the intensification of agricultural activities, especially with regards to fertilizer usage and manure production, the deep aquifer groundwater has a chemical composition that indicates the absence of significant agricultural input. Salinity, dissolved organic C, nitrate and excess nitrogen are all low. This water is also anoxic, with nondetectable dissolved oxygen, detectable hydrogen sulfide, and low ORP. The electron donor responsible for reducing conditions is not known. Groundwater DOC is low, as is sediment solid-phase total S and organic C. Reduced sediment phases, however, are sufficient to create reducing conditions, even for slow redox processes such as solid-phase autotrophy given the age of the water. These observations all indicate that regionally reducing conditions un-related to agricultural activities do exist at the KCD1 site. Rates of denitrification in this deep system are unconstrained but may be slow and controlled by the abundance or reactivity of solid-phase electron donors.

The perched shallow aquifer is impacted by agricultural operations. Total inorganic nitrogen ($NO_3 + NO_2 +$ excess N_2) shows a secular trend with apparent groundwater age, with the highest concentrations in the youngest water. The isotopic composition of high-nitrate waters indicates a wastewater source. Groundwater transport modeling indicates that irrigation dominates recharge in the perched aquifer. Irrigation with dairy wastewater results in the percolation of high-nitrate water to the water table and the penetration of this water to a depth controlled by agricultural pumping (Figure 16). Both the vertical and later transport of irrigation water is controlled by agricultural pumping. The perched aquifer is also strongly stratified with respect to oxidation state, nitrate distribution, and denitrification activity. Denitrification under irrigated fields occurs where oxic high-nitrate irrigation water mixes with older anoxic water. The mixing or "reaction" zone is sharp and at constant depth, and may be controlled by agricultural pumping.

What is the electron donor for the denitrification observed at the oxic-anoxic interface? Sediment organic-C and total-S concentrations in the deep and perched aquifer are comparable and are sufficient (assuming most of the S to be present in reduced phases) to create reducing conditions and support denitrification. At one shallow site (Site 3) upgradient of the main dairy operation, PCR data do indicate the presence of autotrophic bacteria capable of using reduced S as an electron donor, and geochemical modeling is consistent with pyrite oxidation. This evidence is not seen at the other sites, however, and the vertical variability in sediment C and S, does not explain the sharpness or location of the oxic-anoxic interface. Total organic carbon in site groundwaters varies from < 1 to 20 mg/L. (Neither other potential dissolved-phase electron donors such as thiosulfate nor the reactivity or bioavailability of the dissolved organic carbon was characterized.) Geochemical modeling is consistent with organic C oxidation, although simple models that assume shallow and deep waters have similar initial chemical compositions do not match observed compositions tightly. These observations, coupled with the lack of evidence for widespread distribution of autotrophic denitrifying bacteria in active denitrification zones, indicate that heterotrophy dominates the observed denitrification in the agriculturally-impacted perched aquifer. Simulations of irrigation and pumping at the KCD1 site indicate that groundwater flow at this site is strongly vertically compartmentalized. Te location of the redox gradient close to the top of the production well screens suggests that agricultural pumping and lateral groundwater flow in conjunction may be important controls on the development of chemical and redox stratification in the shallow aquifer.

The conceptual model, then, is of a regionally extensive deep aquifer that is naturally reducing and is unimpacted by agricultural operations overlain by a shallow aquifer that in its upper strata is strongly stratified, is reducing, and is the site of active denitrification of dairy-derived nitrate, and that these conditions in the shallow aquifer are driven by irrigation with dairy wastewater and groundwater pumping for dairy operations. This proposition, that denitrification in shallow nitrate-impacted aquifers is driven by dairy operations, is consistent with observations at not only the KCD1 site but also with evidence for denitrification at the MCD and SCD sites. The implication is that to assess net impact of dairy operations on groundwater quality, one must consider denitrification in the saturated zone.

CONCLUSIONS

The three primary findings of this research are that dairy operations do impact underlying groundwater quality in California's San Joaquin Valley, that dairy operations also appear to drive denitrification of dairy-derived nitrate in these groundwaters, and that new methods are available for characterization of nitrate source, transport and fate in the saturated zone underlying dairy operations.

Groundwater quality impact has been demonstrated at three sites, with a site in the southern San Joaquin Valley, KCD1, being the best characterized. High nitrate in groundwaters underlying these dairy sites can be attributed to dairy operations using a number of methods, including

- Chemical composition and nitrogen speciation.
- Nitrate isotopic composition.
- Groundwater dissolved gas content and composition.
- Groundwater age
- Reactive transport and flow modeling

The use of chemical composition, nitrogen speciation, and nitrate isotopic composition are well described in the literature. The use of dissolved gas content to identify manure lagoon seepage is new, and is introduced in this research. Groundwater age and transport simulations can be used to trace contaminants back to their source.

In both northern and southern San Joaquin Valley sites, saturated-zone denitrification occurs and mitigates the impact of nitrogen loading on groundwater quality. At the southern KCD1 site, the location and extent of denitrification in the upper aquifer is driven by irrigation with dairy wastewater and groundwater pumping. The extent of denitrification can be characterized by measuring "excess" nitrogen and nitrate isotopic composition while the location of denitrification can be determined using a PCR bioassay for denitrifying bacteria that developed in this research. The demonstration of saturated-zone denitrification in dairy groundwaters is important in assessing the net impact of dairy operations on groundwater quality.

New tools available for research on dairy groundwater include the determination of groundwater dissolved gas content to distinguish dairy wastewater irrigation from dairy wastewater lagoon seepage, field determination of excess nitrogen to identify denitrification in synoptic surveys and to characterize the extent of denitrification in monitor and production well samples, bioassay of aquifer sediment and water samples for the presence of denitrifying bacteria, characterization of aquifer heterogeneity using direct-push drilling and geostatistical simulation methods. Application of these new methods in conjunction with traditional hydrogeologic and agronomic methods will allow a more complete and accurate understanding of the source, transport and fate of dairy-derived nitrogen in the subsurface, and allow more quantitative estimates of net impact of dairy operations on underlying groundwater.

PUBLICATIONS AND PRESENTATIONS

Peer-Reviewed Presentations

McNab W. W., Singleton M. J., Moran J. E., and Esser B. K. (2007) Assessing the impact of animal waste lagoon seepage on the geochemistry of an underlying shallow aquifer. *Environmental Science & Technology* **41**(3), 753-758.

Singleton M. J., Esser B. K., Moran J. E., Hudson G. B., McNab W. W., and Harter T. (2007) Saturated zone denitrification: Potential for natural attenuation of nitrate contamination in shallow groundwater under dairy operations. *Environmental Science & Technology* **41**(3), 759-765.

Conference presentations

Carle S. F., Esser B. K., McNab W. W., Moran J. E., and Singleton M. J. (2005) Simulation of canal recharge, pumping, and irrigation in a heterogeneous perched aquifer: Effects on nitrate transport and denitrification (abstr.). *25th Biennial Groundwater Conference and 14th Annual Meeting of the Groundwater Resources Association of California (Sacramento, CA; October 25-26, 2005).*

Esser B. K., Beller H. R., Carle S. F., Hudson G. B., Kane S. R., LeTain T. E., McNab W. W., and Moran J. E. (2005) New approaches to characterizing microbial denitrification in the saturated zone (abstr.). *Geochimica et Cosmochimica Acta* **69**(10), A229. 15th Annual Goldschmidt Conference (Moscow, ID, May 20-25, 2005).

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McNab W. W., Jr., Singleton M. J., Esser B. K., Moran J. E., Beller H. R., Kane S. R., Letain T. E., and Carle S. F. (2005) Nitrate loading and groundwater chemistry at a dairy site in California's Central Valley (abstr.). *International Conference on Safe Water 2005 (San Diego, October 21-25, 2005).*

McNab W. W., Singleton M. J., Esser B. K., Moran J. E., Leif R., and Beller H. (2006) Constraining denitrification mechanisms in shallow groundwater at an instrumented dairy site using reactive transport modeling (abstr.). *Nitrate in California's Groundwater: Are We Making Progress (Modesto, California, April 4-5, 2006) (The 17th Symposium in the Groundwater Resources Association of California Series on Groundwater Contaminants).*

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Table 1: KCD2, KCD3, & SCD Site Data

Field Parameters, chemical compositon, groundwater age, recharge temperature, excess air, stable isotopic composition, excess nitrogen

(Unless otherwise indicated, all analytes are reported as mg/L; nitrate is reported as nitrate)

Name	Collection date	pH	DO	TOC	Na^+	K^+	Ca^+	Mg^{++}	Cl^-	SO_4^{-}	NO_3^-	NO_2^-	NH_4^+	excess N_2 (NO_3^- equiv)	Br^-	F^-	Li^-	PO_4^-	$^3H/^3He$ age (yr)	Recharge T (°C)	Excess air (cc STP/g)	$H_2O-\delta^{18}O$ (‰ SMOW)	$NO_3^--\delta^{15}N$ (‰ Air)	$NO_3^--\delta^{18}O$ (‰ SMOW)
KCD2 DW-1	2005/04/26	8.2	0.2		105	1	10	0	64	41	7	0.11	<0.02	2	0.21	0.06	0.005	0.99		15	8.8E-03	-11.1		
KCD3 DW-1	2003/08/21				87	0	54	1	134	57	9	1.22	nd		0.05	0.14	nd					-11.7	17.7	10.6
SCD1 Y-03	2005/03/08	6.8	0.6	18	215	4	124	55	59	199	185	0.41	<0.02	37	0.36	0.11	0.007	<0.04			2.5E-01	-9.8		
SCD1 Y-10	2005/03/08	7.0	5.3	3	82	137	110	81	143	16	42	1.31	137	nd	0.54	0.17	0.008	<0.04		18	9.8E-04	-9.1		
SCD1 Y-13	2003/08/26	7.5			28	5	146	41	48	169	58		<0.02		0.15	0.43	0.005	0.22	>50	16	2.0E-02	-11.0		
SCD1 Y-14	2003/08/26	7.3			63	5	146	55	57	233	167	0.05	<0.02	nd	0.12	0.26	0.003	0.22				-11.5		
SCD1 Y-15	2003/08/26	7.3			50	5	44	54	50	98	62	0.01	<0.02		0.12	0.23	0.006	0.24				-9.7		
SCD1 Y-16	2003/08/26	7.0			48	3	181	43	34	172	201	0.02	<0.02	nd		0.07	0.009	0.29	9	17	1.4E-02	-10.3		
SCD1 Y-17	2003/08/26	7.2			145	6	223	69	75	488	178		<0.02	nd	0.40	0.15	0.004	0.24	9		1.6E-03	-10.5		
SCD1 Y-18	2003/08/26	7.1			132	7	138	45	52	205	207	0.07	<0.02	nd		0.17	0.009	4.44	8	17	8.0E-03	-9.6		

Table 2: KCD1 Site Sediment C, S Data

KCD well cluster	Texture	Depth (ft)	Total C (wt%)	Tot C (2sd)	Carb C (wt%)	Carb C (2sd)	Org C (wt%)	Org C (2sd)	Total S (wt%)	Total S (2sd)	Sulfate S (wt%)	Sulfate S (2sd)	Reduced S (wt%)	Reduced S (2sd)
Site 1	Silty Sand	18	0.079	0.008	0.007	0.002	0.072	0.008	0.057	0.006	0.054	0.011		
Site 1	Clayey Silt	21	0.065	0.007			0.065	0.007	0.009	0.004				
Site 1	Sandy Silt	24	0.042	0.005			0.042	0.005	0.011	0.004				
Site 1	Clayey Silt	26	0.044	0.005			0.044	0.005	0.013	0.004				
Site 1	Sand	33	0.064	0.006			0.064	0.006	0.012	0.004				
Site 1	Sand	38	0.138	0.014	0.006	0.002	0.132	0.014	0.011	0.004	0.017	0.011		
Site 1	Sand	48	0.108	0.011	0.002	0.001	0.107	0.011	0.070	0.007	0.022	0.011	0.047	0.013
Site 1	Silt	61	0.050	0.005			0.050	0.005	0.011	0.004				
Site 1	Sandy Silt	69	0.066	0.007			0.066	0.007	0.022	0.004	0.019	0.011		
Site 1	Silty Sand	76	1.299	0.130			1.299	0.130	0.155	0.016	0.077	0.011	0.078	0.019
Site 1	Sand	77	0.207	0.021			0.207	0.021	0.181	0.018	0.034	0.011	0.147	0.021
Site 1	Sandy Silt	171	0.074	0.007	0.011	0.002	0.064	0.008	0.012	0.004	0.019	0.011		
Site 1	Sand	178	0.072	0.007	0.003	0.002	0.069	0.007	0.016	0.004	0.015	0.011		
Site 1	Silt	185	0.037	0.005			0.037	0.005	0.025	0.004				
Site 2	Sand	16	0.101	0.010			0.101	0.010	0.012	0.004				
Site 2	Sand	21	0.107	0.011			0.107	0.011	0.009	0.004				
Site 2	Silt	22	0.040	0.005			0.040	0.005	0.010	0.004				
Site 2	Sandy Silt	26	0.036	0.005			0.036	0.005	0.009	0.004				
Site 2	Sand	31	0.061	0.006			0.061	0.006	0.009	0.004	0.017	0.011		
Site 2	Clayey Silt	32	0.052	0.005			0.052	0.005	0.010	0.004				
Site 2	Sand	37	0.037	0.005			0.037	0.005	0.010	0.004	0.022	0.011		
Site 2	Sandy Silt	41	0.080	0.008			0.080	0.008	0.007	0.004				
Site 2	Sand	43	0.028	0.005			0.028	0.005	0.012	0.004	0.020	0.011		
Site 3	Sandy Silt	11	0.043	0.005			0.043	0.005	0.011	0.004	0.021	0.011		
Site 3	Silt	14	0.035	0.005			0.035	0.005	0.011	0.004				
Site 3	Sandy Silt	17	0.045	0.005			0.045	0.005	0.041	0.007	0.038	0.005		
Site 3	Sand	20	0.083	0.008			0.083	0.008	0.011	0.004				
Site 3	Sand	27	0.080	0.008			0.080	0.008	0.015	0.004				
Site 3	Sand	32	0.147	0.015	0.014	0.002	0.132	0.015	0.025	0.004	0.035	0.011		
Site 3	Sand	36	0.073	0.007	0.004	0.002	0.068	0.007	0.019	0.004	0.023	0.011		
Site 3	Sand	40	0.059	0.006	0.002	0.001	0.057	0.006	0.018	0.004	0.016	0.011		
Site Temp	Clayey Silt	5	0.187	0.019			0.187	0.019	0.010	0.004	0.019	0.011		
Site Temp	Clayey Silt	8	0.107	0.011	0.001	0.001	0.106	0.011	0.008	0.004	0.016	0.011		
Site Temp	Clayey Silt	8	0.181	0.018			0.181	0.018	0.020	0.004	0.015	0.011		
Site Temp	Sandy Silt	14	0.070	0.007			0.070	0.007	0.009	0.004	0.023	0.011		
Site Temp	Clayey Silt	16	0.058	0.006			0.058	0.006	0.011	0.004	0.021	0.011		
Site Temp	Clayey Silt	23	0.035	0.005			0.035	0.005	0.008	0.004	0.019	0.011		
Site Temp	Sand	27	0.029	0.005			0.029	0.005	0.007	0.004	0.017	0.011		
Site Temp	Clayey Silt	28	0.050	0.005			0.050	0.005	0.008	0.004				
Site Temp	Sand	36	0.057	0.006	0.003	0.002	0.053	0.006	0.008	0.004	0.016	0.011		

Table 3. KCD1 Sediment PCR Data

KCD1 Well Cluster	Depth (ft)	Total *Nir* (gene copies/ 5 g sediment)	Total eubacteria (cells/ 5 g sediment)
Site 1	21	7.9E+03	1.1E+06
Site 1	27	nd	3.9E+06
Site 1	29	1.1E+04	1.0E+06
Site 1	30	5.1E+03	3.9E+05
Site 1	32	3.8E+03	1.9E+06
Site 1	36	1.1E+05	6.7E+06
Site 1	45	9.5E+03	6.9E+05
Site 2	29	9.6E+04	2.0E+06
Site 2	31	1.1E+04	5.4E+05
Site 2	34	1.6E+05	3.8E+06
Site 2	36	2.8E+05	1.2E+07
Site 2	38	2.2E+07	1.7E+08
Site 2	40	1.3E+06	1.9E+07
Site 2	44	5.6E+03	1.4E+05
Site 3	30	6.6E+03	5.9E+05
Site 3	38	3.6E+04	9.6E+05
Site 3	40	3.4E+04	2.6E+06
Site 3	42	9.6E+04	2.1E+06
Site 3	44	3.7E+04	7.4E+05
Site 3	46	1.9E+05	7.5E+06
Site 3	48	1.4E+05	6.9E+06
Site 4	28	2.5E+04	6.9E+05
Site 4	33	3.0E+04	1.1E+06
Site 4	43	1.9E+05	1.8E+06
Site 4	45	9.1E+04	4.9E+05
Site 4	47	7.2E+04	5.2E+05
Site 4	49	4.6E+04	1.7E+06

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Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations

M. J. SINGLETON,*,† B. K. ESSER,† J. E. MORAN,† G. B. HUDSON,† W. W. MCNAB,‡ AND T. HARTER§

Chemical Sciences Division, Lawrence Livermore National Laboratory, Environmental Restoration Division, Lawrence Livermore National Laboratory, and Department of Land, Air, and Water Resources, University of California at Davis

We present results from field studies at two central California dairies that demonstrate the prevalence of saturated-zone denitrification in shallow groundwater with $^3H/^3He$ apparent ages of <35 years. Concentrated animal feeding operations are suspected to be major contributors of nitrate to groundwater, but saturated zone denitrification could mitigate their impact to groundwater quality. Denitrification is identified and quantified using N and O stable isotope compositions of nitrate coupled with measurements of excess N_2 and residual NO_3^- concentrations. Nitrate in dairy groundwater from this study has $\delta^{15}N$ values (4.3–61‰), and $\delta^{18}O$ values (−4.5–24.5‰) that plot with $\delta^{18}O/\delta^{15}N$ slopes of 0.47–0.66, consistent with denitrification. Noble gas mass spectrometry is used to quantify recharge temperature and excess air content. Dissolved N_2 is found at concentrations well above those expected for equilibrium with air or incorporation of excess air, consistent with reduction of nitrate to N_2. Fractionation factors for nitrogen and oxygen isotopes in nitrate appear to be highly variable at a dairy site where denitrification is found in a laterally extensive anoxic zone 5 m below the water table, and at a second dairy site where denitrification occurs near the water table and is strongly influenced by localized lagoon seepage.

Introduction

High concentrations of nitrate, a cause of methemoglobinemia in infants (*1*), are a national problem in the United States (*2*), and nearly 10% of public drinking water wells in the state of California are polluted with nitrate at concentrations above the maximum contaminant level (MCL) for drinking water set by the U.S. Environmental Protection Agency (*3*). The federal MCL is 10 mg/L as N, equivalent to the California EPA limit of 45 mg/L as NO_3^- (all nitrate concentrations are hereafter given as NO_3^-). In the agricultural areas of California's Central Valley, it is not uncommon to have nearly half the active drinking water wells produce groundwater with nitrate concentrations in the range considered to indicate anthropogenic impact (>13–18 mg/L) (*2, 4*). The major sources of this nitrate are septic discharge, fertilization using natural (e.g., manure) or synthetic nitrogen sources, and concentrated animal feeding operations. Dairies are the largest concentrated animal operations in California, with a total heard size of 1.7 million milking cows (*5*).

Denitrification is the microbially mediated reduction of nitrate to gaseous N_2, and can occur in both unsaturated soils and below the water table where the presence of NO_3^-, denitrifying bacteria, low O_2 concentrations, and electron donor availability exist. In the unsaturated zone, denitrification is recognized as an important process in manure and fertilizer management (*6*). Although a number of field studies have shown the impact of denitrification in the saturated zone (e.g., *7, 8–11*), prior to this study it was not known whether saturated zone denitrification could mitigate the impact of nitrate loading at dairy operations. The combined use of tracers of denitrification and groundwater dating allows us to distinguish between nitrate dilution and denitrification, and to detect the presence of pre-modern water at two dairy operations in the Central Valley of California, referred to here as the Kings County Dairy (KCD) and the Merced County Dairy (MCD; Figure 1). Detailed descriptions of the hydrogeologic settings and dairy operations at each site are included as Supporting Information.

Materials and Methods

Concentrations and Nitrate Isotopic Compositions. Samples for nitrate N and O isotopic compositions were filtered in the field to 0.45 μm and stored cold and dark until analysis. Anion and cation concentrations were determined by ion chromatography using a Dionex DX-600. Field measurements of dissolved oxygen and oxidation reduction potential (using Ag/AgCl with 3.33 mol/L KCl as the reference electrode) were carried out using a Horiba U-22 water quality analyzer. The nitrogen and oxygen isotopic compositions ($\delta^{15}N$ and $\delta^{18}O$) of nitrate in 23 groundwater samples from KCD and MCD were measured at Lawrence Berkeley National Laboratory's Center for Isotope Geochemistry using a version of the denitrifying bacteria procedure (*12*) as described in Singleton et al. (*13*). In addition, the nitrate from 17 samples was extracted by ion exchange procedure of (*14*) and analyzed for $\delta^{15}N$ at the University of Waterloo. Analytical uncertainty (1σ) is 0.3‰ for $\delta^{15}N$ of nitrate and 0.5‰ for $\delta^{18}O$ of nitrate. Isotopic compositions of oxygen in water were determined on a VG Prism isotope ratio mass spectrometer at Lawrence Livermore National Laboratory (LLNL) using the CO_2 equilibration method (*15*), and have an analytical uncertainty of 0.1‰.

Membrane Inlet Mass Spectrometry. Previous studies have used gas chromatography and/or mass spectrometry to measure dissolved N_2 gas in groundwater samples (*16–19*). Dissolved concentrations of N_2 and Ar for this study were analyzed by membrane inlet mass spectrometry (MIMS), which allows for precise and fast determination of dissolved gas concentrations in water samples without a separate extraction step, as described in Kana et al. (*20, 21*). The gas abundances are calibrated using water equilibrated with air under known conditions of temperature, altitude, and humidity (typically 18 °C, 183 m, and 100% relative humidity). A small isobaric interference from CO_2 at mass 28 (N_2) is corrected based on calibration with CO_2-rich waters with known dissolved N_2, but is negligible for most samples. Samples are collected for MIMS analysis in 40 mL amber

* Corresponding author address: P.O. Box 808, L-231, Livermore, California, 94550; phone: (925) 424-2022; fax: (925) 422-3160; e-mail: singleton20@llnl.gov.

† Chemical Sciences Division, Lawrence Livermore National Laboratory.

‡ Environmental Restoration Division, Lawrence Livermore National Laboratory.

§ University of California at Davis.

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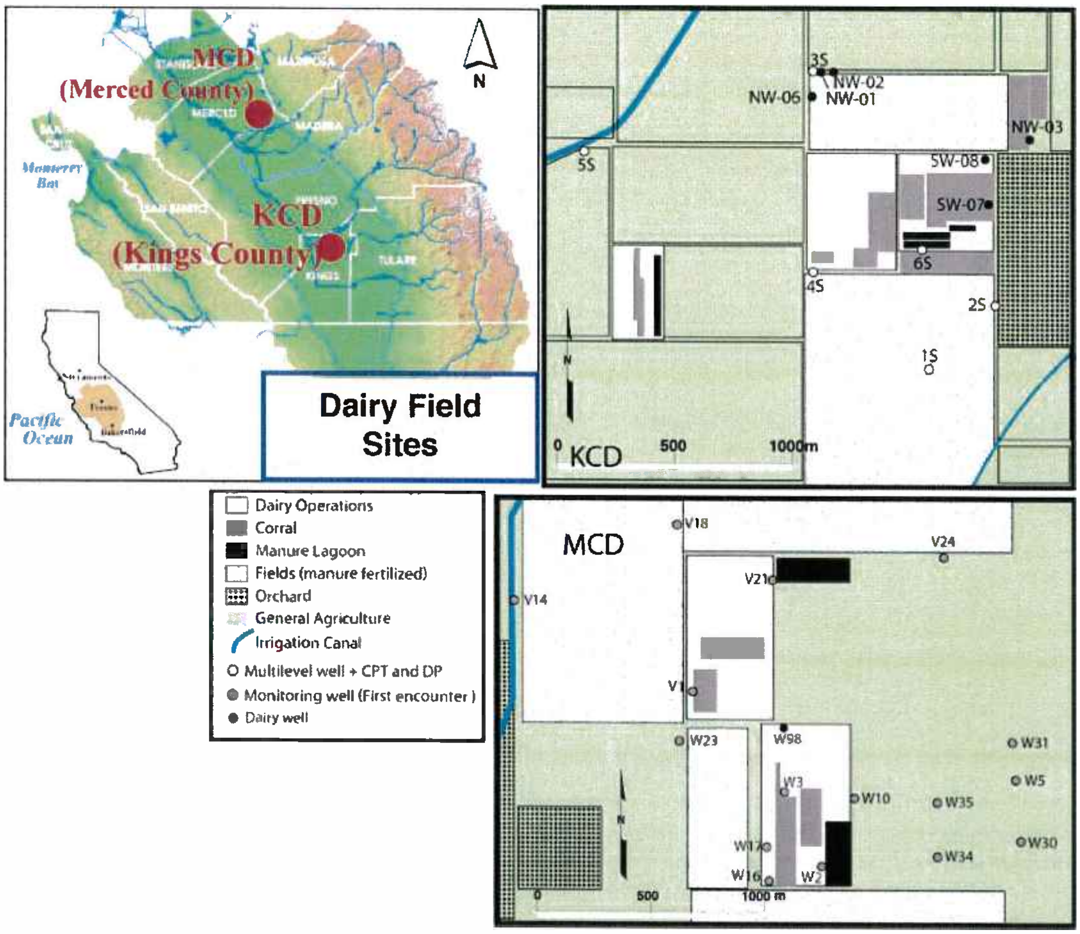

FIGURE 1. Location of dairy study sites, and generalized maps of each dairy showing sample locations relative to lagoons and dairy operations.

glass VOA vials with no headspace that are kept cold during transport, and then analyzed within 24 h.

Noble Gases and $^3H/^3He$ Dating. Dissolved noble gas samples are collected in copper tubes, which are filled without bubbles and sealed with a cold weld in the field. Dissolved noble gas concentrations were measured at LLNL after gas extraction on a vacuum manifold and cryogenic separation of the noble gases. Concentrations of He, Ne, Ar, and Xe were measured on a quadrupole mass spectrometer. The ratio of ^3He to ^4He was measured on a VG5400 mass spectrometer. Calculations of excess air and recharge temperature from Ne and Xe measurements are described in detail in Ekwurzel (*22*), using an approach similar to that of Aeschbach-Hertig et al. (*23*).

Tritium samples were collected in 1 L glass bottles. Tritium was determined by measuring ^3He accumulation after vacuum degassing each sample and allowing 3−4 weeks accumulation time. After correcting for sources of ^3He not related to ^3H decay (*24, 25*), the measurement of both tritium and its daughter product ^3He allows calculation of the initial tritium present at the time of recharge, and apparent ages can be determined from the following relationship based on the production of tritiogenic helium ($^3He_{trit}$):

$$\text{Groundwater Apparent Age (years)} = -17.8 \times \ln(1 + {}^3He_{trit}/{}^3H)$$

Groundwater age dating has been applied in several studies of basin-wide flow and transport (*25−27*). The reported groundwater age is the mean age of the mixed sample, and furthermore, is only the age of the portion of the water that contains measurable tritium. Average analytical error for the age determinations is ±1 year, and samples with ^3H that is too low for accurate age determination (<1 pCi/L) are reported as >50 years. Significant loss of ^3He from groundwater is not likely in this setting given the relatively short residence times and high infiltration rates from irrigation. Apparent ages give the mean residence time of the fraction of recently recharged water in a sample, and are especially useful for comparing relative ages of water from different locations at each site. The absolute mean age of groundwater may be obscured by mixing along flow paths due to heterogeneity in the sediments (*28*).

Results and Discussion

Nitrate in Dairy Groundwater. Nitrate concentrations at KCD range from below detection limit (BDL, <0.07 mg/L) to 274 mg/L. Within the upper aquifer, there is a sharp boundary between high nitrate waters near the surface and deeper, low nitrate waters. Nitrate concentrations are highest between 6 and 13 m below ground surface (BGS) at all multilevel wells (0.5 m screened intervals), with an average concentration of 98 mg/L. Groundwater below 15 m has low nitrate concentrations ranging from BDL to 2.8 mg/L, and also has low or nondetectable ammonium concentrations. The transition from high to low nitrate concentration corresponds to decreases in field-measured oxidation−reduction potential (ORP) and dissolved oxygen (DO) concentration. ORP values are generally above 0 mV and DO concentrations are >1 mg/L in the upper 12 m of the aquifer, defining a more oxidizing zone (Figure 2). A reducing zone is indicated below

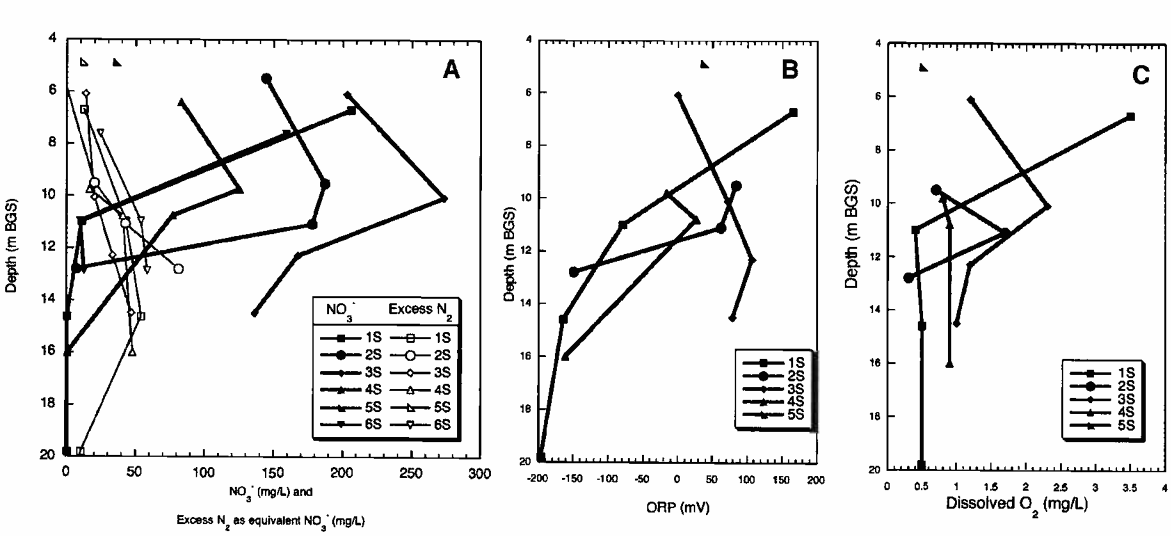

FIGURE 2. (A) Average excess N_2 and nitrate concentrations, (B) oxidation–reduction potential (ORP), and (C) dissolved oxygen in multilevel monitoring wells at the KCD site.

12 m by ORP values as low as −196 mV and DO concentrations <1.2 mg/L. Vertical head varies by less than 10 cm in the upper aquifer multilevel wells.

Nitrate concentrations at MCD monitoring wells sampled for this study range from 2 to 426 mg/L with an average of 230 mg/L. Several wells (W-02, W-16, and W-17) located next to a lagoon and corral have lower nitrate but high ammonium concentrations (Table 1 in Supporting Information). The MCD wells are all screened at the top of the unconfined aquifer except W98, a supply well that is pumped from approximately 57 m BGS. Nitrate concentrations observed for this deeper well are <1 mg/L.

Dissolved Gases. Nitrogen gas, the comparatively conservative product of denitrification, has been used as a natural tracer to detect denitrification in the subsurface (*16–18*). Groundwater often also contains N_2 beyond equilibrium concentrations due to incorporation of excess air from physical processes at the water table interface (*23, 29, 30*). In the saturated zone, total dissolved N_2 is a sum of these three sources:

$$(N_2)_{dissolved} = (N_2)_{equilibrium} + (N_2)_{excess\ air} + (N_2)_{denitrification}$$

By normalizing the measured dissolved concentrations as N_2/Ar ratios, the amount of excess N_2 from denitrification can be calculated as

$$(N_2)_{denitrification} = \left(\left(\frac{N_2}{Ar}\right)_{measured} - \left(\frac{N_{2equilibrium} + N_{2excess\ air}}{Ar_{equilibrium} + Ar_{excess\ air}}\right)\right)Ar_{measured}$$

where the N_2 and Ar terms for equilibrium are calculated from equilibrium concentrations determined by gas solubility. The N_2/Ar ratio is relatively insensitive to recharge temperature, but the incorporation of excess air must be constrained in order to determine whether denitrification has shifted the ratio to higher values (*19*). Calculations of excess N_2 based on the N_2/Ar ratio assume that any excess air entrapped during recharge has the ratio of N_2/Ar in the atmosphere (83.5). Any partial dissolution of air bubbles would lower the N_2/Ar ratio (*30, 31*), thus decreasing the apparent amount of excess N_2.

For this study, Xe and Ne derived recharge temperature and excess air content were determined for 12 of the monitoring wells at KCD and 9 wells at MCD. For these sites, excess N_2 can be calculated directly, accounting for the contribution of excess air and recharge temperature. Site representative mean values of recharge temperature and excess air concentration are used for samples without noble gas measurements. Mean annual air temperatures at the KCD and MCD sites are 17 and 16 °C, respectively (*32*), and the Xe-derived average recharge temperatures for the KCD and MCD sites are 19 and 18 °C. Recharge temperatures are most likely higher than mean annual air temperature because most recharge is from excess irrigation during the summer months. The average amount of excess air indicated by Ne concentrations is 2.2×10^{-3} cm^3(STP)/g H_2O for KCD and 1.7×10^{-3} cm^3(STP)/g H_2O for MCD. From these parameters, we estimate the site representative initial N_2/Ar ratios including excess air to be 41.2 for KCD and 40.6 for MCD. Measured N_2/Ar ratios greater than these values are attributed to production of N_2 by denitrification.

The excess N_2 concentration can be expressed in terms of the equivalent reduced nitrate that it represents in mg/L NO_3^- based on the stoichiometry of denitrification. Considering excess N_2 in terms of equivalent NO_3^- provides a simple test to determine whether there is a mass balance between nitrate concentrations and excess N_2. From Figure 2, there does not appear to be a balance between nitrate concentrations and excess N_2 in KCD groundwater, since nitrate concentrations in the shallow wells are more than twice that of equivalent excess N_2 concentrations in the anoxic zone. There are multiple possible causes of the discrepancy between NO_3^- concentrations and excess N_2 concentrations including (1) the NO_3^- loading at the surface has increased over time, and denitrification is limited by slow vertical transport into the anoxic zone, (2) mixing with deeper, low initial NO_3^- waters has diluted both the NO_3^- and excess N_2 concentrations, or (3) some dissolved N_2 has been lost from the saturated zone. All three processes may play a role in N cycling at the dairies, but we can shed some light on their relative importance by considering the extent of denitrification and then constraining the time scale of denitrification as discussed in the following sections.

Isotopic Compositions of Nitrate. Large ranges in $\delta^{15}N$ and $\delta^{18}O$ values of nitrate are observed at both dairies (Figure 3). Nitrate from KCD has $\delta^{15}N$ values of 4.3–61.1‰, and $\delta^{18}O$ values of −0.7–24.5‰. At MCD, nitrate $\delta^{15}N$ values range from 5.3 to 30.2‰, and $\delta^{18}O$ values range from −0.7 to 13.1‰. The extensive monitoring well networks at these sites increase the probability that water containing residual nitrate from denitrification can be sampled.

Nitrate $\delta^{15}N$ and $\delta^{18}O$ values at both dairies are consistent with nitrification of ammonium and mineralized organic N

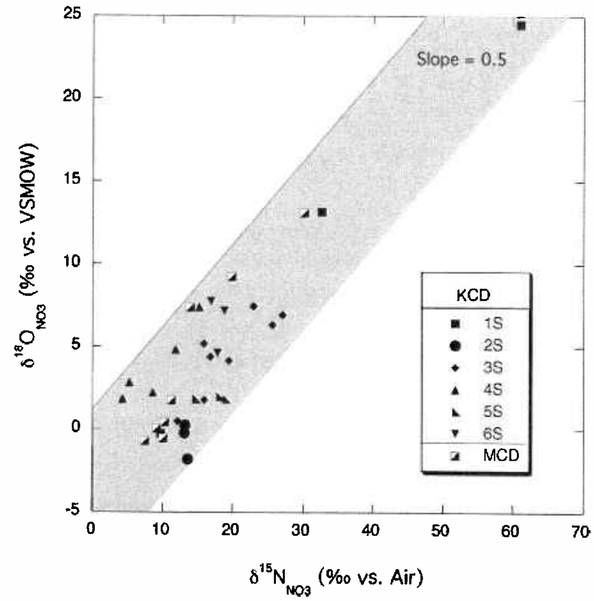

FIGURE 3. Oxygen and nitrogen isotopic composition of nitrate in dairy groundwater from multilevel monitoring wells at KCD and first encounter wells at MCD. The shaded region indicates a slope of 0.5 for a range of starting compositions. Calculated slopes for linear fits to multilevel wells at KCD and first encounter wells at MCD range from 0.47 to 0.60.

compounds from manure-rich wastewater, which is stored and used as a fertilizer at both dairy sites. At some locations, nitrification has been followed by denitrification. Prior to nitrification, cow manure likely starts out with a bulk $\delta^{15}N$ value close to 5‰, but is enriched in ^{15}N to varying degrees due to volatile loss of ammonia, resulting in $\delta^{15}N$ values of 10–22‰ in nitrate derived from manure (*33, 34*). Culture experiments have shown that nitrification reactions typically combine 2 oxygen atoms from the local pore water and one oxygen atom from atmospheric O_2 (*35, 36*), which has a $\delta^{18}O$ of 23.5‰ (*37*). Different ratios of oxygen from water and atmospheric O_2 are possible for very slow nitrification rates and low ammonia concentrations (*38*), however for dairy wastewater we assume that the 2:1 relation gives a reasonable prediction of the starting $\delta^{18}O$ values for nitrate at the two dairies based on the average values for $\delta^{18}O$ of groundwater at each site (−12.6‰ at KCD and −9.9‰ at MCD). Based on this approach, the predicted initial values for $\delta^{18}O$ in nitrate are −0.7‰ at KCD and 1.1‰ at MCD. Samples with the lowest nitrate $\delta^{15}N$ values have $\delta^{18}O$ values in this range, and are consistent with nitrate derived from manure. There is no strong evidence for mixing with nitrate from synthetic nitrogen fertilizers, which are used occasionally at both sites, but typically have low $\delta^{15}N$ values (0–5‰) and $\delta^{18}O$ values around 23‰ (*39*).

Denitrification drives the isotopic composition of the residual nitrate to higher $\delta^{15}N$ and $\delta^{18}O$ values. The stable isotopes of nitrogen are more strongly fractionated during denitrification than those of oxygen, leading to a slope of approximately 0.5 on a $\delta^{18}O$ vs $\delta^{15}N$ diagram (*34*). Nitrate $\delta^{15}N$ and $\delta^{18}O$ values at individual KCD multilevel well sites are positively correlated with calculated slopes ranging from 0.47 to 0.60; the slope of first encounter well data at MCD is 0.66 (Figure 3). These nitrate $\delta^{15}N$ and $\delta^{18}O$ values indicate that denitrification is occurring at both sites. Because a wide range of fractionation factors are known to exist for this process (*40*), it is not possible to determine the extent of denitrification using only the isotopic compositions of nitrate along a denitrification trend, even when the initial value for manure-derived nitrate can be measured or calculated.

Extent of Denitrification. The concentrations of excess N_2 and residual nitrate can be combined with the isotopic composition of nitrate in order to characterize the extent of denitrification. In an ideal system, denitrification leads to a regular decrease in nitrate concentrations, an increase in excess N_2, and a Rayleigh-type fractionation of N and O isotopes in the residual nitrate (Figure 4). In the Rayleigh fractionation model (*41*) the isotopic composition of residual nitrate depends on the fraction of initial nitrate remaining in the system ($f = C/C_{initial}$), the initial $\delta^{15}N$, and the fractionation factor (α) for denitrification:

$$\delta^{15}N = (1000 + \delta^{15}N_{initial})\, f^{(\alpha-1)} - 1000$$

The fractionation factor α is defined from the isotopic ratios of interest ($R = {}^{15}N/{}^{14}N$ and ${}^{18}O/{}^{16}O$):

$$\alpha = \frac{(R)_{Product}}{(R)_{Reactant}}$$

This fractionation can also be considered as an enrichment factor (ϵ) in ‰ units using the approximation $\epsilon \approx 1000 \ln \alpha$. The extent of denitrification can be calculated as $1 - f$. Rather than relying on an estimate of initial nitrate concentration, the parameter f is determined directly using field measurements of excess N_2 in units of equivalent reduced NO_3^-:

$$f = C_{NO_3^-}/(C_{NO_3^-} + C_{excess\ N2})$$

Heterogeneity in groundwater systems can often complicate the interpretation of contaminant degradation using a Rayleigh model (*42*). Denitrified water retains a proportion of its excess N_2 concentration (and low values of f) during mixing, but the isotopic composition of nitrate may be disturbed by mixing since denitrified waters contain extremely low concentrations of nitrate (<1 mg/L). The sample from 1S with a f value close to zero and a $\delta^{15}N$ value of 7.6‰ was likely denitrified and is one example of this type of disturbance. However, in general, groundwater samples from the same multilevel well sites at KCD fall along similar Rayleigh fractionation curves, indicating that the starting isotopic composition of nitrate and the fractionation factor of denitrification vary across the site (Figure 4).

Values of $\delta^{15}N$ and f calculated from nitrate and excess N_2 fall along Rayleigh fractionation curves with enrichment factors (ϵ) ranging from −57‰ to −7‰ for three multilevel well sites at KCD and first encounter wells at MCD. As expected for denitrification, the enrichment factors indicated for oxygen are roughly half of those for nitrogen. The magnitude of these enrichment factors for N in residual nitrate are among the highest reported for denitrification, which typically range from −40‰ to −5‰ (*34, 40*). Partial gas loss near the water table interface at MCD could potentially increase the value of f, resulting in larger values of ϵ. Gas loss is unlikely to affect fractionation factors at KCD since most excess N_2 is produced well below the water table. Considering the large differences observed for denitrification fractionation factors within and between the two dairy sites, it is not sufficient to estimate fractionation factors for denitrification at dairies based on laboratory-derived values or field-derived values from other sites. The appropriate fractionation factors must be determined for each area, and even then the processes of mixing and gas loss must be considered in the relation between isotopic values and the extent of denitrification. Nevertheless, direct determination of the original amount of nitrate using dissolved N_2 values significantly improves our ability to determine the extent of denitrification in settings where the initial nitrate concentrations are highly variable.

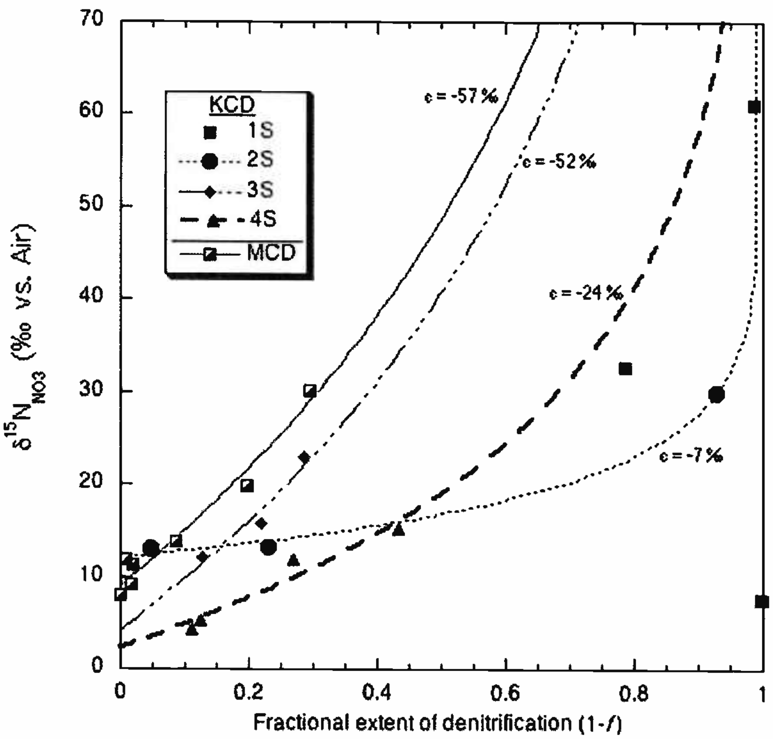

FIGURE 4. Nitrate δ^{15}N values plotted against the fractional extent of denitrification (1 − *f*) based on excess N_2 and residual nitrate. Enrichment factors (ε) are calculated by fitting the Rayleigh fractionation equation to data from three multilevel well sites at KCD and wells at MCD.

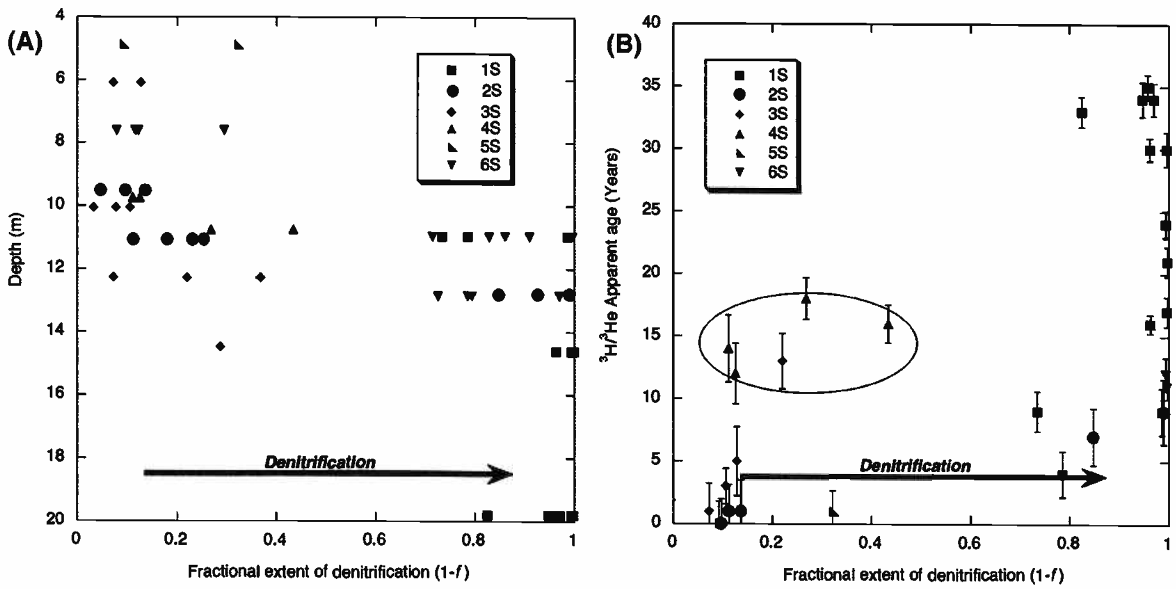

FIGURE 5. Sample depth (A) and ^{3}H/^{3}He apparent age (B) plotted against the fractional extent of denitrification (1 − *f*). Samples at two sites have experienced less denitrification than is typical for samples with ^{3}H/^{3}He apparent age >8 years (circled, see text).

Time Scale of Denitrification. Modern water (i.e., groundwater containing measurable tritium) is found at all multilevel wells completed in the upper aquifer at KCD, the deepest of which is 20 m BGS. The upper aquifer below KCD has ^{3}H/^{3}He apparent ages of <35 years. At well 1D1 (54 m BGS), the lower aquifer has no measurable NO_3^- and tritium below 1 pCi/L, indicating a groundwater age of more than 50 years. The sum of nitrate and excess N_2 is highest in the young, shallow dairy waters at KCD. Samples with ^{3}H/^{3}He ages >29 years were below the MCL for nitrate prior to denitrification. These results are consistent with an increase in nitrate loading at the surface, which followed the startup of KCD operations in the early 1970s.

The extent of denitrification at KCD is related to both depth and groundwater residence times based on ^{3}H/^{3}He apparent ages (Figure 5). There is a sharp transition from high nitrate waters to denitrified waters between 11 and 13 m depth across the KCD site. This transition is also related to the apparent age of the groundwater, as the high nitrate waters typically have apparent ages of between 0 and 5 years, and most samples with ages greater than 8 years are significantly or completely denitrified. There are five samples that do not follow this pattern. These outliers are from sites 3S and 4S where the shallow groundwater has much higher $^3H/^3He$ apparent ages due to slow movement around clay zones at the screened intervals for these samples. The existence of older water that is not significantly impacted by denitrification indicates that it is the physical transport of water below the transition from oxic to anoxic conditions rather than the residence time that governs denitrification in this system.

At the MCD site, groundwater $^3H/^3He$ apparent ages indicate fast transit rates from the water table to the shallow monitoring wells. Most of the first encounter wells have apparent ages of <3 years, consistent with the hydraulic analysis presented by Harter et al. (*5*). The very fast transit times to the shallow monitoring wells at MCD allow for some constraints on minimum denitrification rates at this site. Based on the comparison of the calculated ages with the initial tritium curve, these shallow wells contain a negligible amount of old, ^3H-decayed water. In shallow wells near lagoons (e.g., W-16 and V-21), the observed excess N_2 (equivalent to 71 and 40 mg/L of reduced NO_3^-) accumulated over a duration of less than 1 year, indicating that denitrification rates may be very high at these sites. Complete denitrification of groundwater collected from well W-98 (excess N_2 equivalent to 51 mg/L NO_3^-) was attained within approximately 31 years, but may have occurred over a short period of time relative to the mean age of the water.

Occurrence of Denitrification at Dairy Sites. The depth at which denitrified waters are encountered is remarkably similar across the KCD site. This transition is not strongly correlated with a change in sediment texture. The denitrified waters at all KCD wells coincide with negative ORP values and generally low dissolved O_2 concentrations. Total organic carbon (TOC) concentration in the shallow groundwaters range from 1.1 to 15.7 mg/L at KCD, with the highest concentrations of TOC found in wells adjacent to lagoons. The highest concentrations of excess N_2 are found in nested well-set 2S, which is located in a field downgradient from the lagoons. However, sites distal to the lagoons (3S and 4S) that are apparently not impacted by lagoon seepage (*43*) also show evidence of denitrification, suggesting that direct lagoon seepage is not the sole driver for this process.

The chemical stratification observed in multilevel wells at the KCD site demonstrates the importance of characterizing vertical variations within aquifers for nitrate monitoring studies. Groundwater nitrate concentrations are integrated over the high and low nitrate concentration zones by dairy water supply wells, which have long screened intervals from 9 to 18 m BGS. Water quality samples from these supply wells underestimate the actual nitrate concentrations present in the uppermost oxic aquifer. Similarly, first encounter monitoring wells give an overestimate of nitrate concentrations found deep in the aquifer, and thus would miss entirely the impact of saturated zone denitrification in mitigating nitrate transport to the deep aquifer.

Monitoring wells at MCD sample only the top of the aquifer, so the extent of denitrification at depth is unknown, except for the one deep supply well (W98), which has less than 1 mg/L nitrate and an excess N_2 content consistent with reduction of 51 mg/L NO_3^- to N_2. This supply well would be above the MCL for nitrate without the attenuation of nitrate by denitrification. The presence of ammonium at several of the wells with excess N_2 indicates a component of wastewater seepage in wells located near lagoons, where mixing of oxic waters with anoxic lagoon seepage may induce both nitrification and denitrification. Wells that are located in the surrounding fields have high NO_3^- concentrations, and do not have any detectable excess N_2, a result consistent with mass-balance models of nitrate loading and groundwater nitrate concentration (*5*).

While dairy operations seem likely to establish conditions conducive to saturated zone denitrification, the prevalence of the phenomenon is not known. Major uncertainties include the spatial extent of anaerobic conditions, and transport of organic carbon under differing hydrogeologic conditions and differing nutrient management practices. Lagoon seepage may also increase the likelihood of denitrification in dairy aquifers. The extent to which dairy animal and field operations affect saturated zone denitrification is an important consideration in determining the assimilative capacity of underlying groundwater to nitrogen loading associated with dairy operations.

Acknowledgments

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Supporting Information Available

A table of chemical, isotopic, and dissolved gas results from this study, a plot of apparent age with depth, and detailed descriptions of the study sites. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information for "Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations" by M. J. Singleton[1*], B. K. Esser[1], J. E. Moran[1], G. B. Hudson[1], W. W. McNab[2], and T. Harter[3]

Contents: 7 Pages, 1 Figure, and 1 Table

Description of Dairy Sites

Study Site 1:

Study Site #1 is located at a dairy operation in Kings County, CA (KCD). Manure management practices employed at KCD, with respect to corral design, runoff capture and lagoon management are typical of practices employed at other dairies in the region. KCD has close to the 1000-cow average for dairies in the area, and operates three clay-lined wastewater lagoons that receive wastewater after solids separation. Wastewater is used for irrigation of 500 acres of forage crops (corn and alfalfa) on the dairy and on neighboring farms; dry manure is exported to neighboring farms.

KCD is located in the Kings River alluvial fan, a sequence of layered sediments transported by the Kings River from the Sierra Nevada to the low lying southern San Joaquin Valley of California (*1, 2*). The site overlies an unconfined aquifer, which has been split into an upper aquifer from 3m to 24m below ground surface (BGS) and a lower aquifer (>40 m BGS) that are separated by a gap of unsaturated sediments. Both aquifers are predominantly composed of unconsolidated sands with minor clayey sand layers. The lower unsaturated gap was likely caused by intense regional groundwater pumping, and a well completed in this unsaturated zone has very low gas pressures. There are no persistent gradients in water table levels across the KCD site, but in general, regional groundwater flow is from the NW to SE due to topographic flow on the Kings River fan. The water table is located about 5 m BGS. Local recharge is dominated by vertical fluxes from irrigation, and to a lesser extent, leakage from adjacent unlined canals. Transient cones of depression are induced during groundwater pumping from dairy operation wells.

The regional groundwater is highly impacted by agricultural activities and contains elevated concentrations of nitrate and pesticides (*3, 4*).

KCD was instrumented with five sets of multi-level monitoring wells and one "up-gradient" well near an irrigation canal. These wells were installed in 2002, and sampled between Feb. 2002 and Aug. 2005. The multi-level wells have short (0.5 m) screened intervals in order to detect heterogeneity and stratification in aquifer chemistry. One monitoring well was screened in the lower aquifer, 54m BGS. The remaining monitoring wells are screened in the upper aquifer from 5m to 20m BGS. In addition, there are eight dairy operation wells that were sampled over the course of this study. These production wells have long screens, generally between 9 to 18 meters below ground surface (BGS).

Study Site 2:

The second dairy field site is located in Merced County, CA. The Merced County dairy (MCD) lies within the northern San Joaquin Valley, approximately 160 km NNW from the KCD site. The site is located on the low alluvial fans of the Merced and Tuolumne Rivers, which drain the north-central Sierra Nevada. Soils at the site are sand to loamy sand with rapid infiltration rates. The upper portion of the unconfined alluvial aquifer is comprised of arkosic sand and silty sand, containing mostly quartz and feldspar, with interbedded silt and hardpan layers. Hydraulic conductivities were measured with slug tests and ranged from 1×10^{-4} m/s to 2×10^{-3} m/s with a geometric mean of 5×10^{-4} m/s (*5*). Regional groundwater flow is towards the valley trough with a gradient of approximately 0.05% to 0.15%. Depth to groundwater is 2.5 m to 5 m BGS. The climate is Mediterranean with annual precipitation of 0.5 m, but groundwater recharge is on the order of 0.5–0.8 m per year with most of the recharge originating from excess irrigation water (*3*). Transit times in the unsaturated zone are relatively short due to the shallow depth to groundwater and due to low water holding capacity in the sandy soils. Shallow water tables are managed through tile drainage and groundwater pumping specifically for drainage. The MCD site is instrumented with monitoring wells that are screened from 2-3 m BGS to a depth of 7-9 m BGS. The wells access the upper-most part of the unconfined aquifer, hence, the most recently recharged groundwater (6). Recent investigations showed strongly elevated nitrate levels in this shallow groundwater originating largely from applications of liquid dairy manure to field crops, from corrals, and from manure storage lagoons (6). For this study, a subset of 18 wells was sampled. A deep domestic well was also sampled at MCD. This domestic well is completed to 57 m BGS, and thus samples a deeper part of the aquifer than the monitoring well network.

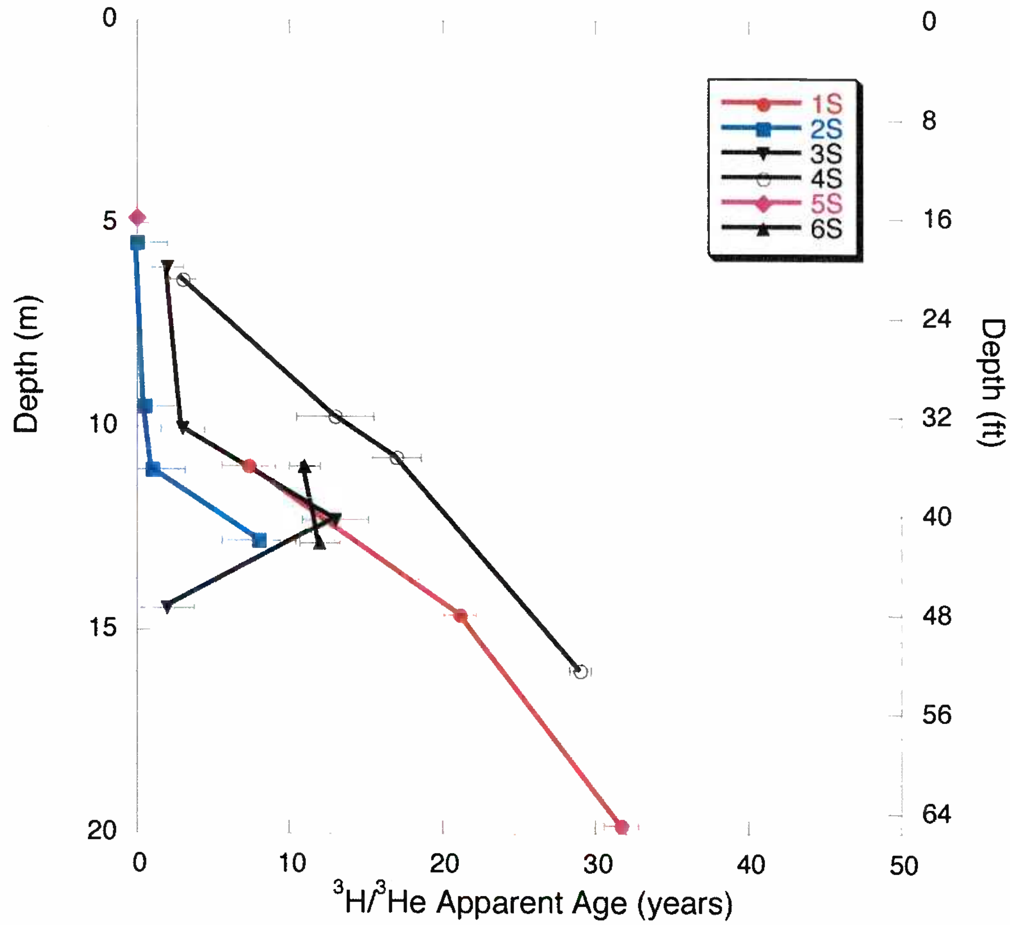

Figure S1. Groundwater $^3H/^3He$ apparent ages from multilevel monitoring wells at KCD. Error bars show analytical error.

Table S1. Chemical, dissolved gas, and isotopic compositions for multilevel groundwater monitoring wells and lagoons. Average values are given for wells sampled more than onc
Excess N_2 values in **bold** are fully constrained by noble gas determinations of excess air and recharge temperature.

Site	Depth of multi-level well (m)	Cl^- (mg/L)	NO_3^- (mg/L)	NH_4^+ (mg/L)	ORP	DO (mg/L)	TOC (mg/L)	$\delta^{18}O$ H_2O (‰ SMOW)	$\delta^{15}N$ NO_3^- (‰ Air)	$\delta^{18}O$ NO_3^- (‰ SMOW)	$^3H/^3He$ age (yr)	+/- (yr)	Excess air determined from Ne (cc STP/g)	Recharge Temp. from Xe (°C)	+/- (°C)	^3H pCi/L	+/- (pCi/L)	N_2/Ar
KCD-CANAL-1		1.5	1.2	0.2		10.0		-12.9								13.3	0.6	
KCD-LAGOON-1		304.5	28.6	360.8		0.4	480.0	-10.2										68
KCD-LAGOON-2		265.2	13.9	292.1		0.5	490.0	-10.0										58
KCD-LAGOON-3		212.2	22.4	181.3		0.5	420.0	-9.9										41
KCD-1O1	54.3	1.9	0.2	<0.1	-264	0.2	0.8	-13.7	7.1		>50		3.40E-03	15	1.2	0.5	0.1	41
KCD-1S1	6.7		206.0		166	3.5		-12.7										46
KCO-1S2	11.0	52.5	11.1	0.3	-79	0.4	2.5	-12.8	46.9	18.8	7.3	1.8	<1E-4	16	1.1	32.0	1.2	62
KCO-1S3	14.6	36.0	0.5	1.3	-164	0.5	1.3	-12.9	7.6		21.1	1.1	2.82E-03	14	1.1	31.4	1.2	63
KCD-1S4	19.8	9.8	0.4	2.5	-196	0.5	1.1	-13.3			31.7	1.1	4.02E-03	16	1.1	28.3	1.1	46
KCD-2S1	5.5	107.7	144.5	<0.1			5.0	-12.3			0.0	2.0	1.70E-03	19	1.0	21.9	0.9	39
KCD-2S2	9.5	95.0	187.2	0.6	84	0.7	4.2	-12.2	13.1	-0.2	0.5	2.2	1.78E-03	22	1.1	19.5	0.8	49
KCO-2S3	11.1	101.1	178.2	0.1	62	1.7	3.0	-12.1	13.2	0.2	1.0	2.1	<1E-4	21	1.1	19.3	0.8	62
KCD-2S4	12.8	72.7	7.1	1.0	-149	0.3	1.8	-12.4	29.9		8.0	2.4	<1E-4	23	1.8	19.8	0.8	10(
KCD-3S1	6.1	170.4	203.1	0.4	0	1.2	5.3	-11.7	14.5	2.4	2.0	1.0	1.42E-03	19	1.1	17.8	0.7	46
KCD-3S2	10.1	255.6	273.6	<0.1	72	2.3	14.2	-11.2			3.0	1.4	6.35E-04	21	1.1	21.2	0.9	49
KCO-3S3	12.3	162.7	167.8	0.5	107	1.2	9.0	-11.9	15.8	5.2	13.0	2.2	1.30E-03	18	1.0	16.4	0.8	53
KCD-3S4	14.5	194.0	136.4	<0.1	79	1.0	5.6	-11.8	22.9	7.4	2.0	1.7	<1E-4	20	1.0	18.6	0.7	59
KCD-4S1	6.4	127.0	83.3	<0.1					8.6	2.2	3.0	0.8	3.35E-04	20	1.0	35.6	1.4	
KCD-4S2	9.8	32.1	125.4	0.4	-16	0.8	1.1	-11.8	4.7	2.3	13.0	2.5	5.07E-03	18	1.3	20.3	0.8	51
KCD-4S3	10.8	42.3	77.1	0.5	27	0.9	1.1	-12.0	13.5	6.1	17.0	1.6	3.54E-03	19	1.2	22.7	0.9	60
KCD-4S4	16.0	35.0	0.9	1.8	-161	0.9	3.5	-13.0			29.0	0.7		18	1.0	46.5	1.7	61
KCD-5S1	4.9	14.5	35.4	1.3	37	0.5	1.5	-13.4	18.9	1.8	<1		<1E-4	18	1.0	12.5	0.6	46
KCD-6S1	12.9	129.3	12.7	20.4		1.0	15.7	-11.9	12.1		12.0	1.3	<1E-4			29.1	1.1	70
KCD-6S2	11.0	140.6	10.1	3.2		1.2	14.6	-11.8			11.0	1.0	<1E-4			33.3	1.2	67
KCD-6S3	7.6	129.5	159.3	0.9			6.7	-11.6	19.0	7.7			2.13E-04			33.9	1.3	51
KCD-NW-01	9-18	140.8	114.7	1.9		1.9		-12.0	15.0									54
KCD-NW-02	9-18	163.4	75.2	3.4		1.3		-12.0	18.2							17.0	0.9	71
KCD-NW-03	9-18	100.3	67.2	<0.1														
KCD-NW-04	9-18	2.8	2.0	<0.1				-13.7			>50		7.72E-04	12	0.9	0.2	0.2	
KCD-NW-06	9-18	92.8	48.6	2.6				-12.2	17.2							22.9	1.2	61
KCD-SW-02	9-18	52.6	91.0	<0.1				-12.7	23.5							24.8	1.4	
KCD-SW-03	9-18	45.1	29.2	1.9		1.5		-12.4	27.3							30.4	1.3	57
KCD-SW-07	9-18	165.5	25.8	<0.1														
KCD-SW-08	9-18	184.1	116.6	2.3		3.8		-10.9	16.9							19.7	0.8	53
MCD-LAGOON		514.0	<0.1	691.8														62
MCD-V-01	7.0	317.8	425.1	<0.1	111	5.6	12.7	-9.3	13.9	7.4	12.0	1.7	<1E-4	25	1.2	36.0	1.4	61
MCD-V-14	7.6	71.4	316.0	<0.1			5.8		11.2	1.7	2.0	2.9	1.26E-03	18	1.0	12.4	0.5	41
MCD-V-18	6.1	77.2	195.5	1.7	193	3.3	8.1		10.1	-0.5						12.2	0.5	39
MCD-V-21	9.1	145.5	163.1	<0.1	147	1.4	22.6	-9.1	19.9	9.2	<1					15.3	0.6	61
MCD-V-24	9.1	30.2	201.5	<0.1	161	7.0	5.4	-10.5	7.4	-0.7	<1		4.31E-04	20	1.0	13.8	0.6	37
MCD-V-99		73.0	303.2	2.4			12.2		10.3	0.4	1.0	2.1	<1E-4	19	1.0	14.5	0.6	39
MCD-W-02	7.0	226.1	2.0	148.5		0.6	12.7	-9.1								17.9	0.7	12(
MCD-W-03	7.0	82.2	341.8	0.7		0.8	14.5	-10.5			3.0	3.1	2.13E-03	17	1.0	13.7	0.6	45
MCD-W-05	7.0	48.3	230.6	<0.1				-10.7	6.8							14.5	0.8	39
MCD-W-10	9.1	55.5	426.1	<0.1	171		11.7	-10.3	9.1	0.0	3.0	3.4	2.52E-03	19	1.1	13.5	0.6	44
MCD-W-16	9.1	298.9	6.1	113.9	176	0.7	9.1	-8.1			<1	0.7	<1E-4			18.9	0.9	13(
MCD-W-17	9.1	136.9	171.7	26.7	208	0.7	9.8	-9.4	30.2	13.1			<1E-4			15.9	0.7	90
MCD-W-23	9.1	80.9	356.1	1.9	121	1.1	10.4	-10.2			2.0	2.8	1.65E-03	20	1.0	13.9	0.5	43
MCD-W-30	9.1	49.1	324.8	<0.1				-9.9	5.3		1.0	2.3	1.23E-03	17	0.8	16.3	0.9	38
MCD-W-31	9.1	40.8	187.9	<0.1				-10.9	8.0		<1		1.82E-03			15.9	0.7	40
MCD-W-34	7.3	63.4	185.6	<0.1				-10.8	7.9		1.0	3.8	2.77E-03	17	0.8	13.7	0.7	41
MCD-W-35	7.3	159.6	304.4	<0.1				-9.7	11.8		<1		1.52E-03	17	0.8	16.3	0.8	41
MCD-W-98	57	69.6	0.4	<0.1			2.1	-10.6			31.0	0.6	1.76E-03	18	1.0	21.8	0.9	64

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Environ. Sci. Technol. **2007**, *41*, 753–758

Assessing the Impact of Animal Waste Lagoon Seepage on the Geochemistry of an Underlying Shallow Aquifer

WALT W. MCNAB, JR.,*,† MICHAEL J. SINGLETON,‡ JEAN E. MORAN,‡ AND BRAD K. ESSER‡

Environmental Restoration Division and Chemical Biology and Nuclear Science Division, Lawrence Livermore National Laboratory, P.O. Box 808, L-530, Livermore, California 94551

Evidence of seepage from animal waste holding lagoons at a dairy facility in the San Joaquin Valley of California is assessed in the context of a process geochemical model that addresses reactions associated with the formation of the lagoon water as well as reactions occurring upon the mixture of lagoon water with underlying aquifer material. Comparison of model results with observed concentrations of NH_4^+, K^+, PO_4^{3-}, dissolved inorganic carbon, pH, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, and dissolved Ar in lagoon water samples and groundwater samples suggests three key geochemical processes: (i) off-gassing of significant quantities of CO_2 and CH_4 during mineralization of manure in the lagoon water, (ii) ion exchange reactions that remove K^+ and NH_4^+ from seepage water as it migrates into the underlying anaerobic aquifer material, and (iii) mineral precipitation reactions involving phosphate and carbonate minerals in the lagoon water in response to an increase in pH as well as in the underlying aquifer from elevated Ca^{2+} and Mg^{2+} levels generated by ion exchange. Substantial off-gassing from the lagoons is further indicated by dissolved argon concentrations in lagoon water samples that are below atmospheric equilibrium. As such, Ar may serve as a unique tracer for lagoon water seepage since under-saturated Ar concentrations in groundwater are unlikely to be influenced by any processes other than mechanical mixing.

Introduction

Animal waste management at dairy facilities often entails storing dairy wastewater in manure lagoons. Irrigation with such lagoon water is a common practice that utilizes readily available fertilizer for forage crops while reducing the stored wastewater volume. The transfer of anoxic lagoon water to aerated unsaturated zone soils leads to the nitrification of ammonia to nitrate, as well as the mineralization of organic nitrogen, and can impact underlying groundwater when nitrogen is added to the fields in excess of the assimilation capacity of the crops (*1*–*3*).

The impact of manure lagoon seepage on groundwater quality is a separate problem from that of fertilizer application but is nonetheless also a groundwater protection concern. Previous studies have indicated that manure lagoons can leak at rates on the order of a few millimeters per day or more based on soil type, construction, and operation (*4*–*10*). Geochemical interactions between the seepage water and groundwater may differ from those involving fertilizer application (*6*, *11*–*13*). For example, nitrate loading from the lagoon will depend on the rate of oxidation of NH_4^+ and organic nitrogen released from the lagoon that, in turn, are affected by subsurface oxidation–reduction conditions and ion exchange characteristics. Distinguishing lagoon seepage from applied manure fertilizer in monitoring wells is difficult because the multitude of possible geochemical reactions create ambiguities with respect to potential tracers.

This study has sought to understand the effects of lagoon seepage on underlying groundwater quality in the context of a putative set of geochemical reactions characterizing the formation of lagoon water as well as the interaction of lagoon water with the groundwater environment. Our study entailed evaluating water quality data collected at an anonymous dairy facility located in Kings County, CA, in the southern San Joaquin Valley (Figure 1). The dairy holds approximately 1000 cows. Three manure lagoons have been active at the dairy since the 1970s, two of which have liners with a 10% clay content while the third is unlined. The largest lagoon measures approximately 100 m × 20 m. The lagoons receive runoff water from the flushing of animal stalls with water pumped from onsite agricultural wells. In turn, lagoon water is mixed with additional pumped groundwater and applied to onsite corn and alfalfa fields. Water depth within the lagoons varies temporally, depending on site operations, but is constrained to a maximum of approximately 3 m to prevent overflow. The site climatic setting is semi-arid, with a mean annual rainfall of approximately 220 mm/year, most of it falling from November through April. The daily summer average temperature is approximately 26 °C, although maximum daytime temperatures of 35 °C are common, while daily average winter temperatures are on the order of 7 °C (*14*).

Groundwater is first encountered in a perched aquifer extending from depths of approximately 3–24 m, separated by an unsaturated zone from a regional aquifer below a 40 m depth. Both aquifers consist of alluvial fan deposits. Measured oxidation–reduction potentials and dissolved gas data delineate the perched aquifer into an upper, aerobic zone above a depth of approximately 11 m below the ground surface (Shallow zone) and a lower, anaerobic zone (Deep zone) subject to denitrification (*13*). Recharge to the perched aquifer stems from nearby unlined irrigation canals, with a mean groundwater flow direction from northwest to southeast. However, agricultural pumping dominates the shallow hydrologic system, so groundwater flow directions are spatially and temporally variable.

Experimental Procedures

Lagoon water and groundwater samples were collected during six sampling events, from the locations indicated in Figure 1, between August 2004 and May 2005. Samples were analyzed for cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Li^+, and NH_4^+) and anions (NO_3^-, SO_4^{2-}, Cl^-, F^-, Br^-, PO_4^{3-}, and NO_2^-) by ion chromatography using a Dionex DX-600. pH, DO, and oxidation–reduction potential were measured in the field using a Horiba U-22 water quality parameter field meter. Dissolved inorganic carbon (DIC) concentrations were estimated in the water samples from charge imbalances and pH using the PHREEQC geochemical model. DIC was also

* Corresponding author phone: (925)423-1423; fax: (925)424-3155; e-mail: mcnab1@llnl.gov.

† Environmental Restoration Division.

‡ Chemical Biology and Nuclear Science Division.

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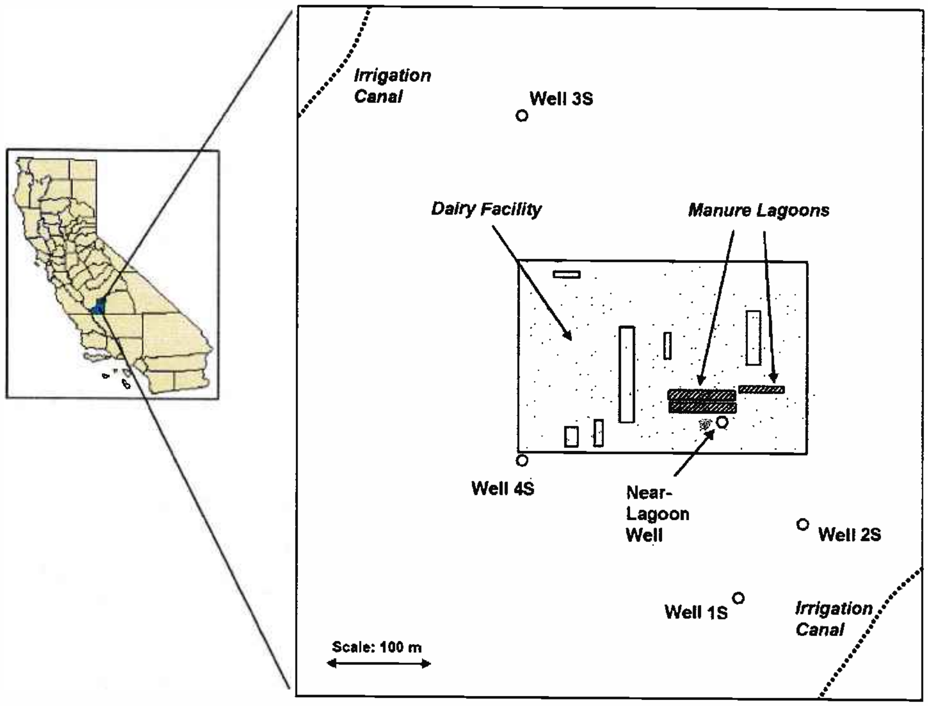

FIGURE 1. Dairy facility map, Kings County, CA. Water quality data from the lagoons and all five monitoring wells were included in the study.

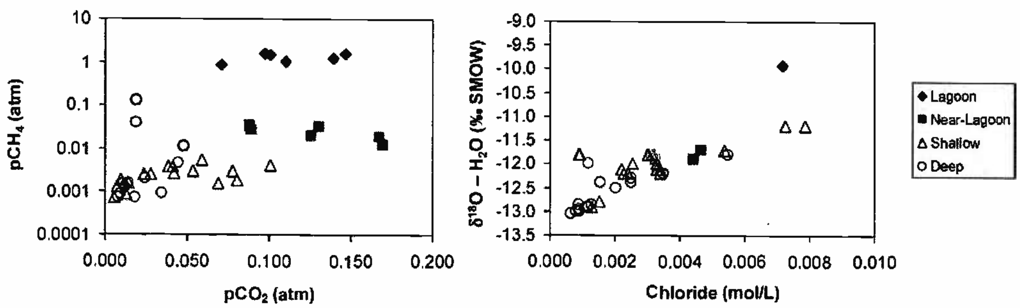

FIGURE 2. Partial pressures of CH_4 and CO_2 in the dairy facility lagoon and groundwater samples (left) and $\delta^{18}O$ and Cl^- (right). SMOW = standard mean ocean water.

quantified in a subset of samples as CO_2 gas pressure after acidification with orthophosphoric acid. δ^2H and $\delta^{18}O$ were determined using a VG Prism II isotope ratio mass spectrometer and are reported in per mil values relative to the Vienna Standard Mean Ocean Water (VSMOW). Oxygen isotope compositions were determined using the CO_2 equilibration method (*15*), and hydrogen isotope compositions were determined using the Zn reduction method (*16*). Dissolved gases (O_2, N_2, CO_2, CH_4, and Ar) were measured by membrane inlet mass spectroscopy– (MIMS (*17*)) or noble gas mass spectrometry.

Geochemical trends in water quality data were interpreted using the PHREEQC geochemical model (*18*). PHREEQC calculates equilibrium water chemistry compositions given an initial water composition, a set of postulated mineral and/or gas phases, and a thermodynamic database of equilibrium reaction constants. For this study, PHREEQC and its associated PHREEQC.DAT database were used to formulate two geochemical processes models: (i) a lagoon water formation model based upon dairy operating practices and a set of assumptions concerning evolution of a multi-component gas phase, oxidation–reduction reaction equilibria, and mineral precipitation and (ii) a seepage model that considers possible ion exchange interactions and mineral precipitation that could occur when seepage water contacts aquifer sediments.

Results

Ideally, a tracer for lagoon seepage should (i) be transported conservatively in groundwater and (ii) be unique to the lagoon environment. While partial pressures of CH_4 and CO_2 measured in site water samples may reflect mineralization of organic matter under anaerobic conditions in the lagoon water (Figure 2), neither indicator is likely to be conservative in groundwater (e.g., CH_4 could be subject to oxidation, while CO_2 is affected by pH). Alternatively, $\delta^{18}O$ and Cl^- are elevated in lagoon water (Figure 2) as a result of evaporation and, for Cl^-, the composition of manure, but both indicators will exist in lagoon seepage as well as applied fertilizer and thus would not provide an unequivocal means of distinguishing the two.

Given these limitations, an alternative approach for identifying lagoon seepage is to evaluate multiple geochemical parameters—major cations, anions, pH, and dissolved gases—together in the context of a geochemical process

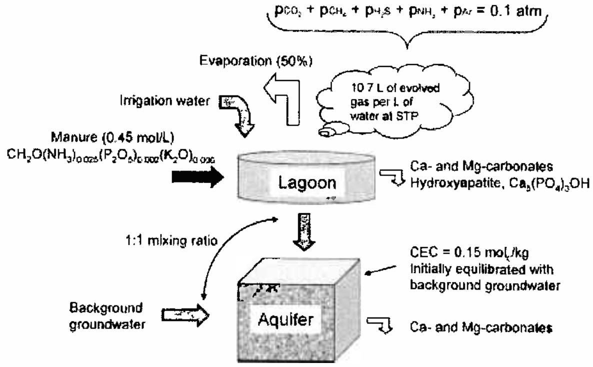

FIGURE 3. Geochemical process model of lagoon water formation and seepage.

model. For example, consider that ion exchange reactions that would remove NH_4^+ and K^+ ions in lagoon seepage (*12*) must be balanced by the release of other cations such as Ca^{2+} or Mg^{2+}, potentially leading to subsequent precipitation of carbonate minerals and an ensuing drop in pH. More broadly, the observed concentrations of those species that would be associated with the mineralization of manure in the lagoon water (NH_4^+, K^+, PO_4^{3-}, and DIC) and those species that could serve as potential indirect tracers of lagoon seepage in the aquifer (pH, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, and dissolved Ar) must be reconciled with process models of manure mineralization reactions in the lagoon—including heterogeneous reactions such as gas evolution and mineral precipitations—and water–aquifer material interactions of lagoon seepage and mixing with underlying groundwater (Ar is included because it can partition into an evolved gas phase, as explained next).

The geochemical modeling scheme is illustrated in Figure 3. Modeling lagoon water formation entailed simulating the mineralization of manure in a starting water composition given by the mean agricultural well water composition (i.e., the water used to flush the animal stalls). Dairy manure is compositionally variable and depends on feed composition, degree of mixing with urine, and storage issues affecting decomposition and preferential loss of volatiles. Reported manure compositions describe nutrient content (nitrogen, phosphorus, and potassium) per unit weight, which is typically less than 5% for dry manure and contains roughly equivalent amounts of nitrogen and potassium with a much smaller phosphorus component (*19, 20*). We assumed a manure stoichiometry of $CH_2O(NH_3)_{0.025}(P_2O_5)_{0.002}(K_2O)_{0.006}$, which has a carbon/nitrogen ratio of approximately 34:1 on a per weight basis, similar to the value of 28:1 reported by Cameron et al. (*1*). In this formulation, both organic nitrogen and NH_4^+ are represented by NH_3.

PHREEQC models aqueous species concentrations under an assumption of thermodynamic equilibrium in the presence of user-selected heterogeneous reactions involving gas phases, mineral equilibria, and ion exchange or surface complexation. To model lagoon water formation, we assumed (i) precipitation of calcium- and magnesium-carbonates (idealized as calcite, $CaCO_3$, and magnesite, $MgCO_3$) as well as hydroxyapatite, $Ca_5(PO_4)_3OH$, upon supersaturation and (ii) evolution of a mixed gas phase consisting of CO_2, CH_4, NH_3, H_2S, and Ar when the sum of the partial pressures of the gas components exceeded a threshold pressure. Ideally, gas bubbles will form when the total gas pressure exceeds local hydrostatic pressure in the lagoon; active gas bubble formation is indeed readily observed in the dairy site lagoons. However, mechanical mixing of the lagoon water during water transfer and the natural movement of air across the surface of the lagoon both facilitate diffusive transport, so a loss of gas phase components at a total pressure less than 1 atm is reasonable given the very low ambient partial pressures of all of the listed gas species in air. Separately, evaporation during lagoon water formation was simulated by removing half of the fluid volume as pure H_2O concurrent with the mineralization of the manure.

Lagoon seepage simulation entailed mixing the lagoon water with the mean composition of anaerobic groundwater (i.e., from depths greater than 11 m) in the presence of an ion exchanger initially in equilibrium with the same anaerobic groundwater. In the absence of site-specific ion exchange data, an exchange capacity of 0.15 mol of charge/kg of soil (*21*) and the default cation exchange selectivity coefficient set utilized by the PHREEQC database for Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+} were assumed. In addition, calcite and magnesite were modeled to precipitate upon supersaturation.

By setting the gas evolution threshold to 0.1 atm, manure loading to 0.45 mol/L, evaporative loss from the lagoon to 50%, and the mixing ratio of lagoon water/groundwater to 1:1, the proposed geochemical model provides a reasonable semiquantitative match to the water quality data set, at an ambient temperature of 25 °C, as indicated in Figure 4. The agricultural water (i.e., starting composition for the lagoon water) and background groundwater compositions are also shown in Figure 4 for comparison. Several key processes are suggested by the modeling results and the observed data.

(i) Gas evolution and mineral precipitation can account for the observed concentrations of mineralized manure components (PO_4^{3-} and DIC), pH, and Ca^{2+} and Mg^{2+} concentrations measured in the lagoon water. The model shows that hydroxyapatite precipitation is a plausible sink for PO_4^{3-} introduced by addition of manure as well as the Ca^{2+} present in the agricultural water. Ca^{2+}, along with Mg^{2+}, can also be removed as carbonates, explaining the low Mg^{2+} content of the lagoon water. Modeling suggests that DIC may be removed from solution by off-gassing (as CO_2 and CH_4) and by precipitation of carbonate minerals in such a manner as to reproduce the observed lagoon water pH.

(ii) Seepage modeling suggests that the high concentrations of NH_4^+ and K^+ found in the lagoon water diminish via ion exchange and dilution after a one 1:1 mixing event, with the exchange reactions releasing Ca^{2+} and Mg^{2+}, which results in calcite and magnesite precipitation and, as a consequence, a pH decline. Calculated calcite saturation indices among site water samples suggest that calcite precipitation is more likely in the lagoon water and in the Near-Lagoon Well than in groundwater at other locations (Figure 5).

Dissolved Ar warrants special mention. In a well-mixed model system, Ar initially dissolved in the agricultural water in equilibrium with the atmosphere partitions into the gas phase generated during lagoon water formation (consisting mainly of a CO_2–CH_4 mixture with a volumetric equivalent of approximately 10.7 L of gas per liter of lagoon water at standard temperature and pressure). Such gas stripping phenomena have been reported for coal bed methane environments (*23*) and ocean sediment pore waters (*24*). MIMS data indicate Ar concentrations in the lagoon water, and while not reduced to negligible levels as predicted by the model, they nonetheless appear to be depleted with respect to the atmosphere even at elevated temperature (Figure 5). In comparison, groundwater samples from both shallow and deep portions of the perched aquifer beyond the vicinity of the lagoon are supersaturated with argon, indicating excess air entrapped during recharge (*25*). The Near-Lagoon water composition is intermediate between two, supporting the 1:1 mixing assumption used in the seepage model.

Groundwater encountered below a depth of 11 m in Well 2S, some 100 m to the east–southeast of the manure lagoons, exhibits indications of lagoon impact such as comparatively low pH and Ar (Figure 6). $\delta^{13}C$– DIC, quantified in a subset

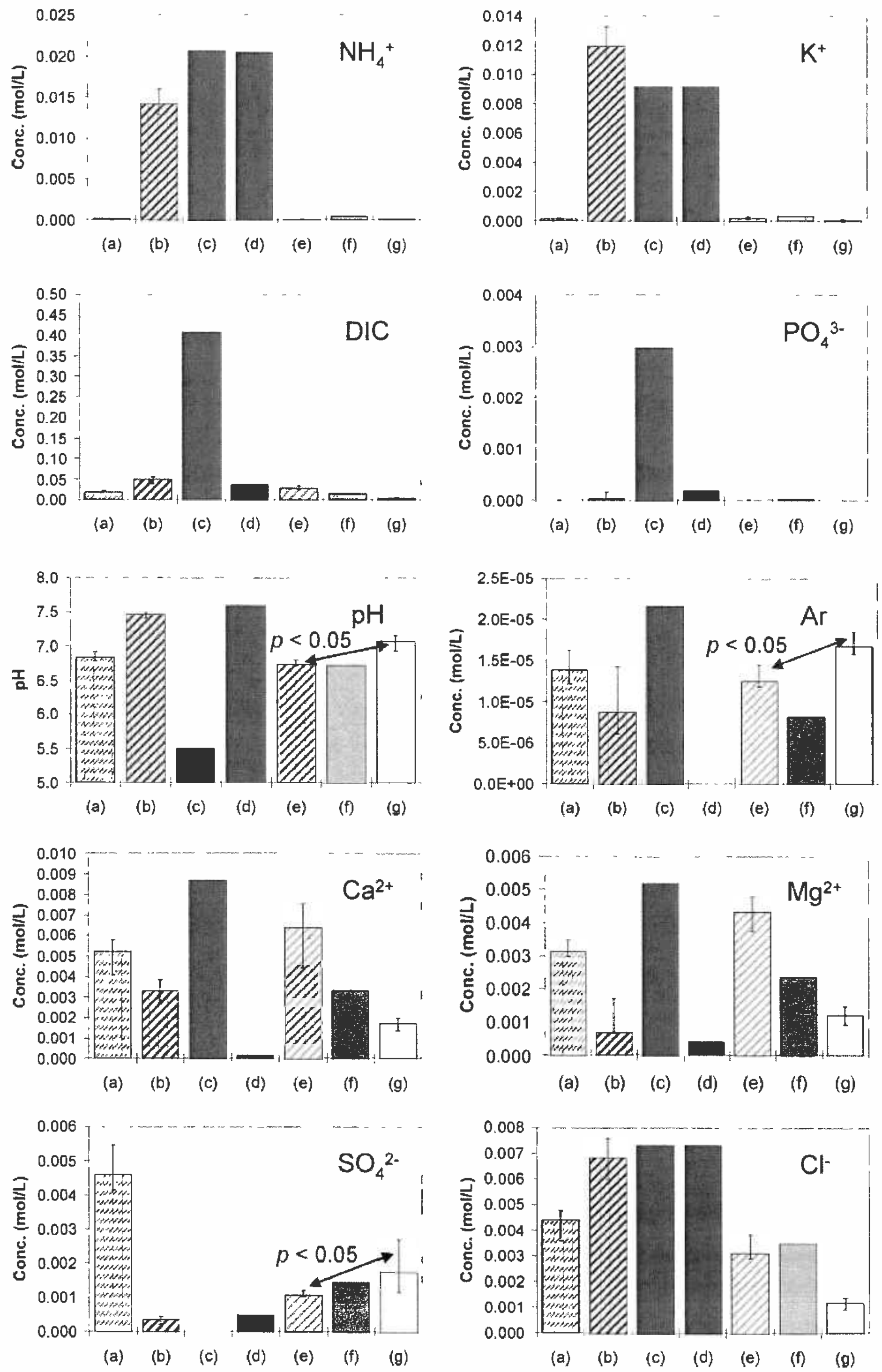

FIGURE 4. Modeling results and dairy site median water characteristics: (a) agricultural water samples, (b) lagoon water samples, (c) lagoon water modeled without any heterogeneous reactions, (d) lagoon water modeled with mineral precipitation and gas evolution, (e) Near-Lagoon Well samples, (f) modeled Near-Lagoon water impacted by seepage, and (f) background groundwater samples collected from depths below 11 m and exclusive of the 2S location. Error bars denote the 25th and 75th percentiles. Differences in parameter value distributions for pH, SO_4^{2-}, and Ar between the Near-Lagoon and background groundwater sets are each statistically significant as indicated by *p*-values based on the Student's *t*-test.

of the data, appears to be elevated in association with the pH and Ar signatures. While $\delta^{13}C$ was not addressed in the geochemical model, isotopically heavy DIC residue in the lagoon water is qualitatively consistent with extensive off-gassing of CO_2 and/or CH_4. As such, data from Well 2S below 11 m were not included in the previous comparisons.

Discussion

The geochemical model for manure lagoon water formation and seepage proposed in this study is based on idealized assumptions that may lead to error. In our judgment, the most problematic assumptions include the following.

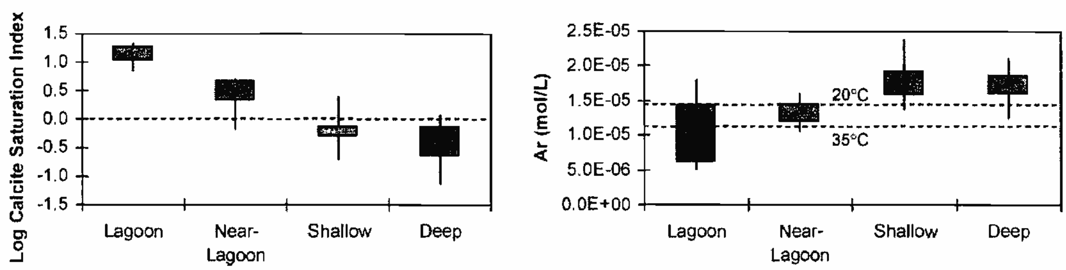

FIGURE 5. Thermodynamic saturation indices for calcite in site water samples, calculated with PHREEQC (left) and Ar concentrations and solubility (*22*) (right). The box-whisker marks correspond to the minimum, maximum, median, lower quartile, and upper quartile values for each group. Deep samples exclude groundwater samples from Well 2S.

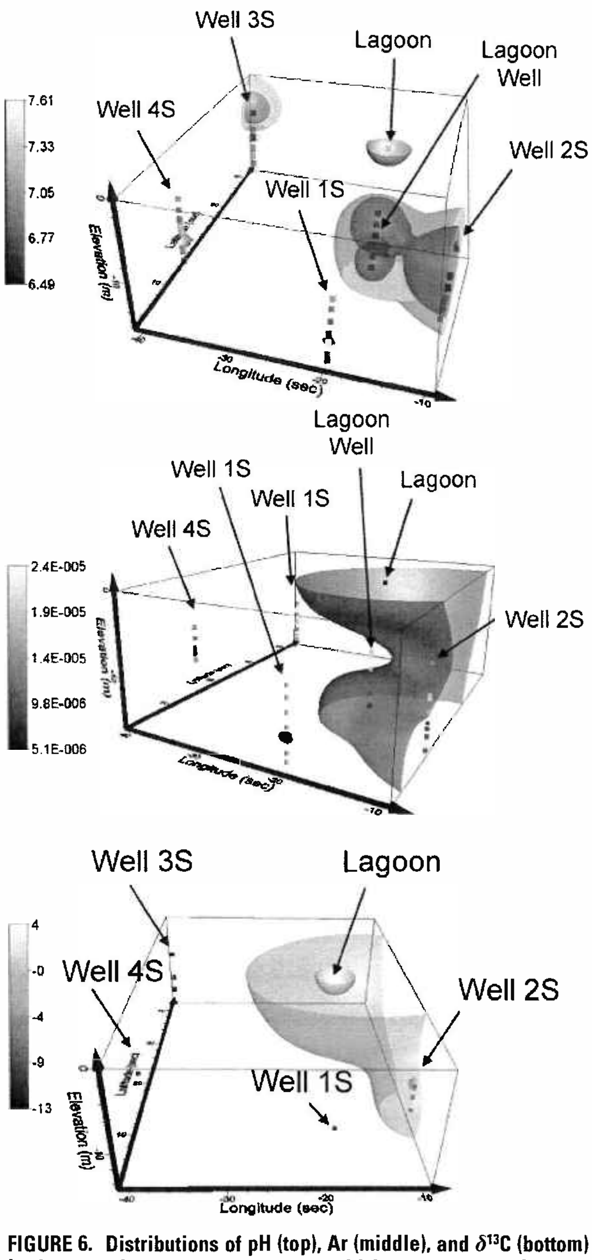

FIGURE 6. Distributions of pH (top), Ar (middle), and $\delta^{13}C$ (bottom) in site groundwater, each consistent with lagoon seepage that may have impacted Well 2S at depths greater than 11 m. Isosurface values for pH correspond to 6.75, 6.8, and 7.3. The isosurface value for Ar corresponds to 3.6×10^{-4} mol/L. The isosurface values for $\delta^{13}C$ correspond to −6.4 and 2.3 per mil.

Perfectly Well-Mixed Lagoon. Some stratification of the lagoons with regard to oxidation−reduction reactions and temperature seems likely, so gas evolution at the surface may reflect a superposition of biogeochemical regimes. Moreover, bubble formation and diffusive gas component losses are separate mechanisms that may operate differently on individual gas phase components depending on the respective diffusion coefficients and other factors. Seasonal and diurnal differences in temperature, microbiological activity in the lagoons, and even the lagoon operation itself will all exert various effects on the rate of off-gassing. This departure from ideality may explain, in part, the inability of the model, with a gas evolution threshold of 0.1 atm, to reproduce the measured CH_4 partial pressures approaching 1 atm (Figure 2).

Thermodynamic Equilibrium within the Lagoon. It is well-recognized that oxidation−reduction processes and some mineral precipitation reactions are slow kinetically. This constraint pertains to all oxidation−reduction reactions occurring in the lagoon—including the assumption of complete mineralization of manure—as well as the precipitation of Mg-rich carbonates that can be kinetically slow (*26*).

Complexation of Ions with Organic Matter. High concentrations of partially degraded manure constituents in the form of organic acids could complex cations such as Ca^{2+} and Mg^{2+} in the lagoon water, affecting their speciation but not considered by the model (*27, 28*).

Cation Exchange Model Used for the Aquifer Material. Hypothetical cation exchange characteristics were assumed.

Solute Transport beneath Lagoons. The compartmentalized geochemical model assumes that lagoon water mixes directly with underlying groundwater without passing through an aerobic vadose zone. While the geochemical data appear consistent with this assumption, there is an absence of soil boring data directly beneath the lagoons to support this assertion.

Despite these caveats, we believe that the proposed model has likely identified evidence of three major processes that affect lagoon water formation and seepage: (i) off-gassing of significant quantities of CO_2 and/or CH_4 during mineralization of manure in the lagoon water, (ii) ion exchange reactions that remove K^+ and NH_4^+ from seepage water in the underlying aquifer, and (iii) phosphate and carbonate mineral precipitation reactions occurring in the lagoon water resulting from an increase in pH and in the underlying aquifer from elevated Ca^{2+} and Mg^{2+} generated by ion exchange. These results are consistent with findings reported in previous studies. For example, significant fluxes of CH_4 (up to 19 mol m^2 day^{-1}) were measured from an anaerobic waste lagoon at a swine operation in southwestern Kansas (*29*), while ion exchange reactions were found to retard the movement of NH_4^+ in lagoon seepage through soils in both field and laboratory studies (*12, 30*), with NH_4^+ occupying more than 20% of the exchange sites in some cases (hence displacing cations such as Ca^{2+}). Moreover, the off-gassing process has suggested a new diagnostic tool—dissolved Ar—to detect gas stripped lagoon water that has migrated in into groundwater. Ar and other noble gases could be particularly useful in distinguishing lagoon seepage from applied fertilizer since lagoon water applied to fields will equilibrate with atmospheric argon prior to infiltration.

Acknowledgments

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Supporting Information Available

Additional details of our analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Assessing the Impact of Animal Waste Lagoon Seepage on the Geochemistry of an Underlying Shallow Aquifer

Walt W. McNab, Jr.[1*], Michael J. Singleton[2], Jean E. Moran[2], and Brad K. Esser[2]

[1]Environmental Restoration Division, Lawrence Livermore National Laboratory
[2]Chemical Biology & Nuclear Science Division, Lawrence Livermore National Laboratory

** Corresponding Author, P.O. Box 808, L-530, Livermore, California, 94551; Telephone (925) 423-1423; Fax (925) 424-3155; Email mcnab1@llnl.gov*

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TITLE Titration and mixing KCD water quality data set

SOLUTION_MASTER_SPECIES
   Ar         Ar           0    1        1

SOLUTION_SPECIES
Ar = Ar
   log_k     0

PHASES
Manure
   CH2O(NH3)0.025(P2O5)0.002(K2O)0.006 + O2 = HCO3- + 0.025NH4+ + 0.004PO4-3 +
0.012K+ + 0.975H+
   log_k     100
Magnesite
   MgCO3 + H+ = HCO3- + Mg+2
   log_k     2.2936
Ar(g)
   Ar = Ar
   log_k  -2.854

SOLUTION_SPECIES
2 NO3- + 12 H+ + 10 e- = N2 + 6 H2O
      #log_k          207.080
      log_k          203.
      delta_h -312.130       kcal
CO3-2 + 10 H+ + 8 e- = CH4 + 3 H2O
      log_k          41.071
      #log_k          45.
      delta_h -61.039 kcal

SOLUTION 1    #Mean agricultural well water
   temp      22
   pH        6.83
   pe        4
   redox     O(-2)/O(0)
   units     mg/l
   density   1
   F         0.23
   Cl        156.03
   Br        0.13
   N         72.42 as NO3-
   S(6)      440.52 as SO4-2
   S(-2)     1e-010 as SO4-2
   P         0.02 as PO4-3
   Li        0.0067
```

```
   Na       216.6
   K        6.39
   Mg       75.99
   Ca       209.61
   C(-4)    1e-010
   C(4)     100 charge
   O(0)     1
   Ar       1e-010 Ar(g)     -2.027
   -water   1 # kg

EQUILIBRIUM_PHASES 1
   Calcite  0 0
   Magnesite  0 0
   Hydroxyapatite 0 0

GAS_PHASE 1
   -fixed_pressure
   -pressure 0.1
   -volume 100
   -temperature 25
   CH4(g)    0
   CO2(g)    0
   H2S(g)    0
   NH3(g)    0
   Ar(g)     0

REACTION 1
   Manure   0.45
   H2O    -22
   1 moles in 200 steps

SELECTED_OUTPUT
   -file              titrate.txt
   -reset             false
   -solution          true
   -distance          true
   -time              true
   -step              true
   -ph                true
   -pe                true
   -totals            C(4)  S(6)  C(-4)  Fe(2)  S(-2)  Ca  Mg
                     Na  K  F  P  Ar  Cl
   -molalities        O2  NH4+  NH3  NO3-
                     N2
   -equilibrium_phases  Calcite  Magnesite  Hydroxyapatite
   -saturation_indices  CH4(g)  CO2(g)  H2S(g)  NH3(g)  N2(g)  Ar(g)
```

```
   -gases          CH4(g)  CO2(g)  H2S(g)  NH3(g)  Ar(g)

SAVE Solution 1

END

SOLUTION 2  #Deep field groundwater
   temp     22
   pH       7.07
   pe       4
   redox    N(0)/N(5)
   units    mg/l
   density  1
   F        0.28
   Cl       42.32
   Br       0.08
   N(0)     34.87 as NO3-
   N(5)     1.75 as NO3-
   S(6)     169.39 as SO4-2
   P        0.02 as PO4-3
   Li       0.0033
   Na       65.18
   K        4.83
   Mg       29.62
   Ca       68.91
   Fe       0.001  Goethite
   C(4)     100 charge
   Ar       1e-010 Ar(g)      -2.027
   -water   1 # kg

EXCHANGE 1
   X      1.0
   -equilibrate with solution 2

SAVE Solution 2
SAVE Exchange 1

END

USE Solution 1
USE Solution 2
USE Exchange 1

MIX 1
   1   1
   2   1
```

```
EQUILIBRIUM_PHASES 2
   Calcite   0 0
   Magnesite  0 0
   Hydroxyapatite 0 0

END
```

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James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT “G”

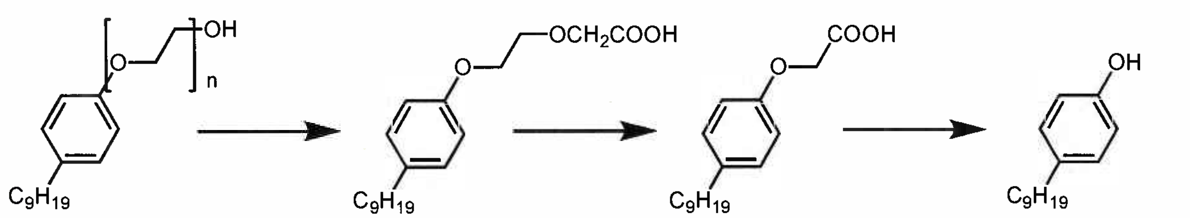
UCRL-TR-222531

LAWRENCE LIVERMORE NATIONAL LABORATORY

Prepared in cooperation with the

CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

California GAMA Program: Fate and Transport of Wastewater Indicators: Results from Ambient Groundwater and from Groundwater Directly Influenced by Wastewater



NPEOs **NP2EC** **NP1EC** **4-nonylphenol (NP)**

June, 2006

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

EXECUTIVE SUMMARY 3
INTRODUCTION 4
SELECTION OF TARGET COMPOUNDS 5
MATERIALS & METHODS 14
SAMPLE COLLECTION 14
ANALYSIS BY SOLID-PHASE EXTRACTION (SPE)-ISOTOPE DILUTION LC/MS/MS 14
ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) 18
RESULTS & DISCUSSION 20
QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) FOR TARGET COMPOUNDS 20
RESULTS FOR TEHAMA COUNTY GROUNDWATER 30
RESULTS FOR GROUNDWATER AT CALIFORNIA DAIRIES 34
RESULTS FOR CHICO GROUNDWATER 35
RESULTS FOR GILROY GROUNDWATER 40
RESULTS FOR LIVERMORE GOLF COURSE GROUNDWATER 47
COMPARING RESULTS FROM TWO AREAS OF RECYCLED WATER APPLICATION 57
REFERENCES 60

EXECUTIVE SUMMARY

A study of the occurrence and transport of wastewater indicator compounds in groundwater is reported here, as part of the California State Water Resources Control Board's Groundwater Ambient Monitoring and Assessment (GAMA) program. One component of the study consisted of analytical methods development for organic compounds of interest as possible tracers of wastewater. Subsequently, the wastewater indicator target compounds were analyzed in groundwater samples from two areas strongly influenced by recharge of tertiary treated wastewater, and from three regions with widely spaced wells and differing land use. Target compounds were analyzed by liquid chromatography/tandem mass spectrometry (LC/MS/MS) and gas chromatography/mass spectrometry (GC/MS), and include endocrine-disrupting compounds such as 4-nonylphenol (NP) and its precursors, and steroid estrogens, pharmaceuticals such as ibuprofen, carbamazepine, and primadone, and personal care products such as triclosan, caffeine, linear akylbenzene sulfonates (LAS), and N, N-diethyl-*m*-toluamide (DEET). These compounds are frequently detected in treated wastewater at concentrations in the microgram per liter (μg/L) range. Reporting limits for the methods used ranged from 3 to 100 nanograms per liter (ng/L).

Wells from two areas where tertiary treated wastewater is used for irrigation, a golf course in Livermore and a farm and public park in Gilroy, were sampled and analyzed for the trace organic compounds that could serve as wastewater indicators. Other chemical and isotopic tracers of wastewater in groundwater were used to identify and quantify the component of produced groundwater that originated as wastewater effluent. At the Livermore golf course site, tritium released by Lawrence Livermore National Laboratory (LLNL) to the municipal sewer system served as an excellent tracer of the wastewater component because it was closely monitored in treatment plant effluent and in groundwater over a 25-year period. At both the Livermore and Gilroy sites, major ions, stable isotope signatures of the water molecule, groundwater age, and stable isotope signatures of nitrogen and oxygen in nitrate, serve to demarcate groundwater that has a component of wastewater recharge. Results for these other tracers indicate that a significant component of wastewater is produced from shallow monitoring wells at both sites. However, of the large number of trace organic compounds analyzed, only a small number of compounds were detected in the same samples, and at very low concentrations. At both sites, alkylphenol ethoxycarboxylic acids (APECs, the precursor compounds of NP) were detected at concentrations greater than 50 ng/L. The pharmaceuticals carbamazepine and primadone were found at a maximum concentration of 110 ng/L at the Gilroy site. Overall, the results indicate efficient removal of wastewater compounds, likely due to sorption and biodegradation in the vadose zone and in the anaerobic zone that exists at depth at both sites.

The occurrence of wastewater indicator compounds was similarly very limited in ambient groundwater, sampled in three regions of differing land use. Domestic wells from Tehama County were entirely free of the target analytes. Results from shallow monitoring wells adjacent to lagoons at three dairy sites suggest that NP may be an indicator of lagoon seepage, although detections of NP may be related to sampling artifacts. Norflurazon and its degradation product, desmethylnorflurazon, served as tracers of groundwater recharged from an area of pesticide application at one dairy site. Twenty three shallow monitoring wells and seven longer-screened drinking water wells in the Chico area were sampled for wastewater indicator compounds, as part of a larger study to determine the source(s) and fate of nitrate. One major potential source of nitrate is discharge from septic systems. Wastewater indicator compounds could potentially serve to distinguish among nitrate sources, as certain target compounds are likely to derive from septic system discharge (caffeine, surfactant-related compounds such as APECs and LAS, ibuprofen and other pharmaceuticals and estrogenic compounds). In all, 14 different target compounds were detected at 11 monitoring wells. Carbamazepine was detected at 4 wells, polycyclic musk compounds and flame retardants were detected at 1 well, caffeine was detected at 2 wells, DEET and NP were detected at one well, and herbicides and their breakdown products were detected at 3 wells. Seven drinking water wells in Chico had no detections of any of the target analytes.

Limitations of the study include: (1) a lack of control over well construction and sampling equipment at some dairy sites and private domestic wells where introduction of contaminants cannot be ruled out, (2) method detection limits for certain compounds (LAS, sterols) that are higher than concentrations expected in groundwater samples, and (3) not all analytes were measured in every sample. A conservative approach was taken in reporting detections in order to minimize the possibility of reporting false positives. The study limitations do not affect the overall conclusions that the occurrence of wastewater indicator compounds in ambient groundwater is extremely rare and that these compounds are substantially removed during recharge to groundwater.

INTRODUCTION

In California, a steep increase in population has been accompanied by an increase in per capita use of pharmaceuticals and personal care products. In the meantime, demand for limited fresh water supplies for use as drinking water has increased. These factors combine to draw public and scientific attention to the environmental fate of trace organic compounds from human wastewater discharges. Since publication of "Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in US Streams, 1999-2000: A National Reconnaissance," (Kolpin et al., 2002), there has been a great deal of interest in the occurrence of pharmaceuticals, personal care products, and other compounds from wastewater in drinking water supplies. Many reports on the fate of trace organic compounds during wastewater treatment and on their occurrence in surface water bodies have appeared in the last several years (e.g., Tixier et al., 2003, Standley et al., 2000, Stamatelatou et al., 2003, Bryrns, 2001, Kolpin et al., 2002). Studies of the fate and transport of these compounds in field studies of groundwater are on the rise, but are still relatively few in number (e.g., Drewes et al., 2002, Fenz et al., 2005, Heberer and Adams, 2004, Hinkle et al., 2005).

Under the State Water Resources Control Board's (SWRCB) comprehensive, state-wide Groundwater Ambient Monitoring and Assessment (GAMA) program, pharmaceutical and other wastewater-derived compounds are analyzed in public drinking water wells by the United States Geological Survey (USGS) at the National Water Quality Laboratory. In addition, a focused study on the fate and transport of wastewater indicator compounds has been carried out by Lawrence Livermore National Laboratory (LLNL) under the GAMA program, and is the subject of this report. The first phase of the study focused on method development, including development of extraction techniques for groundwater samples, extensive analysis of field blanks and equipment blanks, and development of analytical techniques for liquid chromatography/tandem mass spectrometry (LC/MS/MS) and gas chromatography/mass spectrometry (GC/MS). Method development was carried out with the following factors in mind: (1) detection limits needed to be sufficiently low to be consistent with expected concentrations of individual compounds in the ng/L range, (2) specificity and selectivity needed to be high to account for the typically complex groundwater matrix and variable extraction recovery, (3) target analytes had to be selected that were likely to persist in groundwater (based on their physical-chemical and biochemical properties), and (4) quality control issues (mainly blank controls) related specifically to groundwater sampling needed to be addressed.

Selection of sample locations was also carried out to maximize the possibility of collecting meaningful results. Hence two areas known to be strongly affected by recharge of treated municipal wastewater were chosen as study areas. The Livermore golf course and Gilroy farm sites offered an opportunity to compare and contrast results from two areas where tertiary treated effluent has been used for irrigation for more than twenty years. Opportunities to sample groundwater with a very high fraction of recharged wastewater are excellent in these two areas. We focused in particular on shallow monitoring wells at each site where there was a groundwater mound, and where there were multiple lines of geochemical evidence for the presence of recharged wastewater.

In addition, samples of ambient groundwater from shallow and deep aquifers used for private and public water supplies were included to begin to assess the frequency of occurrence of wastewater indicator compounds in areas outside the influence of municipal wastewater irrigation. These included private wells from a relatively undeveloped region in Tehama County, shallow monitoring wells and public supply wells in an area of high nitrate concentrations in Chico, and monitoring wells at three dairy sites.

A key component of the study was to use multiple, complementary techniques for tracing the source and flow of the groundwater along with the various wastewater constituents. To that end, the following analyses were carried out in each study area in addition to analysis of target wastewater indicator compounds: (1) stable isotopes of the water molecule (for source water identification and evidence for evaporation), (2) total dissolved organic carbon and major anions and cations (as indicators of a significant wastewater component), (3) isotopes of N and O in nitrate (wastewater denitrification indicators), and (4) tritium-helium (for groundwater age and source water identification). In this manner, the fate of individual trace organic compounds of interest could be tracked and quantified, since the component of groundwater from a wastewater source and the compounds of interest were quantified in both influent and groundwater samples.

SELECTION OF TARGET COMPOUNDS

Alkylphenol ethoxylate metabolites

Alkylphenol ethoxylates (APEOs), a class of nonionic surfactants, and their metabolites are closely associated with wastewater and treated wastewater, and have attracted attention from the environmental community because they constitute the most prominent group of endocrine-disrupting compounds identified in that matrix. In particular, nonylphenol ethoxylates (NPEOs) constitute the largest subgroup of the APEOs (encompassing more than 80% of the world market). Municipal wastewater treatment (including biological treatment) tends to result in efficient elimination of the parent APEOs but formation of biologically refractory metabolites including the following: alkylphenol mono- and diethoxylates (i.e., n=1 or 2 in Figure 1), alkylphenol carboxylic acids (e.g., NP1EC and NP2EC; Figure 1), and 4-nonylphenol (NP; Figure 1) (Ahel et al., 1994). NP has recently been reported to have a wide distribution in surface waters (Kolpin et al., 2002) and is well documented to be present in effluents of wastewater treatment plants (WWTP) at μg/L concentrations (e.g., Rudel et al., 1998; Johnson and Sumpter, 2001; Ying et al., 2002; Planas et al., 2002). The hormonal and toxicological properties of NP have resulted in the banning of NPEOs for domestic and industrial use in many parts of Europe (Blackburn and Waldock, 1995). The U.S. EPA has recently initiated an effort to encourage a voluntary phase-out of nonylphenol ethoxylate surfactants from detergents (http://pubs.acs.org/cen/news/84/i25/8425notw3.html). APECs have been observed at considerably (e.g., ten-fold) higher concentrations in WWTP effluents than NP (Johnson and Sumpter, 2001). Notably, since APECs have carboxyl groups that are likely to be ionized in a groundwater environment at circumneutral pH, they would be expected to be more soluble and mobile in groundwater than NP.

Caffeine

Caffeine (Figure 1) was chosen as a target compound because it is a unique indicator of human waste that has been widely detected in surface waters and groundwater, and its presence in environmental samples has specifically been linked to WWTP effluent (Seiler et al., 1999 and references therein; Kolpin et al., 2002; Standley et al., 2000; Buerge et al., 2003). Although it is relatively biodegradable (considerably more so than NP), caffeine is nonetheless highly water-soluble and has been observed in the environment near WWTP sources.

Ibuprofen

Ibuprofen (Figure 1) is an acidic pharmaceutical that exhibits a high degree of removal during the waste treatment process, but its high degree of consumption still results in this compound being detected in surface waters and is linked to WWTP effluent, although its frequency of detection and range of detected concentrations appears to be lower than that of caffeine (Kolpin et al., 2002; Tixier et al., 2003; Lindqvist et al., 2005). The lower solubility of ibuprofen in water compared to caffeine may partially explain its lower detection frequency.

Steroid estrogens

Estrogenic steroid hormones such as estrone (E_1) and 17β-estradiol (E_2) (Figure 1) are low-level but distinctive wastewater components that have received attention from environmental community because they are significant contributors to the total estrogenic activity observed in that matrix (Johnson and Sumpter, 2001).

DEET

N,N-diethyl-3-methylbenzamide, also known as N, N-diethyl-*m*-toluamide (DEET), is a broad spectrum insect repellent that is currently the safest and most effective, and therefore the most widely used, topical insect repellent. DEET has been available to the general public since 1957 and as of 1998 there were 225 registered products listing DEET as an active ingredient (USEPA, 1998). The U.S. EPA estimates that approximately 30% of the U.S. population uses a DEET-based insect repellent annually (USEPA, 1998; Fradin, 1998). Total use in 2000 was between 5 and 7 million pounds (Kiely et al., 2004). Because DEET is applied directly to the body or clothing, this limited use pattern makes DEET an "indoor residential" use repellent, where a primary route of introduction to the wastewater is through washing, since essentially all absorbed DEET is metabolized prior to being eliminated in the urine (EPA, 1998). DEET is stable to hydrolysis and is commonly identified in WWTP effluents, surface waters (Kolpin et al., 2002; Weigel et al., 2002) and has also been detected in groundwater impacted by a municipal landfill (Barnes et al., 2004).

Triclosan

Triclosan is one of the most common antibacterial agents added to the wide variety of antibacterial consumer products that includes soaps, deodorants, and toothpastes (Tan et al., 2002), with estimated national usage ranging from 170,000 to 970,000 kg/yr (Halden and Paull, 2005). The combined processes of biodegradation and sedimentation in WWTPs remove approximately 95% of the entering triclosan (Federle et al., 2002; McAvoy et al., 2002; Singer et al., 2002) but high triclosan usage still results in its widespread occurrence in surface waters (Kolpin et al., 2002; Singer et al., 2002; Tixier et al., 2002; Halden and Paull, 2005) and contaminated ground water (Barnes et al., 2004).

Linear Alkylbenzene Sulfonates

Linear alkylbenzene sulfonates (LAS) are anionic surface active agents (surfactants) widely used in common household products, such as laundry detergents and cleaners, with global consumption estimated at 1.8 x 10^9 kg/yr (Karsa, 1998). Commercial North American formulations are actually mixtures composed of homologs of different alkyl chain lengths (C_{10} – C_{14}) and isomers differing in the position of the phenyl group, totaling 26 compounds (Tabor and Barber, 1996). Combined sorption and biodegradation removes 95%-99% of LAS present in raw sewage influent (Berna et al., 1989; Painter and Zabel., 1989) and remaining LAS and metabolites are discharged in the effluent. Once in the environment, low dissolved oxygen concentrations limit primary biodegradation (Halvorsan, 1969; Wagener and Schink, 1987; Krueger et al., 1998) and compositional changes can occur by preferential adsorption of the more hydrophobic congeners (Hand and Williams, 1987) and through enhanced biodegradation of LAS congeners containing longer alkyl side-chains (Swisher, 1963; 1987; Schlehech et al., 2004).

Organophosphate Esters

Organophosphate esters are alkylated and arylated esters of phosphoric acid. This class of chemicals has a variety of industrial applications, such as flame retardants, plasticizers and hydraulic fluids (WHO, 1991; 1998). Tris (2-chloroethyl) phosphate, tris (1,3-dichloroisopropyl) phosphate and triphenyl phosphate were selected as target analytes. Each of these chemicals is classified by the EPA as high production volume chemicals (manufactured or imported into the U.S. in amounts equal or greater than one million pounds per year) and have been identified in effluents of WWTPs, present in both surface waters and ground waters, and resistant to conventional drinking water treatment processes (Fries and Puttmann, 2001; Kolpin et al., 2002; Fries and Puttmann, 2003; Andresen et al., 2004; Barnes et al., 2004; Meyer and Bester, 2004; Stackelberg et al., 2004; Westerhoff et al., 2005; Andresen and Bester, 2006).

Fecal Sterols

Significant amounts of sterols are present in animal feces and the relative amounts are a function of the animal's diet, the ability to synthesize their own sterols, and microbes present in their digestive tract. These factors make fecal sterols, such as coprostanol, useful chemical indicators for identifying contamination from sewage (Dougan and Tan, 1973; Eglinton et al., 1975; Hatcher et al., 1977; Hatcher and McGillivary, 1979; Teshima and Kanazawa, 1978). The desire to distinguish between human and animal (e.g., herbivore) contributions of fecal matter in polluted water led to a technique developed by Leeming et al. (1994, 1996), which involves determining the relative amounts of specific C_{27} and C_{29} sterols present in a particular sample. This approach has been used in a variety of locations and has been useful in tracing sources in which multiple fecal contamination inputs may be present (Gregor et al., 2002; Leeming et al., 1998; Isobe et al., 2002).

Miscellaneous Compounds

In addition to the selected target compounds, the concentrated extracts from the water samples were monitored for non-target organic contaminants during the GC/MS full-scan runs. Compound identifications were made using authentic standards and tentative compound identifications were based on suitable matches using mass spectra database searches and comparisons with published mass spectra. Baseline data were obtained for the study areas and any additional compounds identified in the water samples were useful for future contaminant monitoring. A wide variety of additional anthropogenic compounds were either identified or tentatively identified during the screening process. These include the following: herbicides and herbicide breakdown products (e.g., atrazine, simazine, desethyl atrazine, desisopropyl atrazine, oxadiazon, norflurazon, desmethyl norflurazon), pharmaceuticals (e.g., carbamazepine, primidone), fragrances/personal care products (e.g., HHCB, AHTN, oxybenzone, dometrizole), and industrial chemicals (e.g. benzothiazole, 2-methylthiobenzothiazole, naphthalene).

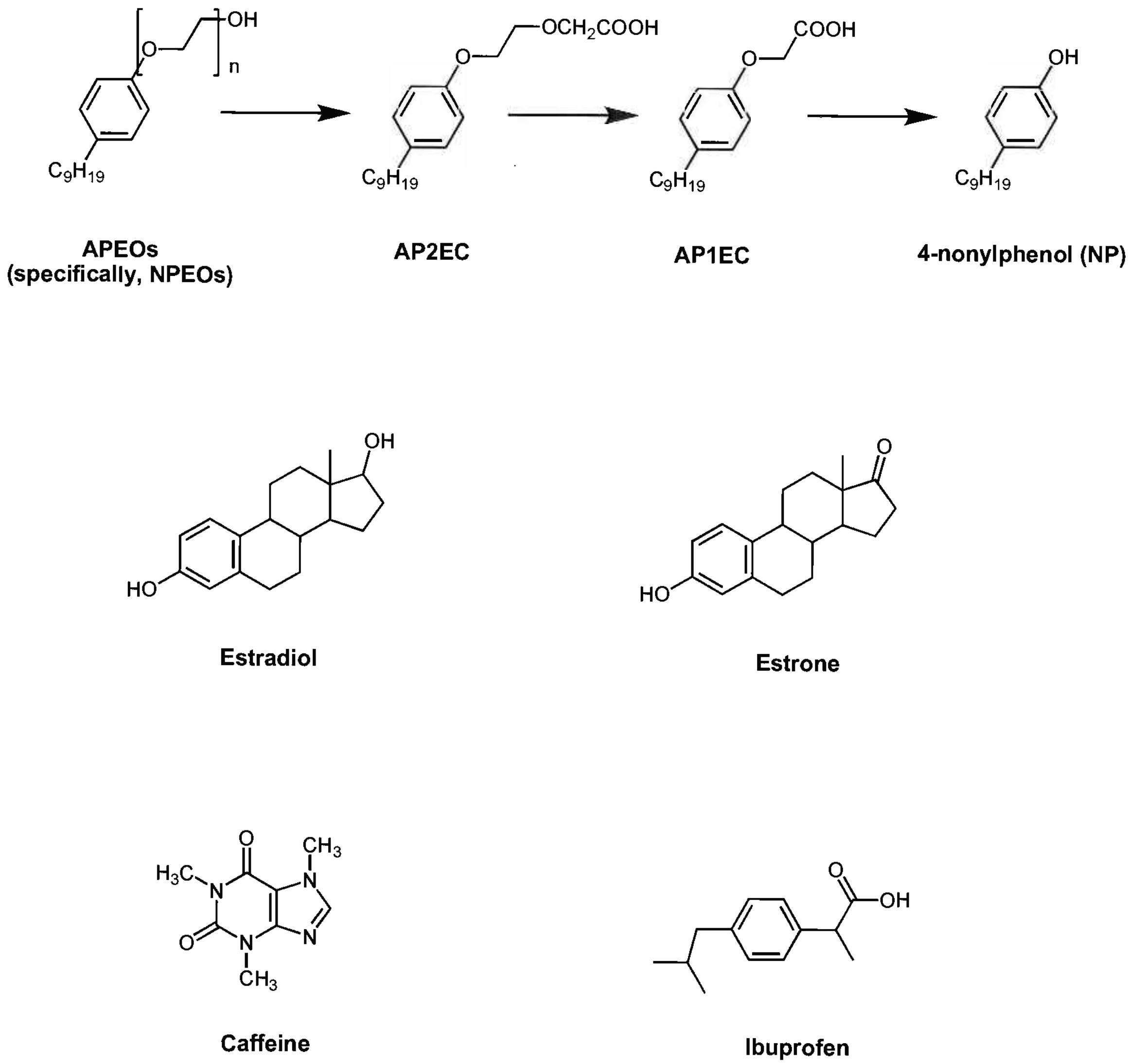


Figure 1. Structures of selected wastewater indicators analyzed by LC/MS/MS for this project. The value of "n" for APEOs is 3 to 20. Not all metabolites in the biodegradation of NPEOs to NP are shown, but the relationships among APEOs, APECs, and NP can be ascertained from the figure.

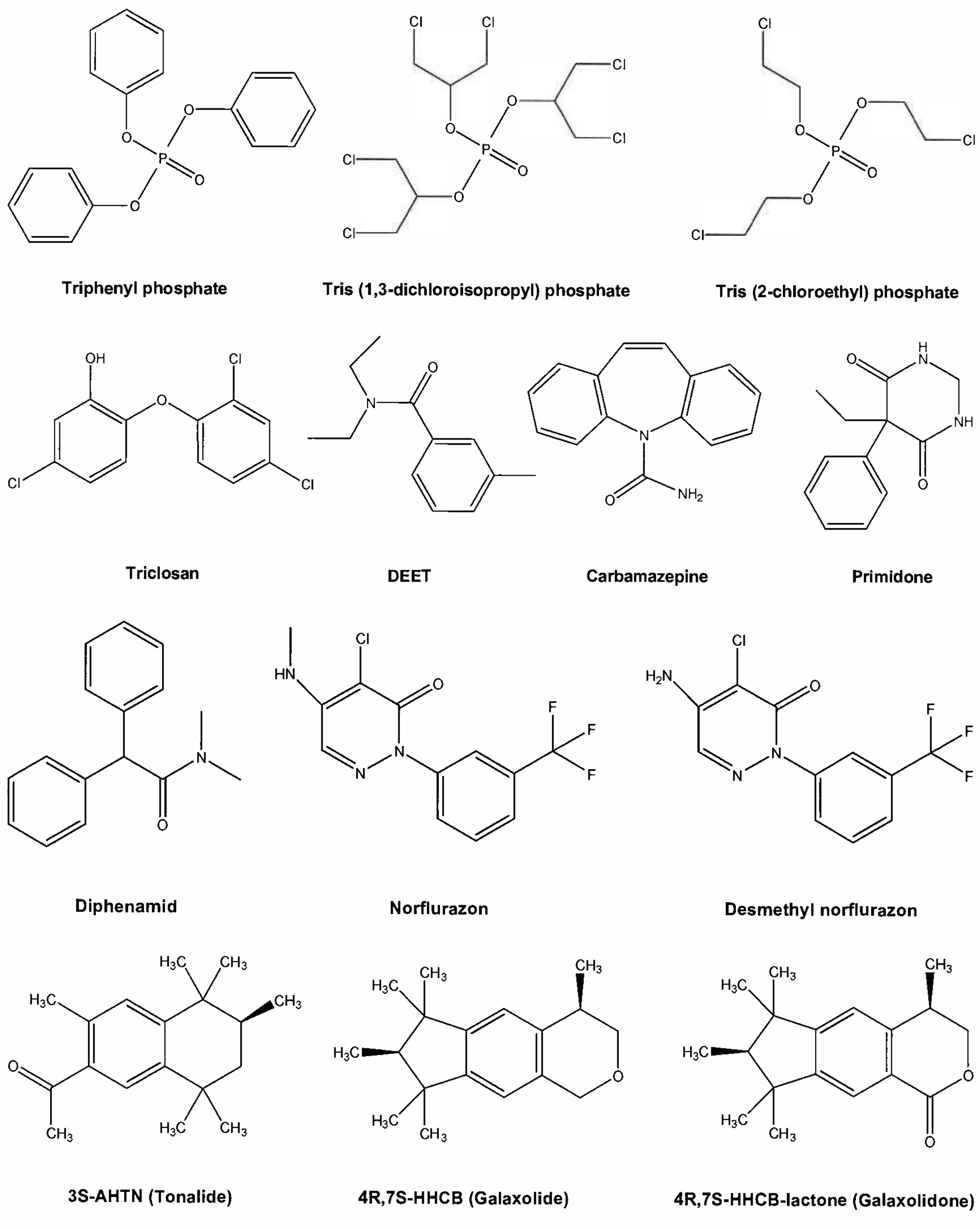
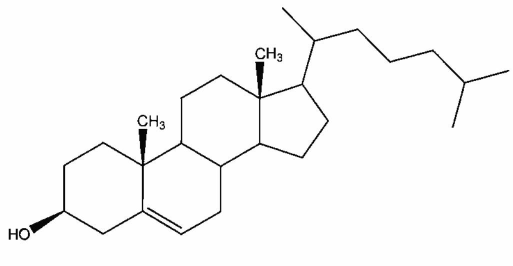
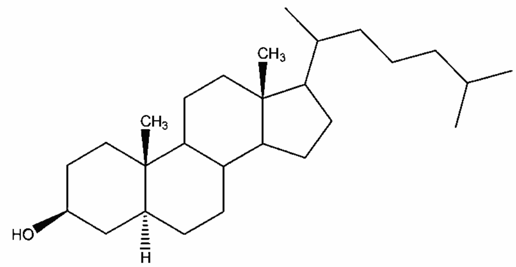


Figure 2. Structures of selected wastewater indicators analyzed by GC/MS.

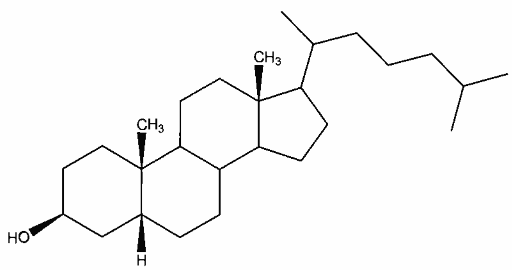
C_{27} Sterols



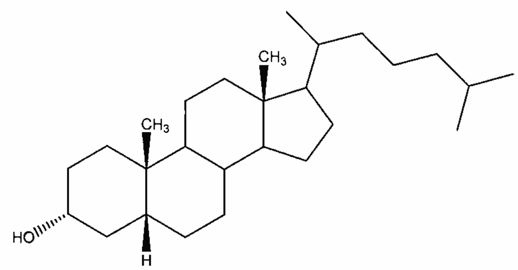
5-Cholesten-3b-ol (Cholesterol)



5a-Cholestan-3b-ol (Cholestanol)



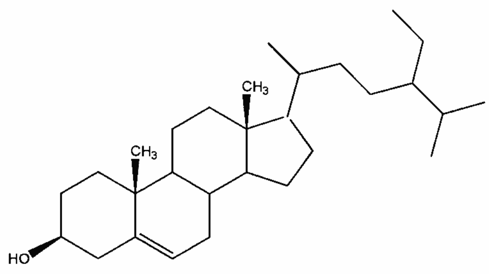
5b-Cholestan-3b-ol (Coprostanol)



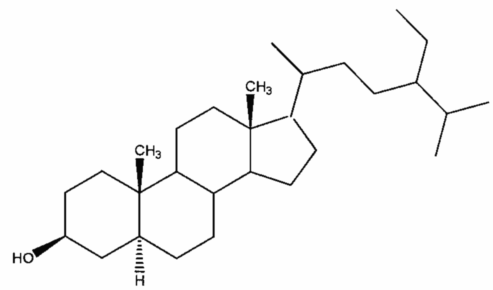
5b-Cholestan-3a-ol (Epicoprostanol)

Figure 2 (cont). Structures of selected wastewater indicators analyzed by GC/MS.

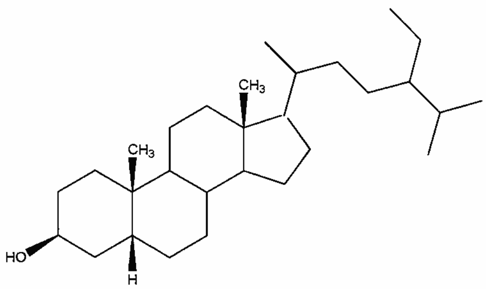
C_{29} Sterols



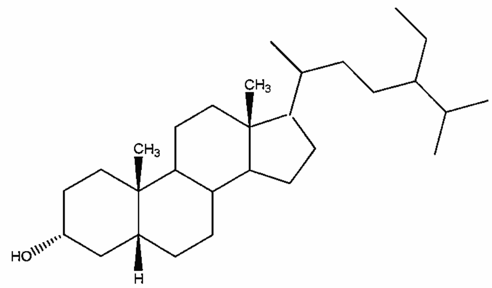
24-Ethylcholesterol



24-Ethylcholestanol



24-Ethylcoprostanol



24-Ethyl-epicoprostanol

Figure 2 (cont). Structures of selected wastewater indicators analyzed by GC/MS.

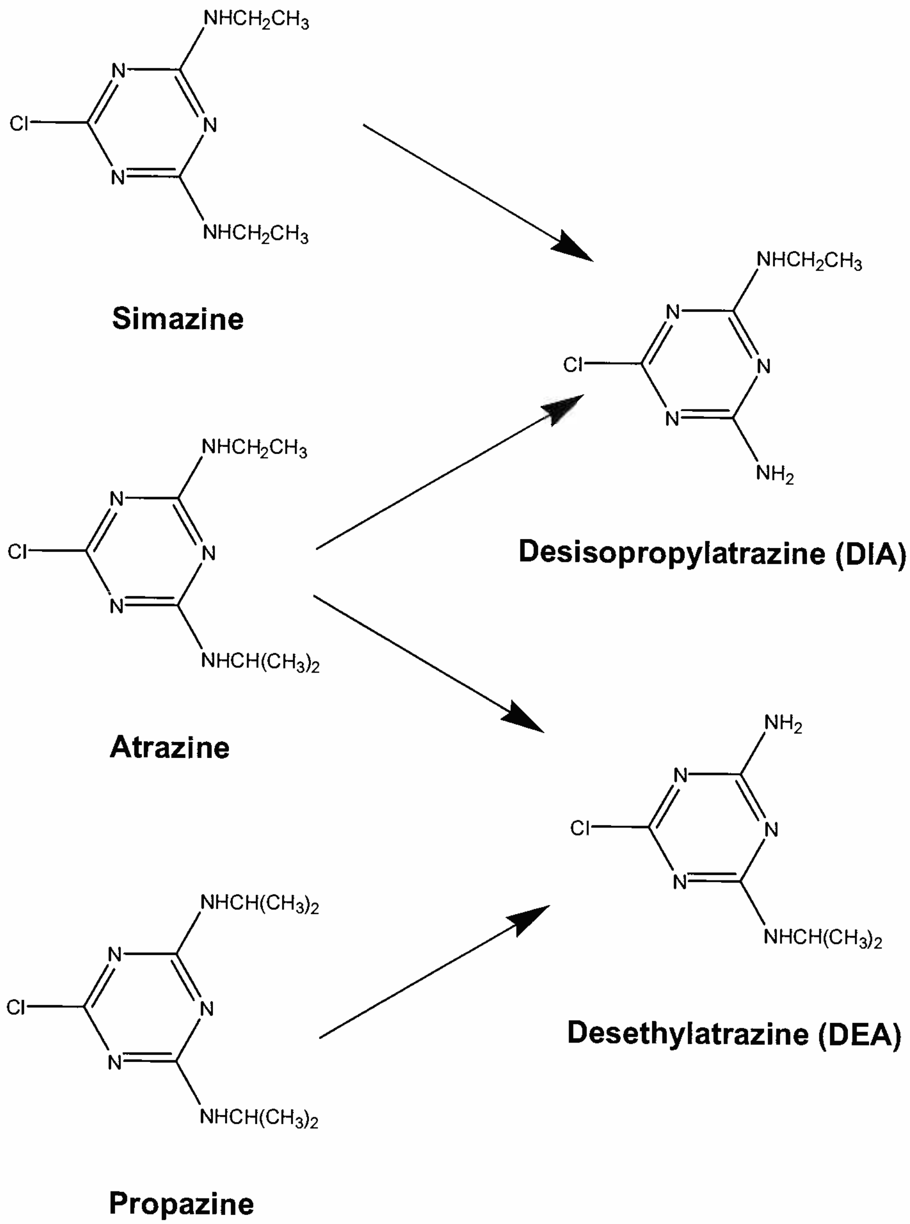


Figure 2 (cont). Structures of selected wastewater indicators analyzed by GC/MS.

MATERIALS & METHODS

SAMPLE COLLECTION

Two water samples were collected at each site in certified precleaned one liter amber I-Chem bottles with Teflon-lined caps. Bottles were typically filled directly from the sampling port. New nitrile gloves were worn by the sampler during sample collection to minimize any trace contamination from the sampler during the sample handling process. The water samples were then placed in a cooler and transported to the lab, where they remained refrigerated at 4°C until extraction. Extraction was carried out within approximately 72 hours of sampling.

A major goal of the study was to examine and minimize artifacts due to sampling equipment and sampling procedures. To that end, individual wells were sampled with stainless steel bailers, single-use Teflon bailers, a low-flow "bladder" pump equipped with polypropylene plastic tubing, and three different Grundfos submersible pumps. Two of the Grundfos pumps were equipped with Teflon-lined tubing. A test was carried out comparing samples collected after well purging by bailing with a Teflon bailer and after well purging by pumping with a Grundfos pump equipped with Teflon-lined tubing. In addition, a large volume of laboratory reagent water was prepared and bailers and pumps were tested by collecting samples of the reagent water. Duplicate samples were collected a frequency of 10%. Trip blanks, which consisted of IsoChem bottles filled with laboratory-cleaned reagent water, were carried with samplers on three occasions and were included to monitor for potential sample artifacts during shipping and storage. All of the wells from the two areas of wastewater irrigation were sampled on at least two separate occasions, and six of the wells from a dairy site were sampled on two separate occasions.

ANALYSIS BY SOLID-PHASE EXTRACTION (SPE)-ISOTOPE DILUTION LC/MS/MS

Spiking of samples with isotopically labeled surrogate compounds

Samples (0.5 L or 1 L) were spiked with appropriate isotopically labeled internal standards. For nonylphenol, the internal standard employed for quantification was [*ring*-$^{13}C_6$]-*n*-nonylphenol (Cambridge Isotope Laboratories, Andover, MA). For the other APEO metabolites studied (NP1EC and NP2EC), the internal standard was $^{13}C_2$-*n*-nonylphenoxyacetic acid (custom-synthesized by Cerilliant, Round Rock, TX); this NP1EC analog was used to represent both NP1EC and NP2EC. For the steroid estrogens 17 β-estradiol and estrone, the internal standard employed for quantification was 17β-estradiol 16,17,17-d_3 (ICN, Pointe-Claire, Quebec). For caffeine, the internal standard used for quantification was caffeine-trimethyl $^{13}C_3$ (Sigma Aldrich, MO). For ibuprofen, the internal standard was ibuprofen-propionic-$^{13}C_3$ (Cambridge Isotope Laboratories, Inc.).

Sample pre-concentration by SPE

Samples were pre-concentrated by solid-phase extraction (SPE)(ENVI-18 disks, Supelco, Bellefonte, PA), followed by elution of the analytes with 10 mL of ultra-pure methanol. This constituted a 50-fold concentration of the analytes for a 0.5-L sample or a 100-fold concentration for a 1-L sample. Additionally, for each batch of samples, a method blank consisting of 0.5-L or 1-L aliquot of reagent water was spiked with internal standards and extracted simultaneously with the aqueous samples. To improve sensitivity for some target analytes (e.g., 17β-estradiol and estrone), an aliquot of the methanol extract was concentrated (e.g., 10-fold from 2 mL to 200 μL) with a gentle stream of nitrogen gas prior to LC/MS/MS analysis.

Analysis by isotope dilution LC/MS/MS

A Waters Model 2690 (Waters Corporation, Milford, MA) HPLC (High Performance Liquid Chromatography) instrument with a Nova-Pak C_{18} column (150 x 2.1 mm, 4-μm particle size; Waters Corporation) was used for chromatographic separation of analytes. The sample injection volume was 25 μL. The mobile phase typically consisted of methanol:water mixtures, with the flow rates ranging from 100-200 μL/min, depending on the analyte of interest. In some cases, chromatographic optimization studies revealed that methanol:water mixtures were not sufficient for good chromatographic separation or retention. For example, chromatographic separation of APECs was achieved with a 65:35 mixture of methanol and 5 mM ammonium acetate (in 90% water:10% methanol).

A triple quadrupole mass spectrometer - Quattro LC™ (Micromass, Manchester, UK) - was employed for mass determination and quantification. Operating conditions included a nitrogen flow rate of 75 L/hr for the nebulizer and a flow rate of 350 L/hr during desolvation. Ion source temperatures were 80^{o}C for the source block and 300^{o}C for desolvation. Compound-specific optimization of MS and MS/MS parameters (e.g., sample cone voltage, capillary voltage, collision energy) for method development involved infusions of standards (typically 10 μL/min for a 200 μg/L standard) and acquisition in full-scan mode or daughter ion mode. Optimized parameters are listed in Table 1. Isotope dilution quantification (with compound-specific corrections for internal standard recovery) was performed in selected reaction monitoring mode for all analytes.

Some method development for acetaminophen was performed, but technical problems precluded regular analysis of this compound in field-collected samples for this project. Both an isotopically labeled acetaminophen standard (Acetyl-$^{13}C_2$, 99%; ^{15}N, 98%) and unlabeled acetaminophen standard were acquired. Standard compound solutions (200 μg/L) were infused through a syringe pump at a flow rate of 20 μL/min for tuning and parameter optimization. Positive electrospray ionization was employed, with a capillary voltage of 3.5 kV and cone voltage of 24 V. For the unlabeled acetaminophen standard, the base peak was at *m/z* 174.2, which corresponds to the parent ion with sodium adduct $[M + Na]^+$; the isotopically-labeled acetaminophen standard had a base peak at *m/z* 177.2, as expected. Observed sensitivity was favorable. Unfortunately, a suitable mass fragment for tandem MS analysis was not produced under the wide range of tuning conditions tested, so the detection limit for acetaminophen was considered too high relative to the concentrations expected in environmental samples.

Table 1. Trace organic compounds of interest.

Compound	Pre-concentration technique[a]	Ionization mode	Instrumentation[b]	Mass fragment or transition for analyte (*m/z*)	Mass fragment or transition for internal std. (*m/z*)[c]	Detection limit[d] (ng/L)
Caffeine	SPE, ENVI-18 disks	Positive Electrospray	LC/MS/MS	*m/z* 195→ *m/z* 138	*m/z* of 198 → *m/z* 140	5-10
4-Nonylphenol	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	*m/z* 219 → *m/z* 133	*m/z* 225 → *m/z* 112	10-15
NP1EC[e]	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	*m/z* 277 → *m/z* 219	*m/z* 279 → *m/z* 219	10
NP2EC[f]	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	*m/z* 321 → *m/z* 219	*m/z* 279 → *m/z* 219[e]	10
17β-estradiol	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	*m/z* 271→ *m/z* 143, 145, 183	*m/z* 274 → *m/z* 145, 185	1-10
Estrone	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	*m/z* 269 → *m/z* 143, 145	*m/z* 274 → *m/z* 145, 185[g]	1-10
Ibuprofen	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	*m/z* 205 → *m/z* 161	*m/z* 208 → *m/z* 163	5-10
DEET	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 119	*m/z* 217[h]	10
Tris (2-chloroethyl)phosphate	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 63	*m/z* 217[h]	100
Tris (1,3-dichloroisopropyl) phosphate	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 75	*m/z* 217[h]	100
Triphenyl phosphate	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 326	*m/z* 217[h]	100
Triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether)	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 290	*m/z* 217[h]	100
Coprostanol[i]	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 215	*m/z* 217[h]	100
Cholesterol[i]	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 275	*m/z* 217[h]	100
Stigmastanol[i]	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 215	*m/z* 217[h]	100

Ethylenediamine tetraacetic acid (EDTA)[j]	Rotary evaporation	Electron Impact	GC/MS	*m/z* 174	*m/z* 180[j]	100
Linear alkylbenzenesulfonates (LAS)[j]	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 185	*m/z* 91[k]	1000
Carbamazepine	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 193	*m/z* 217[h]	20
Primadone	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	*m/z* 146	*m/z* 217[h]	40

[a] SPE media included ENVI-18 disks (Supelco, Bellefonte, PA) and OASIS HLB cartridges (Waters Corporation, Milford, MA).

[b] Liquid chromatography/tandem mass spectrometry, LC/MS/MS. Gas chromatography/mass spectrometry, GC/MS.

[c] Isotopically (i.e., ^{13}C, ^{2}H, ^{15}N) labeled internal standards were employed for isotope dilution liquid chromatography/tandem mass spectrometry unless noted otherwise.

[d] Estimated detection limits are based on solid-phase extraction of a 0.5- or 1-L aqueous sample and account for typical extraction blank concentration levels.

[e] Nonylphenoxyacetic acid (Figure 1), a metabolite of alkylphenol ethoxylates.

[f] Nonylphenoxyethoxyacetic acid (Figure 1), a metabolite of alkylphenol ethoxylates; the internal standard for NP1EC was also used for NP2EC.

[g] The internal standard for 17β-estradiol was also used for estrone.

[h] Internal standard is 5α-cholestane.

[i] C_{27} and C_{29} fecal sterols. Samples are routinely scanned for these sterols, and if observed, 5 other sterol compounds are investigated.

[j] Internal standard is D12-EDTA.

[k] Internal standard is 4-octylbenzene sulfonate.

ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

Spiking of samples with isotopically labeled surrogate compounds

Prior to extraction each water sample was spiked with an isotopically labeled surrogate recovery standard (D5-atrazine, Isotope Laboratories, Andover, MA) to monitor extraction efficiency and chromatographic performance.

Sample pre-concentration by SPE

Extraction and pre-concentration of target wastewater indicators was achieved using Oasis HLB solid phase extraction (SPE) cartridges (3 cc/60 mg, Waters Corporation, Milford, MA). The Oasis HLB cartridge has been successfully used for the extraction of a broad spectrum of organic compounds from a variety of matrices (Liu et al., 2004; Quintana et al., 2004; Benijts et al., 2004) and was a suitable SPE cartridge for the current list of wastewater indicators. Prior to sample extraction, the SPE cartridges were pre-conditioned with 5 mL hexane, 3 mL ethyl acetate, 3 mL methanol and 3 mL Milli-Q water. A short section of precleaned Teflon tubing was inserted into each sample bottle (0.5 – 1 liter) and water samples drawn through the SPE cartridges at a flow rate of ≤1.5 ml/min using a peristaltic pump (Gilson Minipuls 2) equipped with an eight channel pump head, allowing up to eight samples to be extracted simultaneously. After extraction, each SPE cartridge was air dried and a first fraction was eluted with 5 mL ultra-pure ethyl acetate. All target compounds except the LAS surfactants were eluted from the cartridge in an ethyl acetate fraction (fraction 1) and the LAS surfactants were eluted using acetonitrile (fraction 2). This first extract was concentrated with a stream of nitrogen gas, extracts spiked with an internal standard, and final volume adjusted to 50 μL (ethyl acetate). A second fraction, which included the LAS, was eluted using ultra-pure acetonitrile. Fraction 2 was evaporated to dryness using a stream of dry nitrogen gas and residue redissolved in 50 μL dichloromethane containing 0.005M tetrabutylammonium hydrogen sulfate. The LAS-TBA ion pair reacts to esterify the LAS in the injection port. Quantification was performed using an internal standard (4-octylbenzene sulfonate). Typical carryover problems were avoided by following each sample injection with a blank dichloromethane/TBA injection.

Analysis by GC/MS

A 1 μL splitless injection was analyzed using an HP 6890 Series gas chromatograph coupled to an HP 6890MSD (5972 MS) using a Restek Rtx-5ms column (40m x 0.25mm i.d., 0.25 μm film thickness), with the injection port at 280°C and a constant head pressure of 12 psi. The mass spectrometer was operated in selected ion monitoring (SIM) mode for target compound quantification and in full-scan mode for mass spectrometry compound verification. Full-scan runs were also used to screen the extracts for non-target compounds of interest. The temperature program of the GC oven was as follows: isothermal at 65°C for 1 min., 5°C/min. to 310°C, held isothermal at 310°C for 10 min. Helium was used as the carrier gas. The concentrations of the target compounds were determined by using a five-point calibration curve for each analyte, ranging in concentration from 8 to 800 ng/L (based on a 1L water sample) and compounds were quantified using relative response factors of an internal standard (5α-cholestane), with %RSDs ≤20%.

Volatile Organic Compounds

Selected sample locations included analyses for volatile organic compounds in addition to the semivolatile target compounds. The GAMA volatile organic compound (VOC) list, which originally contained 16 compounds, was expanded to 36 compounds. A five-point initial calibration, ranging in concentration from 3.5 ng/L to 176 ng/L, was checked daily with a midpoint continuing calibration check. Detection limits were variable but all compounds in the current target list were calibrated down to a level of 3.5 ng/L. The reporting limit was set at 5 ng/L. Replicates were run at a frequency of 10% and samples with analytes exceeding the linear calibration range were diluted accordingly and rerun. Analytical procedures and QA considerations follow those reported by Moran et al. (2005).

EDTA

The current method for EDTA works well only for waters low in total dissolved solids. This method involved spiking the water samples with an isotopically labeled internal standard (D_{12}-EDTA, Cambridge Isotope Laboratories, Inc.). Each sample was then concentrated by rotary evaporation to approximately 2 mL. The concentrated samples were transferred to 10 mL test tubes with Teflon-lined screw caps. Formic acid (0.5 mL) was added to each, and samples reduced to dryness under a stream of dry nitrogen gas. The dried residue was dissolved in 1 mL of a BF_3/MeOH solution (10%) and reacted at 85°C for 45 min. to methylate the EDTA and D_{12}-EDTA. This solution was cooled to room temperature and diluted with 2.5 mL of a 2% potassium bicarbonate solution, then solvent extracted using two 0.5 mL portions of dichloromethane to extract the methylated EDTA and methylated D_{12}-EDTA. The extracts were combined and prepared for analysis using GC/MS by adjusting the extract volume to 50 μL. GC/MS analyses were performed on the dichloromethane extracts using a Hewlett Packard 6890 GC coupled to a Hewlett Packard 6890 MSD (5972 MSD) using an HP-5 ms open tubular column (30 m x 0.25 mm i.d., 0.25 μm film thickness). The injection temperature was set at 280°C and the GC oven program was as follows: isothermal at 65°C for 2 min., then ramped at 5°C/min. to a final temperature of 310°C and held isothermal for 10 min. Injection volumes were 1 μL using a constant column head pressure of 12 psig. Selected ion monitoring (SIM) with electron impact was employed for quantification. A six-point calibration curve for EDTA was used (D_{12}-EDTA as internal standard), ranging in concentration from 100 ng/L to 10,000 ng/L. Good linearity was obtained (e.g., $r^2 = 0.999$). Method blanks had EDTA amounts below the reporting limit (~ 40 ng/L). This method works well and recoveries are high only with waters low in total dissolved solids. The presence of salts interferes with the methylation reaction, resulting in very low or no recoveries of EDTA and the internal standard.

RESULTS & DISCUSSION

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) FOR TARGET COMPOUNDS

LC/MS/MS calibration

Internal standard calibration curves (3-point to 5-point) for NP, caffeine, NP1EC, and NP2EC were highly linear over the concentration range relevant to samples analyzed. Representative calibration curves are presented in Figures 3-5. For NP, caffeine, NP1EC, and NP2EC, calibration curves typically covering the concentration ranges of 10 to 250, 10 to 1000, or 10 to 2500 ng/L (assuming a sample size of 1 L) had r^2 values between 0.996 and 0.99997. Internal standard calibration curves (5-point) for 17β-estradiol, estrone, and ibuprofen were linear over the concentration range relevant to samples analyzed, with r^2 values greater than 0.99.

Surrogate recoveries

For 147 samples (including well water samples, replicates, trip blanks, and equipment blanks) analyzed for NP by isotope dilution LC/MS/MS, recovery of the ^{13}C-labeled surrogate compound averaged 68 $\pm$ 25% (mean $\pm$ standard deviation) and had a median value of 69%. The surrogate compound was spiked into samples at a concentration of either 0.5 or 1 μg/L (depending on the sample size). For 154 samples analyzed by isotope dilution LC/MS/MS for caffeine, recovery of the ^{13}C-labeled surrogate compound averaged 14 $\pm$ 9% and had a median value of 13%. The surrogate compound for caffeine was spiked into samples at a concentration of either 0.1 or 0.2 μg/L (depending on the sample size). The relatively poor recovery for caffeine probably reflects that this compound is too polar to be effectively captured by the octadecyl silica solid phase extraction discs that were used for this project. For 17 samples analyzed for AP1EC and AP2EC by isotope dilution, LC/MS/MS, recovery of the ^{13}C-labeled surrogate compound averaged 139 $\pm$ 25% and had a median value of 144%. The surrogate compound was spiked into samples at a concentration of either 0.5 or 1 μg/L (depending on the sample size). The cause of the high recovery for the APEC surrogate compound is not known, but could potentially be associated with signal enhancement related to the sample matrix. One advantage of the isotope dilution technique is that it corrects for signal enhancement (or signal suppression) on a compound-specific and sample-specific basis.

For groundwater samples analyzed by GC/MS, recovery of the surrogate compound (D5-Atrazine) averaged 98 $\pm$ 8% (mean $\pm$ standard deviation for n=90).

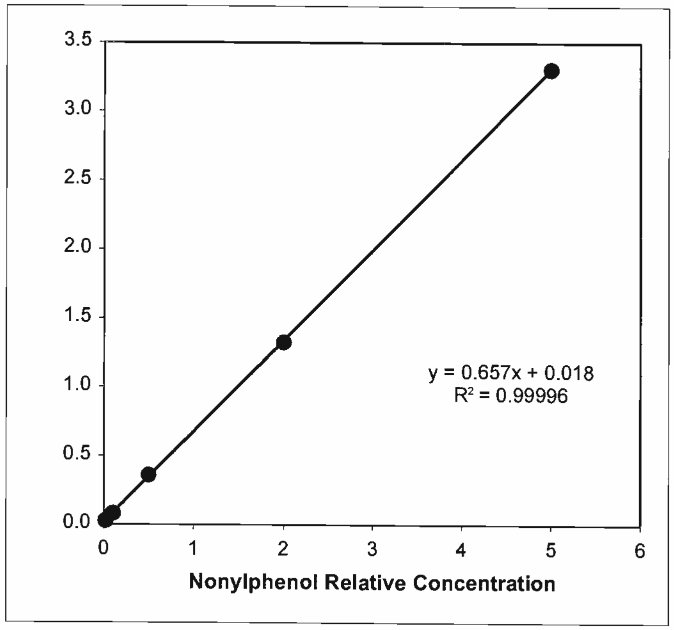


Figure 3. Internal standard calibration for NP. Standard concentrations (accounting for a 1-L sample processed through SPE) range from 10 to 2500 ng/L.

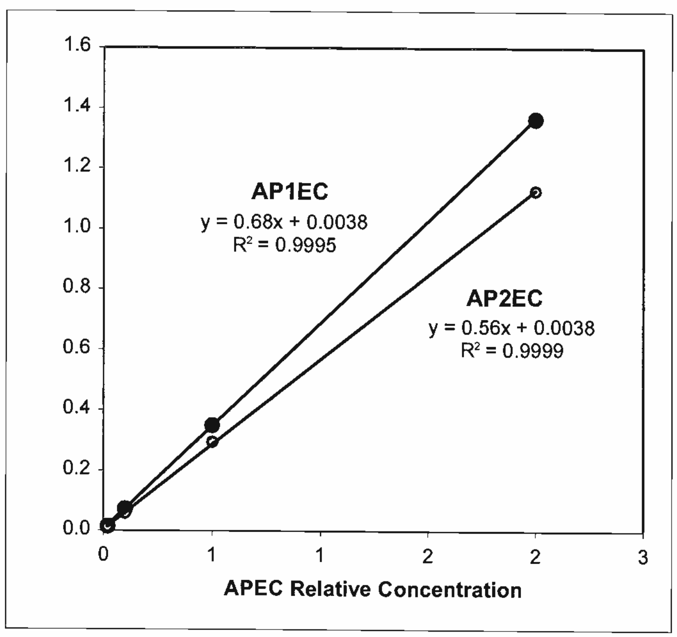


Figure 4. Internal standard calibration for AP1EC and AP2EC. Standard concentrations (accounting for a 1-L sample processed through SPE) range from 10 to 1000 ng/L.

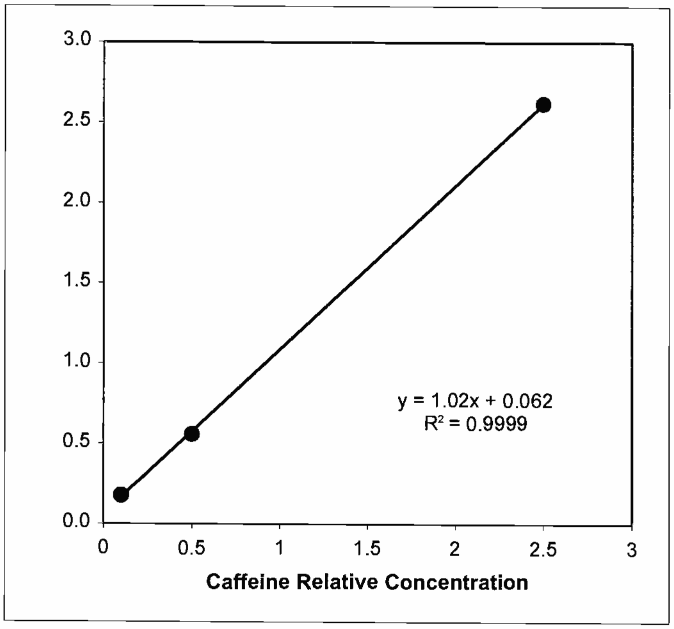


Figure 5. Internal standard calibration for caffeine. Standard concentrations (accounting for a 1-L sample processed through SPE) range from 10 to 250 ng/L.

Reporting conventions for LC/MS/MS (detection limits)

Accurate method detection limits should reflect more than the absolute sensitivity of the analytical instrumentation (the instrumental detection limit). Specifically, for compounds that can occur at low levels as laboratory contaminants, method detection limits should also reflect the background level of such contamination. Thus, for caffeine, detection limits were established as the highest concentration among method blanks analyzed in a sample batch. This concentration (10-15 ng/L) is considerably higher than the absolute sensitivity of the LC/MS/MS method, but effectively minimizes the possibility of false positive detections. For NP, two levels of detection limits were established: (1) the highest concentration among method blanks analyzed in a sample batch (as for caffeine) and (2) double that concentration. To illustrate, if the highest method blank concentration for NP was 10 ng/L, a sample with 8 ng/L was reported as <10 ng/L, a sample with 15 ng/L was reported as <20 ng/L, and a sample with 22 ng/L was reported as 22 ng/L. This reporting convention was based on the best professional judgment of the analyst, and reflects the observation that there were a number of samples with NP concentrations in the range of the method blank, and the analyst did not consider these to be sufficiently above background to be confidently reported. It should be noted that, even with this conservative reporting convention, detection limits were still quite low as compared to conventional EPA analysis of organic priority pollutants.

Method and Trip blanks

Method blanks are defined for this project as reagent water samples that are processed through the entire laboratory analysis procedure (i.e., spiking with surrogate compounds, solid-phase extraction, and analysis by LC/MS/MS). A method blank was run with each extraction batch (typically 4 or 5 groundwater samples).

For the method blanks analyzed, caffeine concentrations were typically less than 5 to 10 ng/L and always less than 15 ng/L. As discussed in the previous section, the highest method blank for an LC/MS/MS analysis batch was used to establish the detection limit (at least for certain compounds). For NP, method blank concentrations were typically less than 10 ng/L and always less than 37 ng/L. Method blanks did not contain detectable levels of NP1EC, NP2EC, ibuprofen, or estrogenic compounds (i.e., above 3 ng/L for NPEC's or above 11 ng/L for other compounds).

None of the target compounds was detected by either GC/MS or by LC/MS/MS in any of the five trip blanks.

Equipment Blanks

The results of the series of equipment blanks should serve as a cautionary tale. Of the target analytes, NP is arguably the most likely target compound to suffer such artifacts because this compound is included in the manufacture of a range of plastics. As shown in Table 2, some sampling equipment resulted in NP contamination that clearly exceeded the concentrations observed in method blanks. In particular, two samples of reagent water that had passed through a Grundfos pump (samples 103943 and 103944) had 200 ng/L NP concentrations, which is at least 20-fold higher than concentrations in method blanks. This artifact was observed despite the fact that this pump included Teflon-lined tubing, which is the optimal material for minimizing plasticizer contamination. In addition, NP was observed at concentrations less than 50 ng/L in blank samples collected using both the stainless steel and Teflon bailers, and in blank water stored in a plastic bucket (Table 2). Only the ¾" Teflon bailer and bladder pump blanks were free of NP at the 20 ng/L level. Hence, for NP, it is very difficult to completely rule out the possibility of sampling artifacts; detections must be viewed with caution and ideally confirmed by multiple samplings with different equipment. Other LC/MS/MS-analyzed compounds such as caffeine and ibuprofen were not detected in equipment blanks.

For compounds analyzed by GC/MS, all of the plastic bailer blanks were significantly cleaner than the stainless steel bailer blanks (see Table 2); this may be attributed to the fact that some organic compounds sorb to the stainless steel and are transferred to subsequent samples. Some of the compounds identified in the stainless steel bailer blank appear to come from a typical sunscreen lotion, and being somewhat oily in composition, would have a tendency to persist. The stainless steel bailer blank samples also contained compounds usually associated with plastics (e.g., butyl citrate, triphenylphosphine oxide and benzyl butyl phthalate).

Table 2. Results from equipment blank experiments

Sample Type	Compounds Detected (ng/L)
method blank	none
trip blank	none
stainless steel bailer	N-butyl-benzenesulfonamide, benzyl butyl phthalate, Diphenyl sulfone
1/2" teflon bailer	NP (40)
3/4" teflon bailer	N-butyl-benzenesulfonamide, phthalates
bladder pump	N-butyl-benzenesulfonamide (100,000), Diphenyl sulfone, phthalates
Grundfos pump 1 (Teflon tubing)	NP (200), Diphenyl sulfone
Grundfos pump 2 (Teflon tubing)	NP (20), N-butyl-benzenesulfonamide

N-butyl-benzenesulfonamide was detected at relatively high concentrations (up to 100 μg/L) in blank water samples that had been stored in a new plastic bucket, pumped through a Grundfos pump with new Teflon-lined tubing, pumped with the bladder pump, and passed through a ¾" Teflon bailer. N-butyl-benzenesulfonamide is a plasticizer used in polymerization of polyamide compounds, and was not a target analyte. Diphenyl sulfone and some phthalates were also detected in these samples at lower concentrations. Only one sample, passed through a narrow (1/2") teflon bailer, did not have detections of any contaminants by GC/MS.

Results for Groundwater Samples

Results for groundwater samples are discussed in five sections: (1) Tehama County private wells, (2) Chico area monitoring and drinking water wells, (3) dairy site monitoring wells, (4) Gilroy wells, and (5) Livermore wells. Analytical results, along with well information for the five regions, are shown in Table 3. The latter two regions include local areas where tertiary treated wastewater has been used for irrigation for at least two decades. Monitoring wells from those areas are most likely to show the effects of transport of wastewater compounds. Multiple isotopic tracers and wastewater indicator compounds were analyzed in 8 monitoring wells from wastewater irrigation areas in Gilroy and 10 such wells in Livermore. In addition, trace organic compounds of interest as wastewater indicators have been analyzed in 93 samples, 20 of which are from shallow monitoring wells in Chico, 35 from private domestic wells in Tehama County (26), Chico (2), and Livermore (7), 5 from public drinking water wells in Chico, and 33 from dairy monitoring wells.

Following the results section, there is a discussion of the major factors affecting the fate and transport of wastewater indicators, and a comparison between results from Livermore and Gilroy, as well as a comparison between results from those areas and the regions that are outside of the area of influence of wastewater irrigation.

Many target analytes were not detected in any of the well water samples. For example, no groundwater samples contained ibuprofen or estrogenic compounds at detectable concentration levels (i.e., above 11 ng/L). In addition, none of the sterols were detected in groundwater samples.

Table 3. Analytical results for target compounds. Blank fields indicate compound was not analyzed in that sample. UCM = Unresolved complex mixture of organic material. * Detection is likely a sampling artifact, as discussed in text.

LLNL ID	Collection Date	Well ID	TOC	Caffeine	Nonylphenol	NP1EC	NP2EC	Chloroform	Carbamazepine	Primadone	Desmethyl norflurazon	Nor flurazon	Additional Detections (concentration)
			mg/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
Tehama County													
102836	4/19/2005	SWRCB-691-Tehama		<15	24*	<3	<3				<10	<10	
102885	4/26/2005	SWRCB-726-Tehama		<15	<10						<10	<10	
102886	4/26/2005	SWRCB-775-Tehama		<15	<10						<10	<10	
102890	4/27/2005	SWRCB-780-Tehama		<15	<10						<10	<10	
102891	4/27/2005	SWRCB-729-Tehama		<15	<20						<10	<10	
102892	4/27/2005	SWRCB-730-Tehama		<15	<10						<10	<10	
102893	4/27/2005	SWRCB-751-Tehama		<15	<10						<10	<10	
102894	4/28/2005	SWRCB-764-Tehama		<15	<10						<10	<10	
102917	5/3/2005	SWRCB-744-Tehama		<15	690* (<1μg/L)	<3	<3				<10	<10	
102918	5/4/2005	SWRCB-754-Tehama		<15	<10						<10	<10	
102919	5/4/2005	SWRCB-755-Tehama		<15	<10						<10	<10	
102920	5/4/2005	SWRCB-753-Tehama		<15	<10						<10	<10	
102921	5/10/2005	SWRCB-792-Tehama		<15	<10						<10	<10	
102922	5/10/2005	SWRCB-803-Tehama		<15	<20						<10	<10	
102928	5/11/2005	SWRCB-808-Tehama		<10	<20						<10	<10	
102929	5/11/2005	SWRCB-821-Tehama		<10	<10						<10	<10	
102930	5/16/2005	SWRCB-841-Tehama		<10	<10						<10	<10	
102931	5/19/2005	SWRCB-844-Tehama		<10	<10						<10	<10	
102932	5/19/2005	SWRCB-801-Tehama		<10	<10						<10	<10	
102933	5/19/2005	SWRCB-838-		<10	<10						<10	<10	

LLNL ID	Collection Date	Well ID	TOC	Caffeine	Nonylphenol	NP1EC	NP2EC	Chloroform	Carbamazepine	Primadone	Desmethyl norflurazon	Nor flurazon	Additional Detections (concentration)
		Tehama											
102934	5/24/2005	SWRCB-871-Tehama		<10	<10						<10	<10	
102935	5/25/2005	SWRCB-816-Tehama		<10	<10						<10	<10	
102945	6/1/2005	SWRCB-890-Tehama		<10	<20						<10	<10	
102946	6/1/2005	SWRCB-876-Tehama		<10	28*						<10	<10	
102947	6/1/2005	SWRCB-781-Tehama		<10	<10						<10	<10	
102948	6/1/2005	SWRCB-786-Tehama		<10	<20						<10	<10	
Chico													
103023	10/25/2005	DMW-11	1	<7	<10				230		<10	<10	
103022	10/25/2005	DMW-13	1	<7	<10				<20		<10	<10	
103021	10/13/2005	MW-21	1	<7	<20				<20	<40	<10	<10	UV absorbing sunscreen agents of oxybenzone and parsol MCX (2-ethylhexyl cinnamate), polycyclic musk compounds AHTN (tonalide) and HHCB (galaxolide), and the HHCB transformation product HHCB-lactone (galaxolidone), flame retardant tris (1,3-dichloroisopropyl) phosphate
103020	10/13/2005	102-A	<0.5	<7	<10				<20	<40	<10	<10	
103019	10/5/2005	MW-28	1						<20	<40	<10	<10	
103018	10/5/2005	MW-22	<0.5	<6	<5				39	<40	<10	<10	
103017	10/5/2005	DMW-7	<0.5	<6	<5				<20	<40	<10	<10	
103014	10/5/2005	MW-25	1	<6	<5				<20	<40	<10	<10	
103013	10/5/2005	DMW-18	1	16	6	<3	<3		<20	<40	<10	<10	
103012	8/18/2005	CWS 52-01	<0.5	<10	<36				<20	<40	<10	<10	UCM
103011	8/18/2005	CWS 30-01	<0.5						<20	<40	<10	<10	UCM
103010	8/18/2005	CWS 27-01	<0.5						<20	<40	<10	<10	
103009	8/18/2005	CWS 47-01	<0.5						<20	<40	<10	<10	
103008	8/18/2005	CWS 68-01	<0.5						<20	<40	<10	<10	

LLNL ID	Collection Date	Well ID	TOC	Caffeine	Nonylphenol	NP1EC	NP2EC	Chloroform	Carbamazepine	Primadone	Desmethyl norflurazon	Nor flurazon	Additional Detections (concentration)
103007	8/18/2005	CWS 59-01	1						<20	<40	<10	<10	
103006	7/14/2005	DMW-2	1	<15	<36				<20	<40	140	<10	
103005	7/13/2005	DMW-3	2	<10	<36				<20	<40	<10	<10	
103004	7/13/2005	2-D1	<0.5	<10	<36				<20	<40	<10	<10	
103003	7/13/2005	2-I1	<0.5	<10	<36				<20	<40	<10	<10	
103002	7/13/2005	2-S1	1	<10	110	<3	<3		<20	<40	<10	<10	DEET (16)
103001	10/13/2005	FCMW2	1	<14	<10				<20	<40	<10	<10	
103000	10/12/2005	DMW-14	1	<7	<10				<20	<40	<10	<10	UCM, desisopropyl atrazine (25), simazine (6)
102999	10/12/2005	DMW-15	1	<7	<10				120	<40	<10	<10	
102998	10/12/2005	46-S1	<0.5	<7	<10				<20	<40	<10	<10	
102997	10/12/2005	DMW-16	1	<7	<10				<20	<40	<10	<10	atrazine (33), desethylatrazine (12)
102996	10/5/2005	DMW-6	<0.5	<6	<5				30	<40	<10	<10	
102995	10/5/2005	DMW-5	1	<6	<5				<20	<40	<10	<10	
102994	6/14/2005	DMW-17	1	<10	<36				<20	<40	<10	<10	
102993	6/14/2005	022N001E28J002M		30	<36	4	<3		<20	<40	<10	<10	UCM
102992	6/14/2005	MEADOWS PARK	<0.5	<10	<36				<20	<40	<10	<10	
Dairies													
102685	3/8/2005	MCD V1	13	<15	<30			11			<10	<10	
102673	3/7/2005	MCD V14	6	<15	67			<5			<10	<10	
102981	6/7/2005	MCD V18		<10	<20						<10	<10	
102675	3/7/2005	MCD V18	8	<15	130			18			<10	<10	
102677	3/7/2005	MCD V21	23	<15	<30			<5			<10	<10	carbon disulfide (90)
102676	3/7/2005	MCD V24	5	<15	78			<5			<10	<10	
102674	3/7/2005	MCD V99	12	<15	<60			8			<10	<10	
102988	6/7/2005	MCD W2		<10	29						<10	<10	
102689	3/8/2005	MCD W2	13	<15	<60			<5			<10	<10	carbon disulfide (13)
102690	3/8/2005	MCD W3	15	<15	<30			6			<10	<10	
102679	3/7/2005	MCD W10	12	<15	<30			7			<10	<10	
102985	6/7/2005	MCD W16		<10	80						<10	<10	
102684	3/8/2005	MCD W16	9	<15	<60			<5			<10	<10	carbon disulfide (38)
102986	6/7/2005	MCD W17		<10	25						<10	<10	

LLNL ID	Collection Date	Well ID	TOC	Caffeine	Nonylphenol	NP1EC	NP2EC	Chloroform	Carbamazepine	Primadone	Desmethyl norflurazon	Nor flurazon	Additional Detections (concentration)
102683	3/8/2005	MCD W17	10	<15	<30			<5			<10	<10	carbon disulfide (33)
102678	3/7/2005	MCD W23	10	<15	<30			11			<10	<10	
102680	3/8/2005	MCD W98	2	<15	<60			4975			<10	<10	carbon disulfide (17)
102687	3/8/2005	SCD Y3	18	<15	4700			<5			<10	<10	carbon disulfide (30)
102686	3/8/2005	SCD Y10	3	<15	<30			<5			<10	<10	
103379	8/25/2005	KCD DAIRY									<10	<10	
103353	8/25/2005	KCD PVT									<10	<10	
103351	8/25/2005	KCD LAGOON3						27					carbon disulfide (790), coprostanol, cholesterol, stigmastanol
103380	8/25/2005	CANAL									<10	<10	
102634	2/15/2002	KCD 1S2	2	<15	120			<5			<10	<10	
102632	2/15/2005	KCD 1S3	1	<15	210			<5			<10	<10	carbon disulfide (9.3)
102631	2/15/2005	KCD 1S4	1					<5			<10	<10	carbon disulfide (27)
103352	8/25/2005	KCD 2S1		460*	45			26			14500	9500	dichlorobenzamine (20), 3,4,Dichlorophenyl isocyanate (58)
102627	2/16/2005	KCD 2S2		<15	<60			6			5900	9600	dichlorobenzamine (690)
102628	2/15/2005	KCD 2S3		<15	63			10			1900	4300	dichlorobenzamine (440),3,4,Dichlorophenyl isocyanate (2100)
102633	2/15/2005	KCD 2S4						<5			<10	<10	carbon disulfide (37)
102623	2/16/2005	KCD 3S1	4	<15	<60			85			60	<10	
102624	2/16/2005	KCD 3S2	14	<15	72			<5			910	30	
102629	2/16/2005	KCD 3S3	6					<5			330	14	
102630	2/16/2005	KCD 3S4	6					<5			175	10	
102625	2/16/2005	KCD 4S2	1	<15	66			<5			<10	<10	
102636	2/17/2005	KCD 4S3	1										
102639	2/17/2005	KCD 4S4	1	<15	330			<5			<10	<10	carbon disulfide (17)
102849	4/26/2005	KCD 5S1						<5					MTBE (360)
102626	2/17/2005	KCD 5S1		<15	95			<5			<10	<10	MTBE (350), 3-Chlorophenyl isocyanate (150), 3,4,Dichlorophenyl isocyanate (30)
103348	8/25/2005	KCD TEMP1	12	245*	510			<5			<10	<10	carbon disulfide (8.6)
102887	5/10/2005	KCD TEMP1						<5					carbon disulfide (9.5)
102635	2/17/2005	KCD TEMP1		<15	770			<5			<10	<10	carbon disulfide (25)

LLNL ID	Collection Date	Well ID	TOC	Caffeine	Nonylphenol	NP1EC	NP2EC	Chloroform	Carbamazepine	Primadone	Desmethyl norflurazon	Nor flurazon	Additional Detections (concentration)
103349	8/25/2005	KCD TEMP2	12	890*	450			<5			<10	<10	
102888	5/10/2005	KCD TEMP2						<5					carbon disulfide (6.5)
102637	2/17/2005	KCD TEMP2		<15	3000			<5			<10	<10	carbon disulfide (93)
103350	8/25/2005	KCD TEMP3	5					<5					carbon disulfide (9.1)
102638	2/17/2005	KCD TEMP3						<5			<10	<10	carbon disulfide (6.3)
Gilroy													
103446	10/4/2005	Bolsa-2		<6	67	4	12	8	<20	E40	<10	<10	MTBE (25)
103445	10/4/2005	Bloom-1		7	74	<3	<3	<5	<20	<40	<10	<10	
103444	9/28/2005	MW-24			27	<3	<3	<5	<20	<40	<10	<10	
101768	8/19/2003	MW-24				<3	<3						
103443	9/28/2005	MW-22		<6	60	840	125	<5	150	E40	<10	<10	diphenamide, MTBE (43)
101767	8/19/2003	MW-22			28	1700	800						
103442	9/28/2005	MW-21		<6	36	8	13	40	150	E40	<10	<10	MTBE (7.2)
101766	8/19/2003	MW-21			23	<3	<3						
103441	9/26/2005	CH-3		<6	120	<3	<3	414	<20	<40	<10	<10	
103440	9/26/2005	CH-2		<6	150	<3	<3	340	<20	<40	<10	<10	
103439	9/26/2005	CH-1		<6	225	<3	<3	225	<20	<40	<10	<10	
Livermore													
103560	11/9/2005	2J2	2	<7	<10	125	18		<20	<40	<10	<10	benzothiazole (22), desisopropyl atrazine (16), simazine (83)
101792	8/25/2003	2J2		<7		140	170						
103559	11/9/2005	1P2	1	<7	<10	4.5	<3		<20	<40	<10	18	benzothiazole (35), desisopropyl atrazine (36), simazine (110), oxadiazon
101794	8/26/2003	1P2		<7		<10	<10						
101796	8/28/2003	2R1		<7		60	90						
101798	8/28/2003	11C3		<7		<10	<10						
101793	8/25/2003	2Q1		<7		<10	<10						
101795	8/25/2003	11B1		<7		<10	<10						

RESULTS FOR TEHAMA GROUNDWATER

Twenty six groundwater samples, collected from Tehama County wells as part of the SWRCB GAMA Voluntary Domestic Well program, were received through the Spring of 2005. The samples were collected by SWRCB personnel using the collection protocol described previously. Samples were collected at ports upstream of holding tanks, and represent a small subset of the >200 wells included in the Voluntary Domestic Well program for Tehama County. Figure 6 shows the locations of the wells that were sampled for wastewater indicator compounds.

In summary, no *target* analyte was detected with confidence in any of the well water samples. One relatively high level detection of nonylphenol can be attributed to the sampling container (not the standard I-Chem bottle), which had a black phenolic cap instead of a Teflon-lined cap. The result for that sample is reported as '< 1 μg/L'. Two more samples with nonylphenol detections below 30 ng/L cannot be excluded as readily, but results from the blank studies provide ample evidence for suspecting that the source of the nonylphenol may be contamination of the sample during or after sampling.

The samples did not contain ibuprofen or estrogenic compounds at detectable concentration levels (i.e., above 10 ng/L). Extraction method blank samples did not contain detectable levels of ibuprofen or estrogenic compounds. Notably, surrogate recoveries in groundwater for the isotopically labeled ibuprofen standard varied considerably.

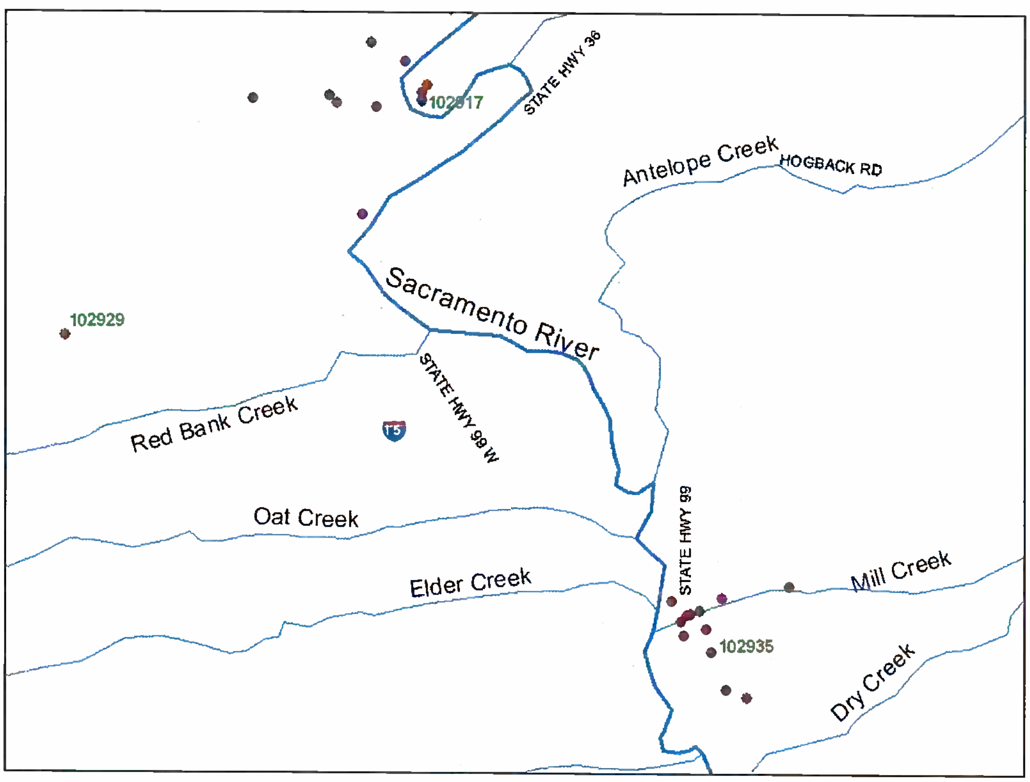


Figure 6. Map showing locations of private domestic wells sampled for wastewater indicator compounds. Numerical labels refer to three samples discussed in the text.

Duplicate water samples were also extracted by solid phase extraction using Waters Oasis HLB cartridges, and analyzed by GC/MS. None of the GC/MS target analytes were detected in these water samples. Total extracts were screened with the mass spectrometer in full-scan mode and no additional compounds of interest were detected, but elemental sulfur was present in a few of the extracts (likely indicating that sulfide was present in the samples). Three GC/MS total ion chromatograms (TICs) for Tehama are shown in Figures 7-9. Figure 7 is the chromatogram of the total extract for sample 102935 and is representative of most water samples analyzed from this study area. Peak labels identify the surrogate compound and internal standard. Additional peak labels identify a second extraction surrogate, which was added during this time as a method development check, and some minor contaminants, including butylated hydroxytoluene (BHT), several phthalates, and a trace compound from the injection port septum. No target compounds were detected in the GC/MS run and the concentrations of the minor contaminants were similar to those observed in the method blanks.

Figure 8 is the TIC from sample 102929. The total extract of this sample is unique because it contains an anomalously high level of one particular phthalate, bis (2-ethylhexyl) phthalate (a non-target analyte), with a concentration estimated at 4 μg/L. Phthalates are common plasticizers and routine artifacts in concentrated organic extracts but the level of this one particular phthalate in this sample was quite high. Bis (2-ethylhexyl) phthalate may have been in this water sample but it is very likely that this phthalate could have been introduced during the initial sampling or later on during sample handling and extraction.

Figure 9 is the TIC from sample 102917. The total extract of this sample contained a high concentration of elemental sulfur, along with lesser amounts of the S_6 and S_7 allotropes (these allotropes could have been formed in the injection port of the GC). Except for the typical phthalates and other low-level contaminants, no target compounds were identified in the analysis by GC/MS.

As mentioned above, none of the priority target compounds were detected (e.g., DEET (N,N-diethyl-3-methylbenzamide), tris (2-chloroethyl) phosphate, tris (1,3-dichloroisopropyl) phosphate, triphenyl phosphate, triclosan, and C_{27} and C_{29} fecal sterols). In addition to the above target compounds, the mass spectrometer was run in full-scan mode and a general survey was performed on each sample extract. Most water samples were quite clean and not significantly different from the method blanks.

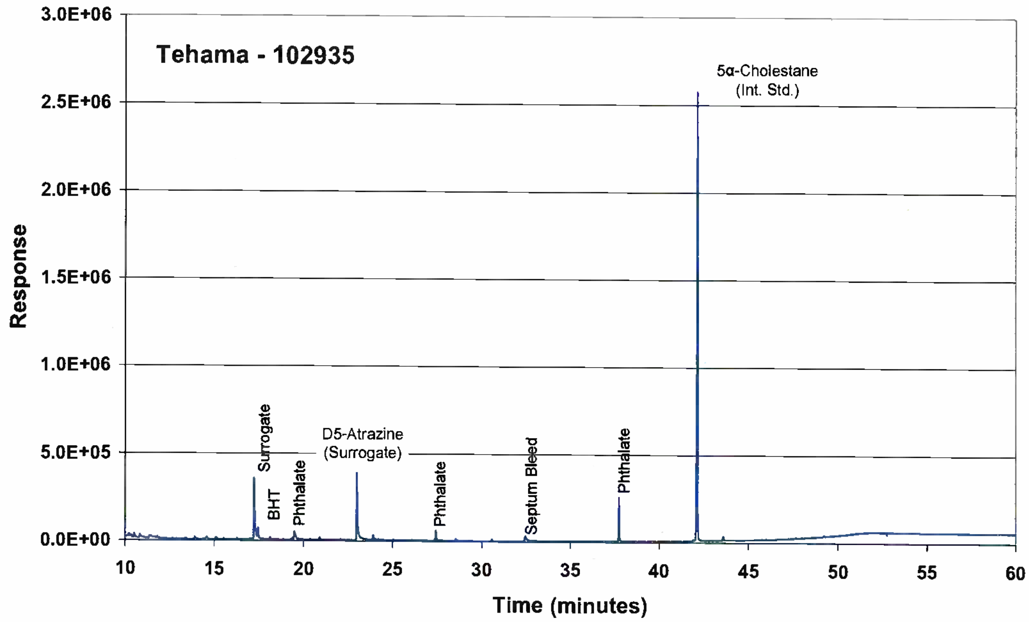


Figure 7. TIC of sample 102935. This GC/MS chromatogram is representative of the typical water extract from the Tehama study area.

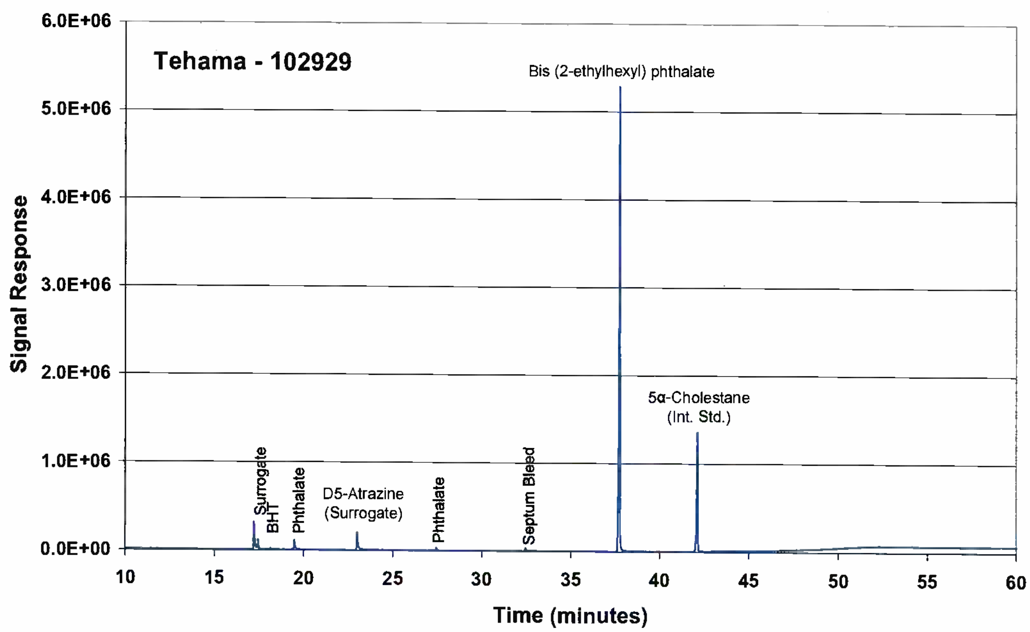


Figure 8. TIC of sample 102929, showing an unusually large amount of bis (2-ethylhexyl) phthalate.

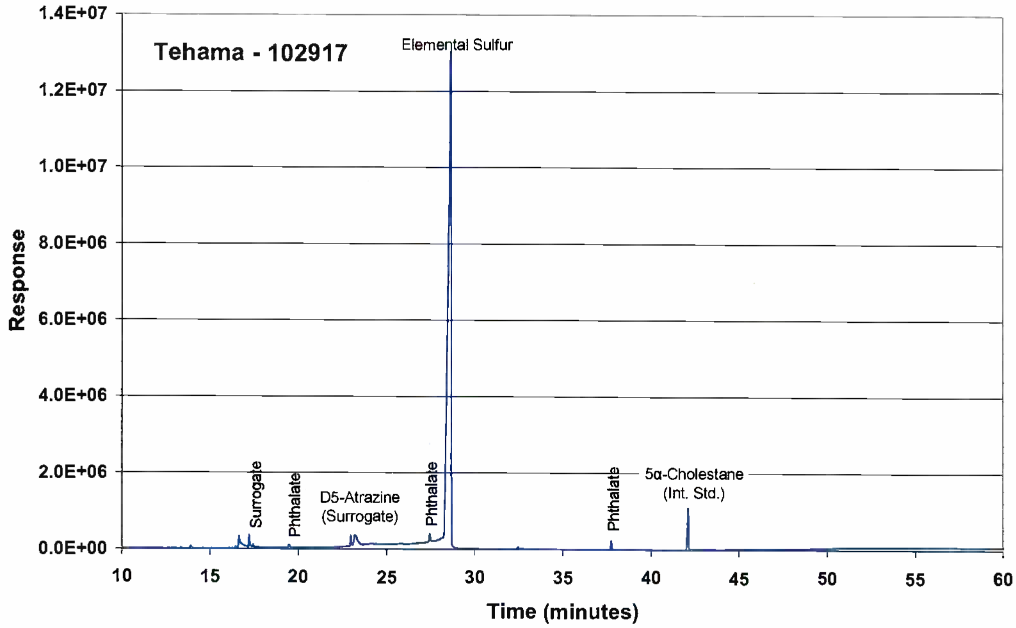


Figure 9. TIC of sample 102917. This sample had a high concentration of elemental sulfur.

RESULTS FOR GROUNDWATER AT CALIFORNIA DAIRIES

Thirteen monitoring wells from a Kings County dairy, 12 monitoring wells from a Merced County dairy and 2 monitoring wells from a Stanislaus County dairy were sampled for a large number of chemical and isotopic constituents, including trace organic compounds and low level VOCs (see Esser et al., 2006 for a complete description of analytes and results). The main goal of the sampling at dairy sites was to ascertain the fate and transport of nitrate (Esser et al., 2006). Trace organic compounds were analyzed in an effort to determine whether groundwater contains tracers of the various dairy operations. For example, one might expect C_{27} and C_{29} sterols to be useful as tracers of groundwater influenced by manure lagoon seepage or by irrigation return flow from fields fertilized by liquid or solid manure.

The Kings County dairy site was instrumented and studied extensively in the nitrate study (Esser et al., 2006). Overall, groundwater from the Kings County dairy is remarkably free of VOCs, considering that these are shallow wells in an area of significant human activity. Low-level MtBE is found at the highest concentration in the well nearest to an unlined irrigation canal (350 ng/L), and is almost certainly sourced from boating activity on the Kings River, which feeds the canal. Carbon disulfide is found frequently at diary wells, and likely has a natural source. It occurs in wells producing chemically reduced groundwater and not in wells with significant dissolved oxygen concentrations.

Nonylphenol was detected at several Kings County dairy monitoring wells, with the highest concentrations detected in temporary wells adjacent to manure lagoons that are sampled by bailing or using a low flow bladder pump. Lower concentrations were also found in shallow monitoring wells in dairy fields. In Merced County diary monitoring wells, NP was detected at a maximum concentration of 80 ng/L in wells adjacent to manure lagoons. NP was not detected in wells distant from manure lagoons at the Merced County site. At the Stanislaus county dairy, the well adjacent to the lagoon had a high concentration of NP (3000 ng/L), while the result for the well in the field was <30 ng/L. NP may therefore be an indicator of the influence of lagoon seepage in recently recharged groundwater. However, in dairy monitoring well samples, NP occurrence as a sampling artifact cannot be ruled out. The temporary wells adjacent to lagoons at the Kings County site are especially likely to produce compromised samples since they are ¾" piezometers with slots in the PVC over 2' intervals, and cannot be purged or sampled using a submersible pump.

Caffeine was detected in only three of 33 dairy monitoring wells in which it was analyzed. The three wells with detections are those adjacent to or downgradient from manure lagoons at the Kings County dairy site. (On a separate sampling occasion, the same wells were non-detect at <15 ng/L for caffeine.)

As mentioned above, the ratios of certain sterols can be useful in fingerprinting sources of fecal material. For example, C_{27}: coprostanol is a human fecal biomarker, and cholesterol, cholestanol, C_{29}: 24-ethylcoprostanol is an herbivore fecal biomarker. To calculate the proportion of human vs. herbivore fecal contribution, the most useful formula is the following: (coprostanol/(coprostanol + 24-ethylcoprostanol))x100. If this ratio is <30, then the observed sterols are likely 100% herbivore-derived, if it is >75, then they are likely 100% human-derived. The calculated ratio from the lagoon effluent at the Kings County Dairy is ~25, and therefore indicates an exclusively herbivore source, as expected. However, there were no detections of any of the sterol compounds at dairy site wells. Therefore, while the tracer is present in lagoon water, biodegradation of these compounds in the unsaturated zone makes detections in groundwater unlikely.

Of greater interest are the detections of pesticides and pesticide degradation products in dairy monitoring wells. At the Kings County dairy site, norflurazon and its degradation product, desmethylnorflurazon, were detected in a subset of the monitoring wells. Norflurazon was applied to a corn field in excess of the intended amount approximately two years prior to sampling. Figure 10 shows the locations of wells with detections of norflurazon and desmethylnorflurazon (2S and 3S), along with the approximate area where the over-application occurred. The 2S set of nested wells shows a pattern of decreasing concentrations of norflurazon with depth. In the same samples, the relative proportions of norflurazon:desmethylnorflurazon decrease from 1.6 to 0.6 to 0.4, suggesting that conversion to the degradation product takes place during transport in the saturated zone. Overall, significant removal of constituents presumed to be present in manure lagoon water (which is used for crop fertilization) seems to take place during recharge and transport to wells.

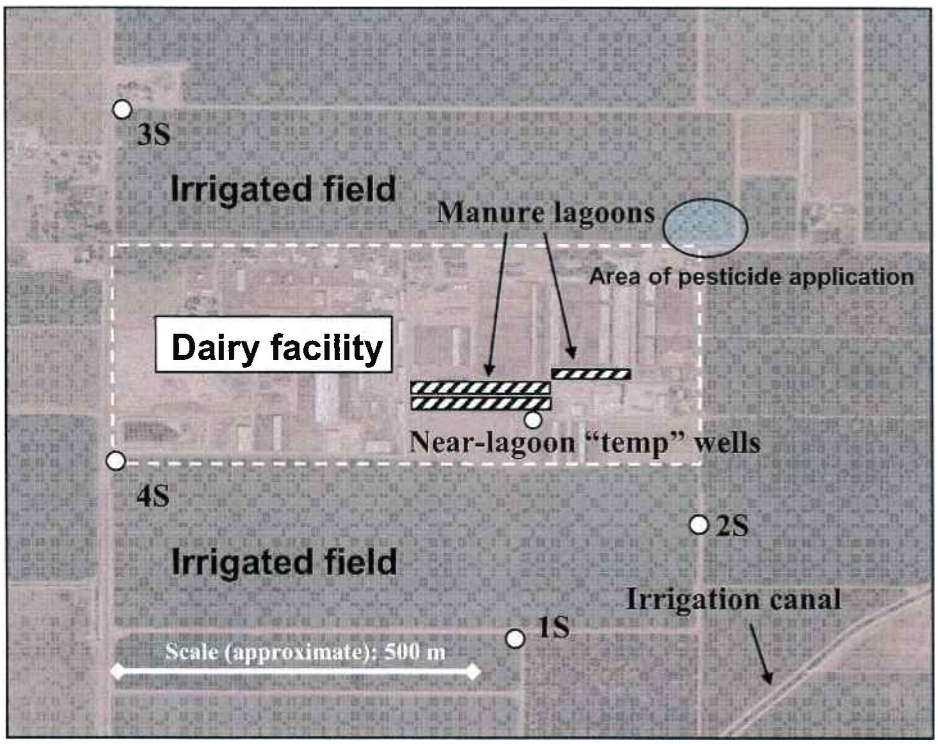


Figure 10. Location map for Kings County dairy site. Nonylphenol was detected at high concentrations in near-lagoon "temp" wells. Pesticides and degradates were found in 2S and 3S nested wells.

RESULTS FOR CHICO GROUNDWATER

Twenty three shallow monitoring wells and seven longer-screened drinking water wells in the Chico area were sampled for trace organics, as part of a larger study to determine the source(s) and fate of nitrate (Figure 11). High nitrate concentrations have been detected in the study area for the past two decades (http://www.buttecounty.net/cob/nitratefiles/execsum.htm; Butte County Environmental Health), and the monitoring wells were installed to monitor for nitrate. One potential major source of nitrate is discharge from septic systems, which serve as onsite wastewater treatment systems over a significant part of the study area. The other potential major source of nitrate is from fertilizer applied for agriculture over many preceding decades. Some target compounds are much more likely to come from septic system discharge than from agricultural irrigation return flow (caffeine, surfactant-derived compounds such as APECs and LAS, ibuprofen and other pharmaceuticals and estrogenic compounds), others are more likely to be present in irrigation return (herbicides and their breakdown products). Wastewater indicator compounds could thus potentially serve as a way to distinguish nitrate sources.

In all, 14 different target compounds were detected at 11 monitoring wells. Carbamazepine was detected at 4 wells, polycyclic musk compounds and flame retardants were detected at one, caffeine was detected at 2 wells, DEET and NP were detected at one well, and herbicides and their breakdown products were detected at 3 wells. Each of the detections is discussed below. Seven drinking water wells in Chico had no detections of any of the target analytes.

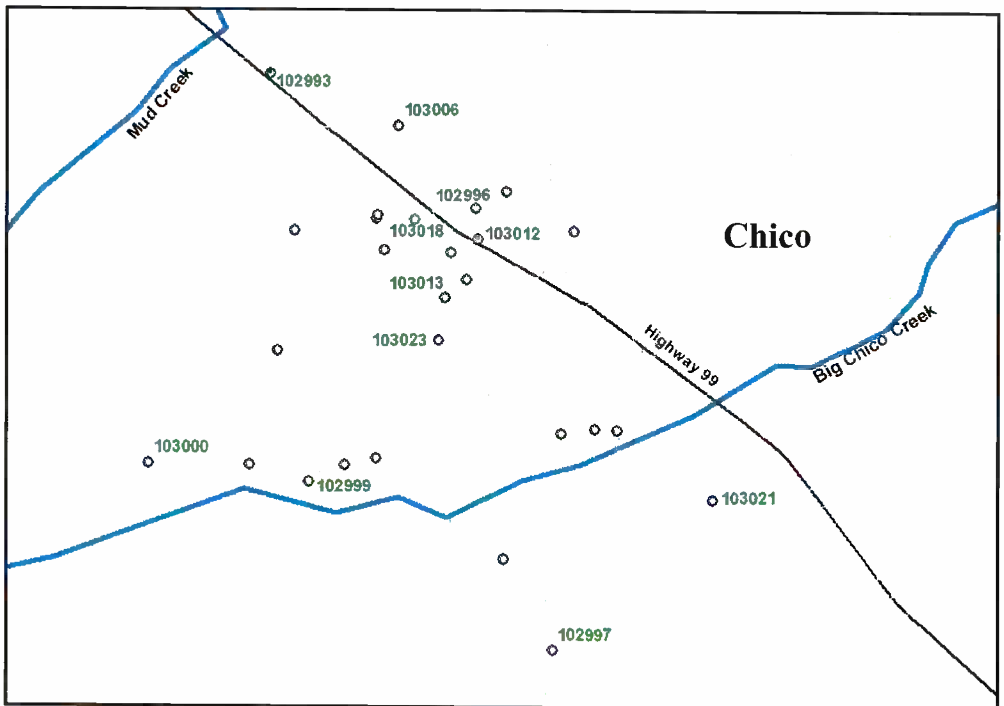


Figure 11. Map showing locations of private domestic wells sampled for wastewater indicator compounds. Numerical labels refer to samples discussed in the text.

Several GC/MS TICs for Chico are provided in Figures 12-15. A large number of chromatographically unresolved organic compounds are present in sample 102993. The GC/MS chromatogram of this sample is shown in Figure 12 and this chromatogram consists primarily of a large, smooth "hump" in the baseline with a few resolved peaks. This is known as an unresolved complex mixture (UCM) and is made up of hundreds of chromatographically unresolved compounds. Other than caffeine, detected at 30 ng/L by LC/MS/MS, no target compounds were detected and no additional non-target compounds could be identified in the chromatogram. The bulk of the organic compounds consist of polycyclic and polyalkylated hydrocarbons, perhaps with some oxygenated moieties, consistent with dissolved naturally-occurring organic matter or biologically reworked organic matter. Except for the two additional samples 103012 and 103013, both of which had evidence of trace amounts of a UCM, the remaining extracts possessed relatively flat baselines. In sample 103013, caffeine and NP were detected at 16 and 6 ng/L, respectively.

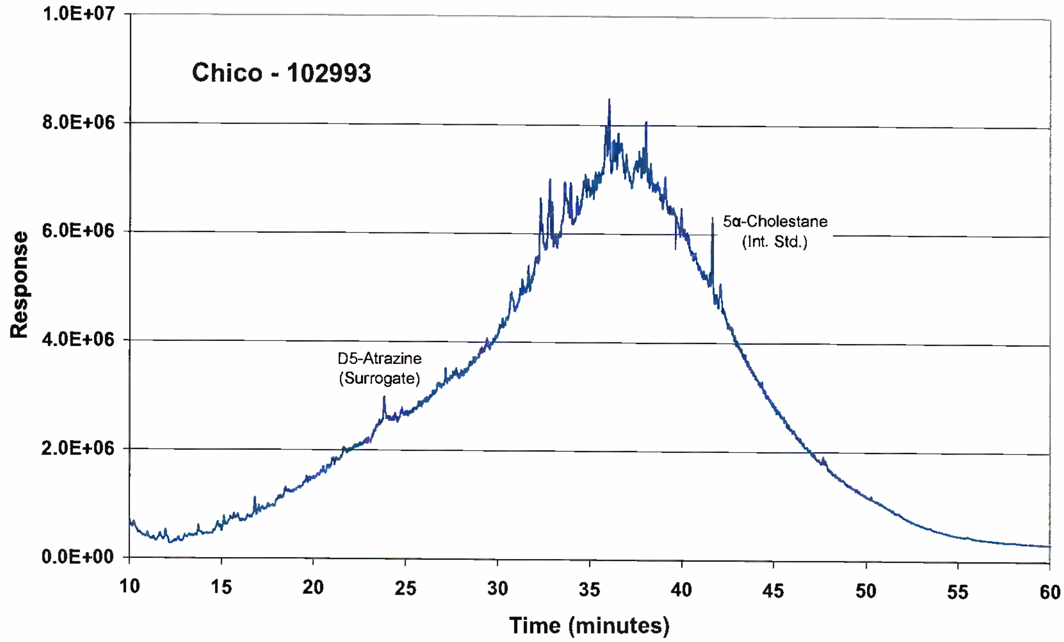


Figure 12. TIC of Chico sample 102993 showing the large amount of unresolved organic material present in this water sample. For scale, the internal standard in this sample represents 1 µg/L.

Three samples from the Chico study area contained low levels of herbicides or herbicide breakdown products. Two water samples contained triazine herbicides. Shown in Figure 13 is the TIC of sample 103000. This sample contained desisopropyl atrazine (25 ng/L) and a trace amount of simazine (6 ng/L) but no additional groundwater organic tracer compounds were found. Sample 102997 contained atrazine (33 ng/L) and desethylatrazine (12 ng/L). Except for the parent triazine herbicides and the breakdown products, the GC/MS TIC was clean and no additional compounds were found. Desmethylnorflurazon was present in sample 103006 at a concentration of 140 ng/L but the parent herbicide norflurazon was not detected. These three samples did not have detections of any of the wastewater indicator compounds, and are all located on the outer fringe of the study area, where irrigation return flow from agriculture is most likely to affect shallow groundwater.

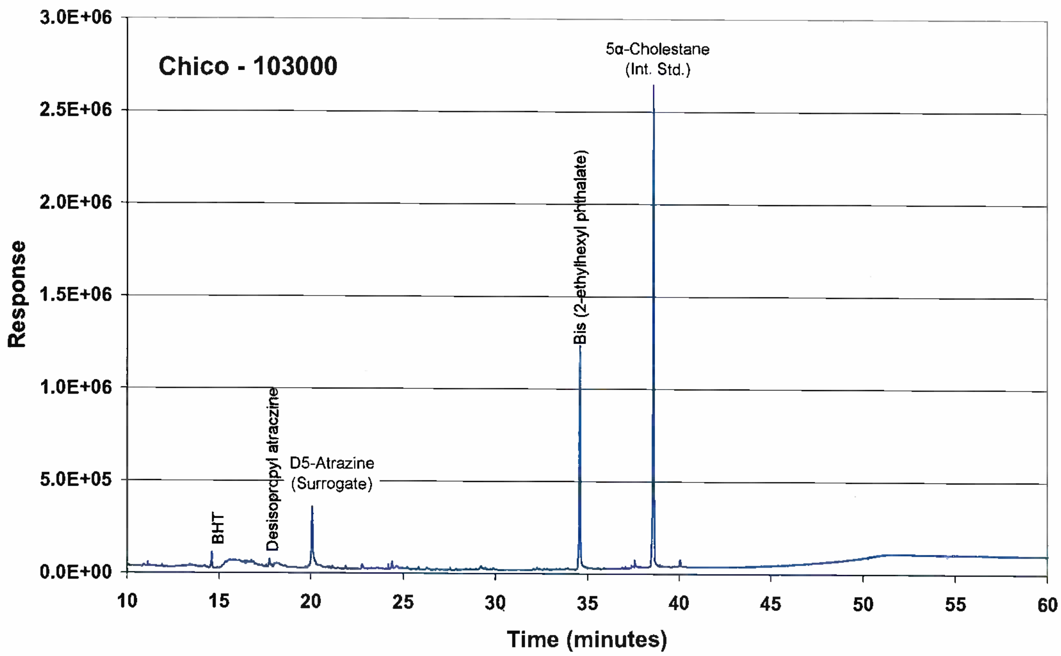


Figure 13. TIC of sample 103000, showing internal standard, surrogate compound, and desisopropyl atrazine (25 ng/L).

Two samples (102999 and 103023) contained the antiepileptic drug carbamazepine at levels > 100 ng/L. Carbamazepine is an anticonvulsant that has been used as a tracer of municipal wastewater effluent in both surface and ground waters (Clara et al., 2004). Recent studies suggest that it is one of the most refractory of the high-use pharmaceuticals, and is likely to persist in groundwater (e.g., Drewes et al., 2002, Fenz et al., 2005). It was also detected at lower levels in the GC/MS selected ion monitoring (SIM) analyses of samples 102996 and 103018 but definitive mass spectra in the full scan runs were not obtained. The presence of carbamazepine in these samples suggests that the shallow groundwater in the central part of the study area has a component of wastewater, perhaps from septic discharge, although a direct connection between septic systems and the wells with occurrences cannot be made with the data at hand. Both NP (110 ng/L) and DEET (16 ng/L) were detected in sample 103002

One of the GC/MS target compounds, tris (1,3-dichloroisopropyl) phosphate, was detected in sample 103021 at a concentration of 27 ng/L. This compound is a commonly used flame retardant chemical and typically found in effluent from waste water treatment plants. The concentration of this compound was determined in the SIM analysis but it is shown in Figure 14 as one of the minor peaks in the full-scan run. A definitive mass spectrum provided absolute compound verification. This water sample also contained the common UV absorbing sunscreen agents oxybenzone and parsol MCX (2-ethylhexyl cinnamate), the two most commonly found polycyclic musk compounds AHTN (tonalide) and HHCB (galaxolide), and the HHCB transformation product HHCB-lactone (galaxolidone). The total polycyclic musk concentration was estimated at 180 ng/L. The polycyclic musks are common fragrance compounds present in a wide variety of consumer personal care products. In this sample, the detections of sunscreen agents as well as the polycyclic musk compounds may be the result of contamination of the sample during sample collection. Numerous polycyclic musk fragrances have been found in wastewater effluents. Once discharged, these compounds can end up as trace contaminants in a variety of surface waters (Bester et al., 1998; Simonich et al., 2000; Osemwengie and Steinberg, 2001; Artola-Garicano et al., 2003; Buerge et al., 2003; Heberer, 2003; Ricking et al., 2003; Peck and Hornbuckle, 2004; Bester, 2005).

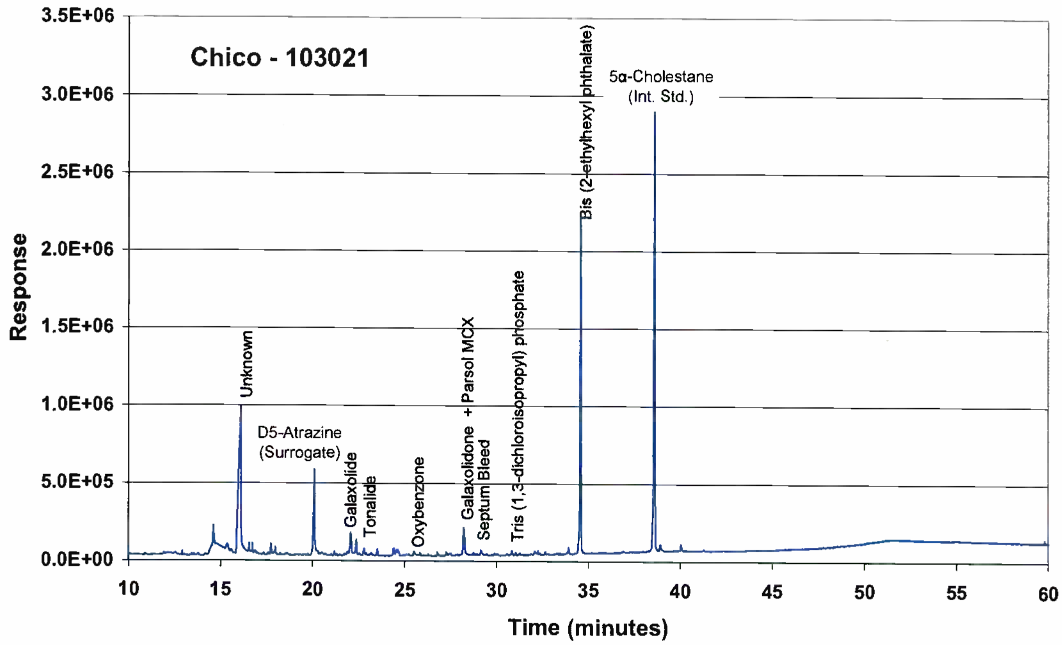


Figure 14. TIC of sample 103021, showing polycyclic musks, sunscreen compounds and tris (1,3-dichloroisopropyl) phosphate.

Figure 15 is the GC/MS chromatogram of the total extract for sample 103011 and is representative of the remaining samples from this study area, including the seven drinking water supply wells sampled. No target compounds were detected in the GC/MS SIM analysis and the extract was free of any GC/MS nontarget compounds. Peak labels identify the surrogate and internal standard and the typical minor contaminants, including butylated hydroxytoluene (BHT), several phthalates, and a trace compound from the injection port septum.

In summary, the small number of low-level detections of different trace organic compounds in shallow wells from the Chico area are difficult to interpret in connection with specific sources. The infrequent detections of carbamazepine, nonylphenol, and caffeine suggest that transport of wastewater, possibly from septic discharge, affects groundwater locally, at individual wells that sample recent recharge. (The monitoring wells included in this study are screened just below the water table and most have tritium-helium groundwater ages of less than 2 years.) The lack of detections in many of the shallow monitoring wells and in drinking water wells suggests that transport of wastewater indicator compounds is not widespread. Future work should include closer inspection of discharge and transport of wastewater indicator compounds from individual septic systems to potentially affected groundwater.

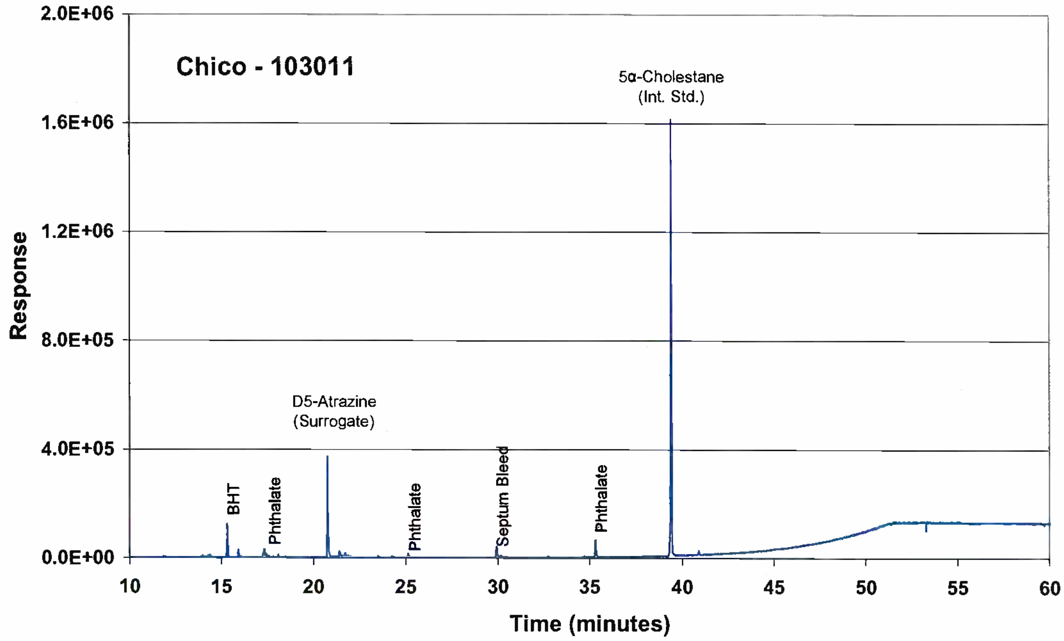


Figure 15. TIC of sample 103011. The GC/MS chromatogram is representative of the clean water extracts from the Chico study area.

RESULTS FOR GILROY GROUNDWATER

The South County Regional Wastewater Authority (SCRWA) operates a wastewater treatment, disposal, and water recycling facility for the cities of Morgan Hill and Gilroy. Biosolids are removed from the site and disposed of elsewhere, while secondary effluent is discharged to percolation over a 394-acre area around the facility. The capacity of both the wastewater treatment facility and the recycled water distribution system are presently being expanded to include a greater volume of water and areas of non-potable re-use. During the study period, the SCRWA distributed roughly 700 acre-ft of tertiary treated recycled water per year to three customers for non-potable uses, all irrigation. Two of the areas irrigated with treated wastewater, Christmas Hill Park and a farm, were sampled for this study. Treated wastewater has been used for irrigation at the farm site since 1999 and at the park since 2002. Groundwater occurs at depths of less than 20' below ground surface at both sites, and groundwater levels are influenced by rainfall, irrigation, and regional pumpage. Groundwater flow is in a south-southeast direction. Five wells in the farm location and three wells in Christmas Hill Park were sampled and analyzed for the full suite of trace organic compounds, along with general minerals, tracers of water (stable isotopes and groundwater age), and tracers of nitrate fate and transport (Figure 16).

Relatively high chloride, sulfate, and sodium concentrations are obvious indicators of the presence of recycled water. In general, total dissolved solids concentrations in groundwater from the study area exceed the concentrations observed in Llagas subbasin groundwater. Enrichment of salts in the vadose zone occurs during evapotranspiration, which is highest during periods of irrigation. Complex patterns of recharge from both irrigation return and precipitation that vary in time make interpretation of dissolved ion concentrations difficult. Therefore, salt concentrations are not reliable indicators of the presence or absence of a wastewater component and are even less reliable as tracers for quantifying the fraction of well water that originated as wastewater.

Tritium-helium groundwater ages in shallow wells are all 15 years or less, and the well showing the strongest influence of recycled water (MW-22 sample ID 103443), has a groundwater age of only 3 years, confirming a direct and fast connection between the well water and the recharge source (mainly applied irrigation water). Groundwater ages from wells in the immediate vicinity increase sharply as a function of depth to the top perforation (Table 4), and groundwater produced from a well with a top perforation at 100 ft. is tritium dead (indicating that it recharged more than about 50 years ago). A clay confining unit has been observed at a depth of approximately 100 ft in previous hydrogeologic characterization studies (DWR Bulletin 118).

Figure 16. Aerial photograph of Gilroy and surrounding area. The location of the SCRWA facilities is indicated with a red label; well locations are labeled with sample IDs discussed in the text.

$\delta^{18}O$ that is enriched by about +1 ‰ in wells affected by recycled water recharge compared to shallow wells upgradient of the area of recycled water application (Figure 17) is another way in which the recycled water stands out. This shift in $\delta^{18}O$ is also likely due to evaporation, either at the treatment plant or after water is applied to fields. Strongly enriched $\delta^{18}O$ and $\delta^{15}N$ of nitrate (Figure 18) are additional indicators of the influence of the recycled water on the produced groundwater. The trend in the observed shift, along a slope of roughly 0.5 on a plot of $\delta^{18}O$ versus $\delta^{15}N$, is characteristic of denitrification. A denitrification step was added to the SCRWA treatment process in 1995.

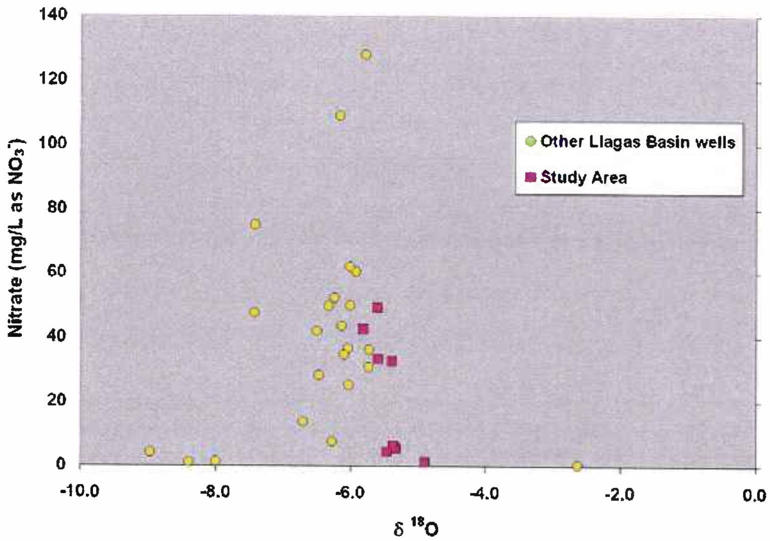


Figure 17. The ratio of nitrate versus stable isotope signatures of oxygen in wells from the region affected by wastewater irrigation (pink symbols) and in other shallow wells in the Llagas Basin (yellow symbols). Wastewater-influenced groundwater is shifted to more enriched isotopic values compared to ambient groundwater.

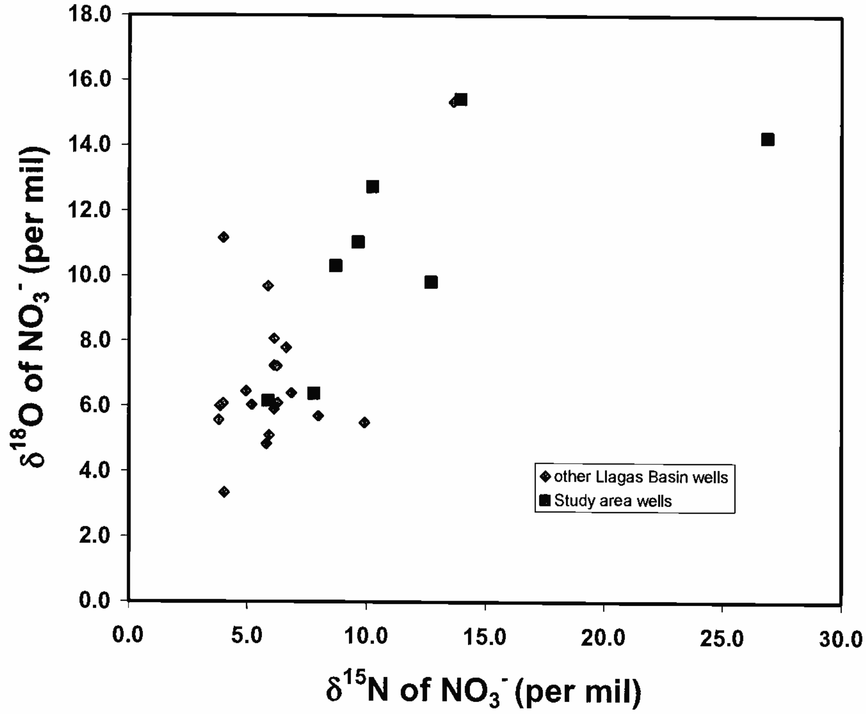


Figure 18. Nitrogen and oxygen isotope ratios in nitrate show a pattern characteristic of denitrification in samples influenced by recharge of wastewater.

Most significantly, the NP precursors NP1EC and NP2EC were detected in two shallow monitoring wells (labeled 103443 and 103442 in Figure 19 and Table 3). Samples acquired one year apart from the same wells showed similar results (Table 3). The relatively high concentration observed in 103443, a sample estimated to be nearly 100% wastewater-derived, suggests that these surfactant-derived metabolites are transported through the vadose and saturated zones. In addition, there were detections of the endocrine-disrupting compound nonylphenol at concentrations up to 225 ng/L. Low level detections of NP in these wells may or may not be sampling artifacts. Low-level NP was also detected in Christmas Hill Park wells, although none of the other target compounds were detected in that area.

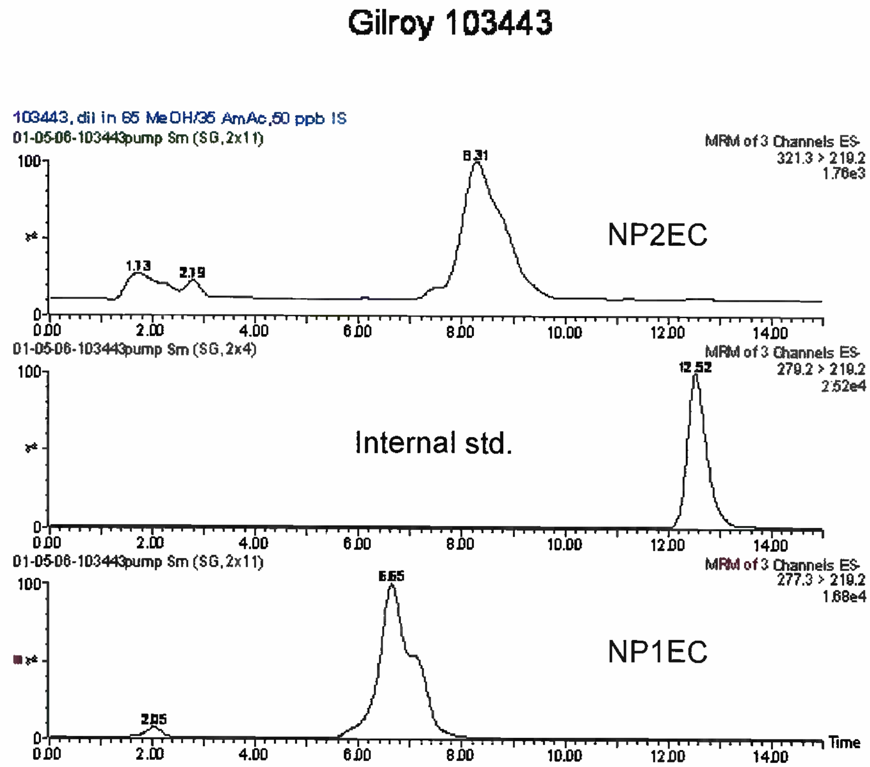


Figure 19. LC/MS/MS chromatogram of NP1EC (*m/z* 277→219) and NP2EC (*m/z* 321→219) in a Gilroy groundwater sample . The effective concentration of the internal standard (*m/z* 279→219) is 1 μg/L. The likely reason that the NP1EC and NP2EC peaks are broader than the internal standard peak (which is a labeled form of AP1EC) is that the former peaks represent mixtures of isomers whereas the internal standard peak represents a single compound only.

Figure 20 is the TIC from sample 103443. Two fatty acids (dodecanoic and tetradecanoic acid) were found and a moderate UCM was present, which made it difficult to obtain definitive mass spectra for some of the compounds. Carbamazepine was detected in the concentrated extract and primidone was tentatively identified. Both of these compounds are anticonvulsant pharmaceuticals that have been found to be nearly conservative ground water tracers (Drewes et al., 2002; 2003), and therefore useful for tracing sewer exfiltration (Stamatelatou et al., 2003; Clara et al., 2004; Heberer and Adam, 2004; Fenz et al., 2005; Hinkle et al., 2005). There is a consensus in these recent publications on the fate and transport of pharmaceuticals in the groundwater that these antiepileptics and perhaps some metabolites appear to be some of the best organic tracers of groundwater contamination from municipal wastewater. The compound diphenamid was also tentatively identified in the extract. Diphenamid is a common amide herbicide and the identification was based on the mass spectrum. Carbamazepine and primidone were also detected in samples 103442, and sample 103446 had only primidone above the reporting limit (Figure 21). For the remaining samples (103439-103441, 103444-103445) no target compounds were detected in the GC/MS SIM runs and no additional non-target compounds were detected in GC/MS full-scan runs. Caffeine was not detected (6 ng/L detection limit), suggesting a high removal rate in the soil or aquifer material. Likewise, many of the other target compounds, likely to be present in the irrigation water, were absent in groundwater samples.

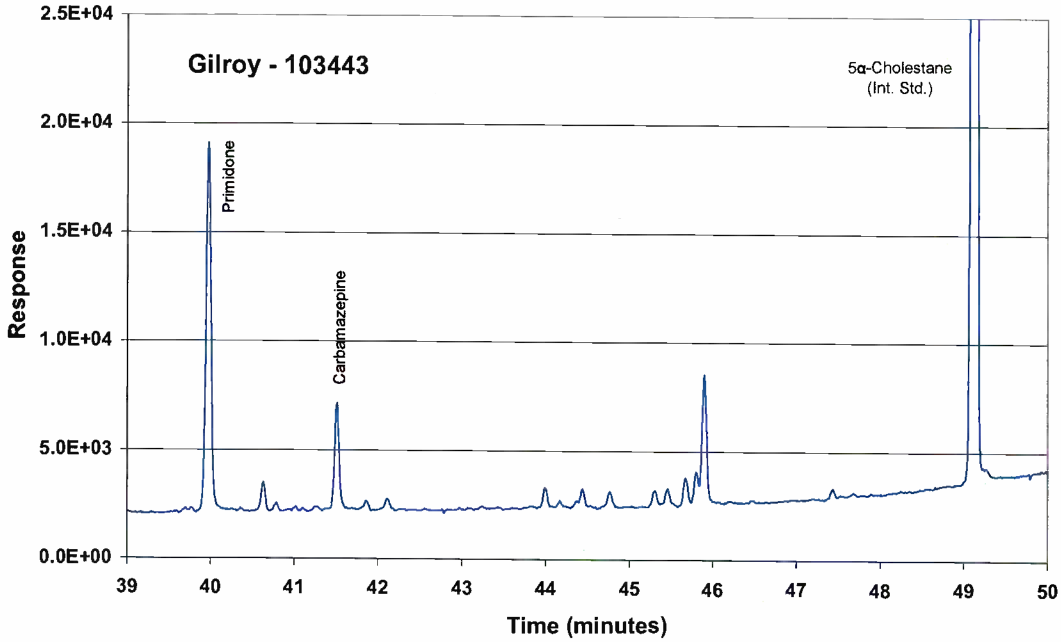


Figure 20. TIC of sample 103443, showing the anticonvulsants primidone and carbamazepine.

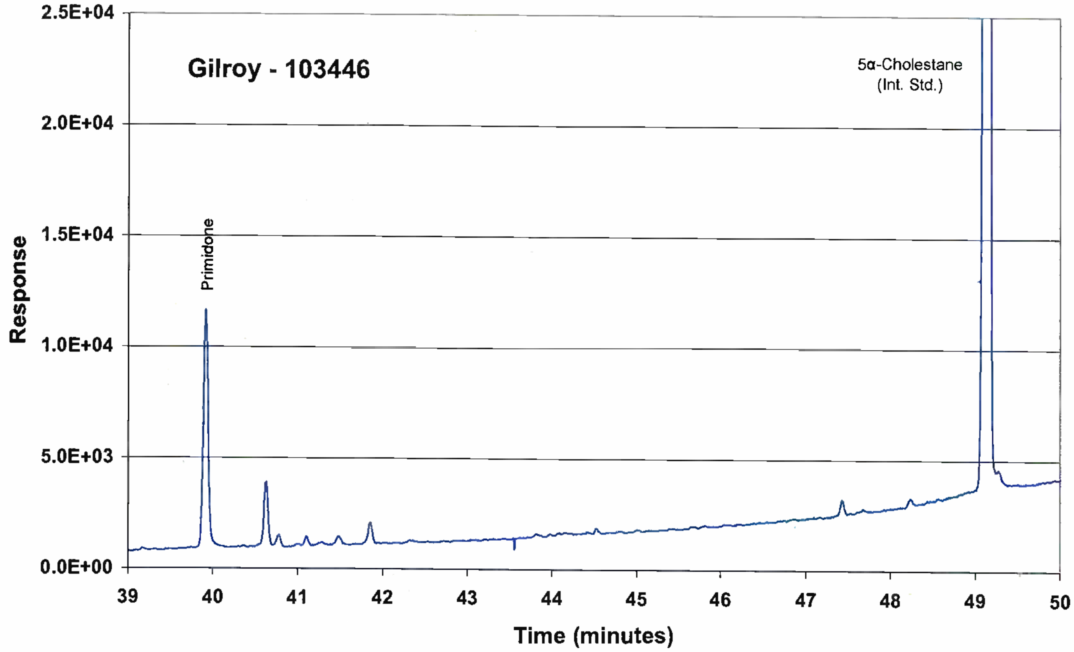


Figure 21. TIC of sample 103446, showing common plasticizer contaminants and primidone.

RESULTS FOR LIVERMORE GOLF COURSE GROUNDWATER

Livermore Water Reclamation Plant

Recycled water has been used at the Las Positas Golf Course (LPGC) in Livermore, California (Figure 22) since 1978 to provide turf irrigation for the golf course in what is a relatively arid climate. Average yearly precipitation at LPGC is approximately 15" per year and occurs primarily in the winter (Figure 23). Irrigation is necessary in the summer and approximately 36" per year of recycled water is required to maintain vegetation at the LPGC. Since 1978, irrigation of this area with treated wastewater has dominated the overall water budget.

LLNL has had regular, permitted releases of tritium to the LWRP, which have been carefully monitored by LLNL and by the LWRP. Since the release of radioactive materials into the environment is a source of community concern, LLNL developed detailed and aggressive environmental monitoring programs to monitor radioactive material releases. It is the combination of the tritium releases combined with detailed monitoring programs that makes the LPGC an interesting site to examine the fate and transport of wastewater indicators. It is appropriate to note that the release of trace amounts of tritium is not unique to LLNL. Many large cities have far larger annual tritium releases to their wastewater systems. Again, these other releases are carefully regulated, but do not receive the level of monitoring that LLNL has put in place.

In the mid 1970s, the city of Livermore began a program to recycle wastewater and use the water to irrigate the LPGC. A group of 10 monitoring wells were installed to evaluate wastewater impacts on the local groundwater. Additionally, these wells were regularly monitored for tritium (^{3}H). Overall volumes of irrigation water have been recorded along with total flows through the Livermore Water Reclamation Plant (LWRP). These data have been used to accurately calculate the ^{3}H concentration in the applied irrigation water as a function of time. This was accomplished by performing two carefully monitored tritium releases from LLNL and following the ^{3}H through the LWRP. Combining these data with ^{3}H-^{3}He groundwater age results, it was possible determine both the age and the degree of dilution from other water sources. This information was critical in the evaluation of observed concentrations of trace organic compounds from wastewater.

Figure 22. Aerial view of study site with monitoring well locations highlighted. Numbered sites refer to sample IDs discussed in the text.

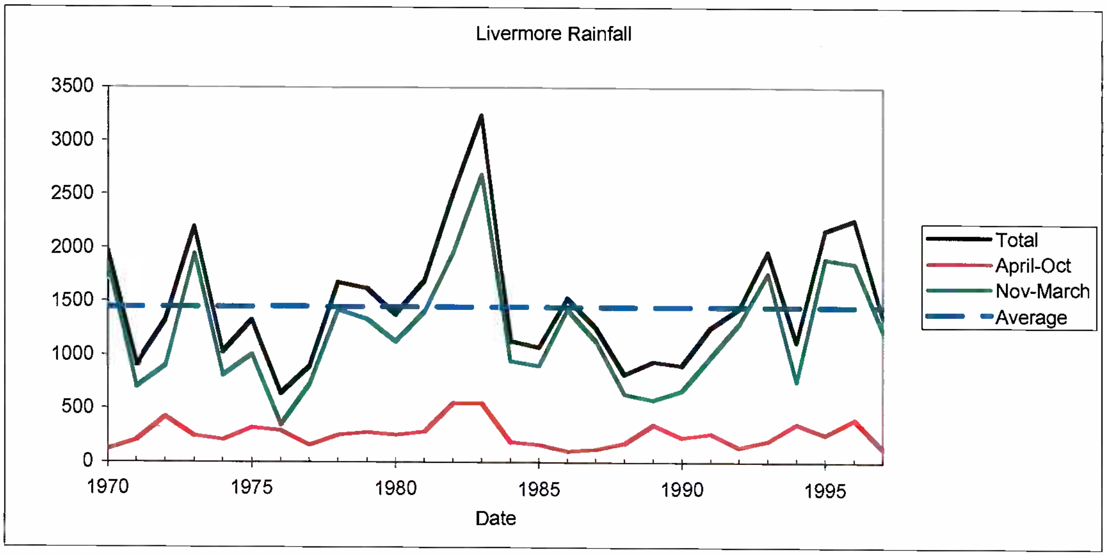


Figure 23. Rainfall trends for the study area since 1970.

The monitoring results show the clear connection between the application of recycled water and the local shallow groundwater (Figure 24). The overall trend in tritium releases from LLNL is decreasing. While the LLNL tritium releases have always been well below regulatory limits, the general goal of programs using tritium at LLNL has been to reduce releases as much as can be reasonably achieved. Figure 24 shows a close match between the monitoring wells and the recycled water. As will be discussed, the relationship between the tritium concentration observed in the monitoring wells and the irrigation water is relatively complex, nevertheless, the presence of the tritium tracer provides a clear indication of the connection.

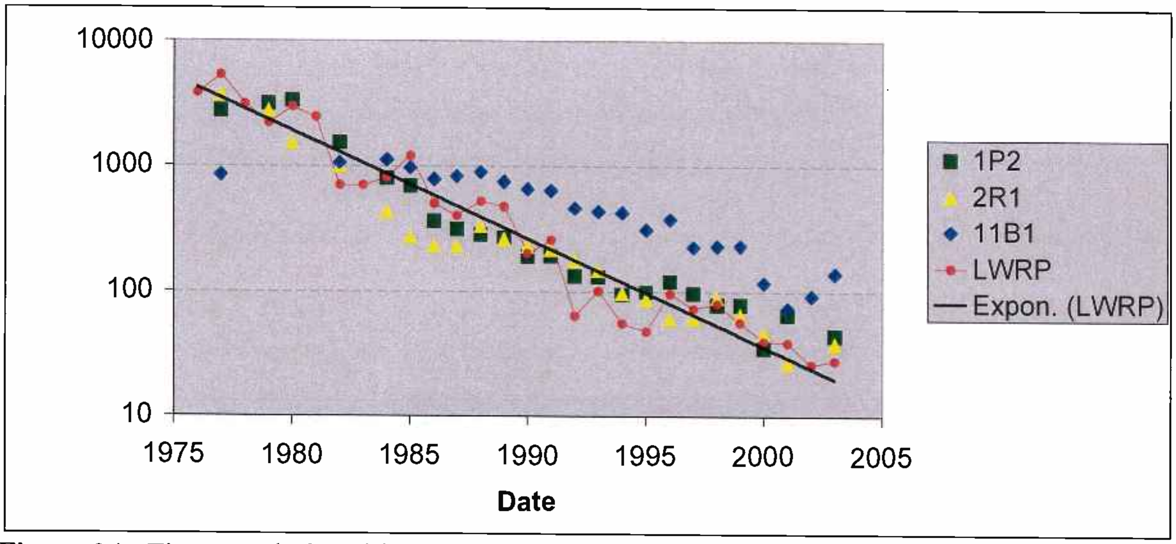


Figure 24. Time trends for tritium concentrations in LWRP effluent and selected monitoring wells.

Additional Isotopic Tracers of the Wastewater Component

Other isotopic tracers help to constrain the relationship between the sampled groundwater and its potential sources. The stable isotopes of H and O can potentially be used to identify contributions from local precipitation and wastewater from the LWRP. Most of the water used in the Livermore Valley comes from the State Water Project and consists of precipitation that fell in the Sierra Nevada at high altitude. This water is significantly depleted in the heavier stable isotopes of H and O when compared to local precipitation in the Livermore Valley. The ratio of oxygen isotopes in water ($\delta^{18}O$, expressed as ‰ deviation from standard mean ocean water) is about -7.5 for precipitation and -9.5 for wastewater from the LWRP. The data for O and H stable isotopes is shown in Figure 25. Evaporation of the applied irrigation water also produces shifts in the H and O isotopic compositions. The initial water compositions are connected by a line of slope 8, evaporation enriches both δ^2H and $\delta^{18}O$ along a line of slope 5. These data suggest that the samples represent a strongly evaporated mixture of wastewater and local precipitation. However, the uncertainties preclude an accurate determination of the mixing ratio of the two water sources.

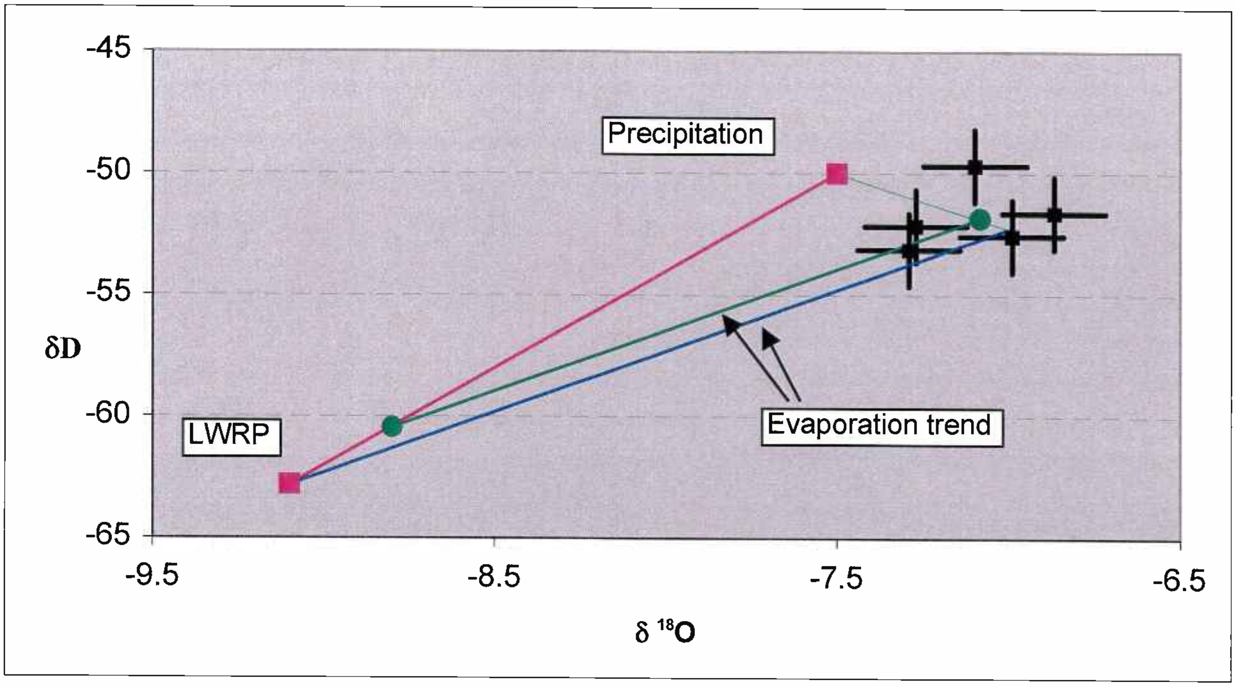


Figure 25. Isotopic signatures for LWRP effluent and LPGC groundwater samples.

The isotopic composition of N and O in the nitrate present in the groundwater samples also shows the contribution of a wastewater component. Denitrification occurring during treatment leads to the correlated enrichment of $\delta^{15}N$ and $\delta^{18}O$ in the remaining nitrate. All of the groundwater samples from the golf course area, but not from other areas in Livermore, show this effect (Figure 26).

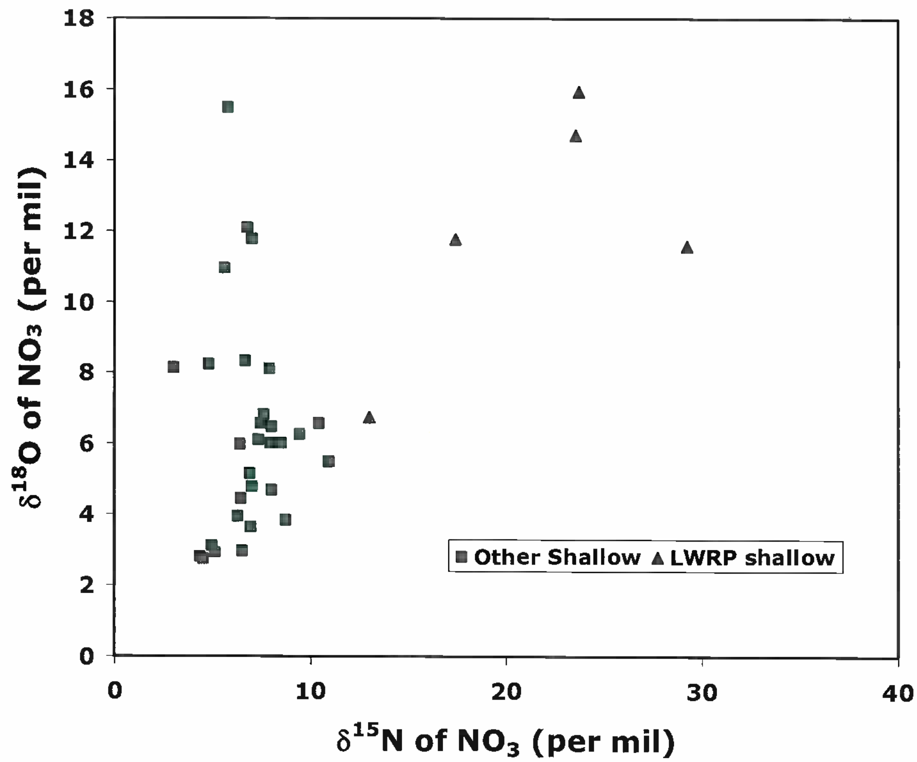


Figure 26. Shallow wells whose recharge source is treated wastewater from LWRP have isotopic signatures of nitrate that are distinct from other wells and indicate isotopic fractionation mediated by denitrification.

The ^3H concentrations measured in groundwater fall between the two sources (LWRP water and precipitation) and one can calculate that the fraction of the groundwater due to the LWRP contribution ranges from 27 to 67%, and is 50% for sample 2J2. The initial estimate of 36" of irrigation water versus 15" of precipitation is easily reconciled with this result when evaporation is taken into account. Irrigation water applied in the summer undergoes much greater evaporation than does winter precipitation. This model predicts significant enrichment in nonvolatile dissolved components such as chloride. The LWRP wastewater averages 161 mg/L of Cl^- over the period 1975 – 2000. The recovered groundwater samples show values greater than or equal to the LWRP value for Cl^- (>400 mg/L). Thus, even though precipitation accounts for about half of the water, evaporation of the LWRP source more than makes up for this dilution. In summary, the recovered groundwater samples for this study were derived from a mixture of wastewater and local precipitation that infiltrated from surface application between about 1980 and 1995. While local precipitation causes some dilution of the wastewater, evaporative enrichment has produced net enrichments of nonvolatile dissolved components such as Cl^-.

Results of Wastewater Indicator Analyses in LWRP Effluent and at LPGC Wells

One liter water samples were collected from two locations (E2R Outlet and UV Outlet) at the Livermore Water Reclamation Plant (LWRP). These samples were extracted using Waters Oasis HLB solid phase extraction cartridges and components eluted with 5 mL ethyl acetate. The eluents were adjusted to 1 mL and screened by GC/MS. LWRP effluent samples were also analyzed by LC/MS/MS using the procedures described previously.

In general, the findings for LWRP effluent are similar to findings (both the types of compounds and their concentrations) from previous studies of tertiary treated wastewater (e.g., Johnson and Sumpter, 2001). For example, caffeine was detected at approximately 1 μg/L, NP concentrations were 2 to 4 μg/L, AP1EC and AP2EC were detected at approximately 20 μg/L and 60 μg/L, respectively. Estrone 3-sulfate, estrone, and 17β-estradiol were not detected in LWRP effluent, despite detection limits in the low ng/L range. Removal of these compounds during advanced treatment is likely.

TICs were obtained for each sample. There was no significant difference in compositions or concentrations of the two extracts from the E2R and UV Outlet. Figure 27 shows the TIC of the E2R Outlet with some of the major compounds labeled. These compounds were identified using a combination of authentic standards, published mass spectra (e.g., Bester et al., 1997; 1998), and best mass spectra fits to mass spectra library databases (e.g., NBS Mass Spectra Library). Prominent unidentified compounds are labeled with key ion fragments. Full-scale response represents approximately 10 μg/L of analyte.

In addition to compounds detected by LC/MS/MS, other compounds of interest shown on the TIC are the following: benzothiazole and 2-(methylthio)-benzothiazole (Bester et al., 1997), N,N-diethyl-3-methylbenzamide (DEET, insect repellent); at least two polycyclic musk fragrances HHCB and AHTN (Bester et al., 1998); the alkyl- and aryl-phosphate fire retardants (tris (2-chloroethyl) phosphate, tris (1,3-dichloroisopropyl) phosphate and triphenyl phosphate), which have been shown to have low removal rates in simulated waste treatment processes (Westerhoff et al., 2005); and pharmaceuticals such as diphenylhydramine (antihistamine, diphenylhydramine hydrochloride is the active ingredient in Benadryl), gemfibrozil (lipid regulating agent) and carbamazepine (anti-seizure medication). [Note: No. 28 refers to cluster of five compounds with similar mass spectra (common ion fragments of m/z 107, 135, 165 and 193) and which are presumed to be structurally-related isomers.]

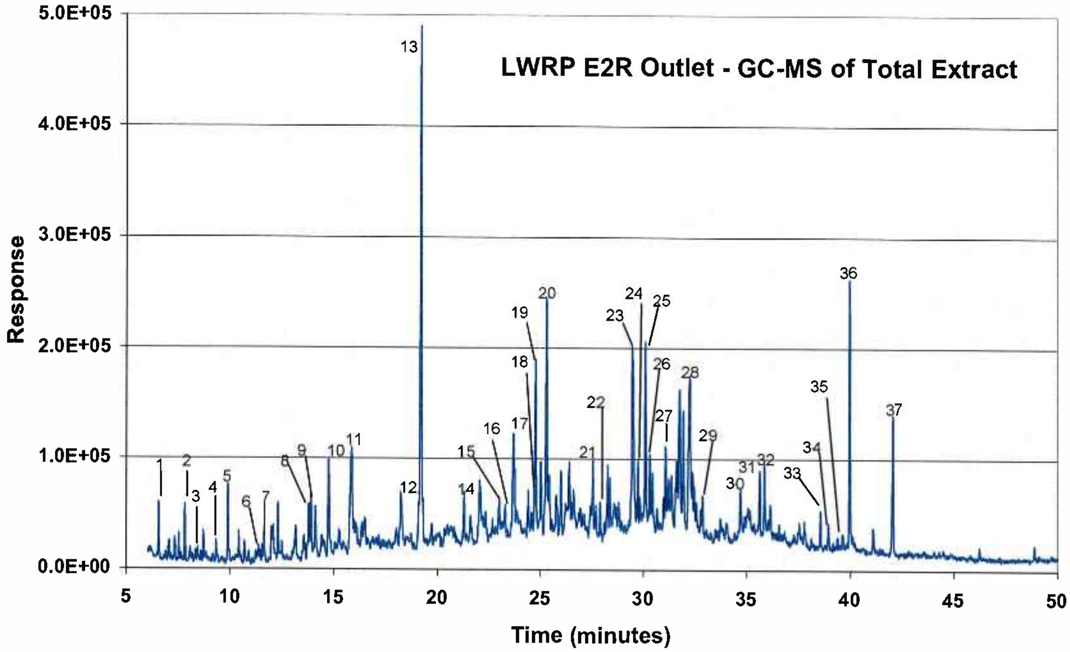


Figure 27. GC/MS TIC of total extract from E2R Outlet, Livermore Water Reclamation Plant with major peaks identified.

1. Benzaldehyde
2. Dichlorobenzene
3. 3,3,5-Trimethylcyclohexane
4. Acetophenone
5. Tetramethylpyrazine
6. Camphene hydrate
7. 2-(1,1-Dimethylethyl)-cyclohexanol
8. Benzothiazole
9. 4-(1,1-Dimethylethyl)-cyclohexanone
10. (68,80,83,107,109,135)
11. Dimethylphenol
12. 57,82,85,125
13. 57,69,109,151,169
14. 77,79,107
15. N-Cyclohexyl-2-pyrrolidone
16. N,N-Diethyl-3-methylbenzamide (DEET)
17. 2-(Methylthio)-benzothiazole
18. Benzophenone
19. 109,151,213
20. 91,119,157,191
21. Tris (2-chloroethyl) phosphate
22. N-Butylbenzenesulfonamide
23. HHCB
24. AHTN
25. 89,109,151
26. Diphenylhydramine
27. Gemfibrozil
28. 107,135,165,193
29. Elemental sulfur
30. 58,91,119,134
31. 145,173
32. 58,257,272
33. Tris (1,3-dichloroisopropyl) phosphate
34. Carbamazepine
35. Triphenyl phosphate
36. Tris (2-butoxyethyl) phosphate
37. Bis (2-ethylhexyl) phthalate

Wells from the Livermore golf course were sampled by pumping and bailing. Teflon-lined pump tubing, and Teflon bailers were employed. Only two wells had detections of target compounds (well 2J2 with sample ID 103560, and well 1P2 sample ID 103559). After two rounds of sampling in which NP detections were determined to be sampling artifacts, subsequent samples collected with Teflon-lined pump tubing showed no detections of NP with a reporting limit of 10 ng/L. Most significantly, NP1EC and NP2EC were detected at concentrations of 130 ng/L and 18 ng/L, respectively, in well 2J2 (103560; Figure 28). Well 1P2 (103559) had a very low-level detection of NP1EC (4.5 ng/L). Compared to concentrations determined in LWRP water, these concentrations are more than 100-fold lower.

Livermore 103560

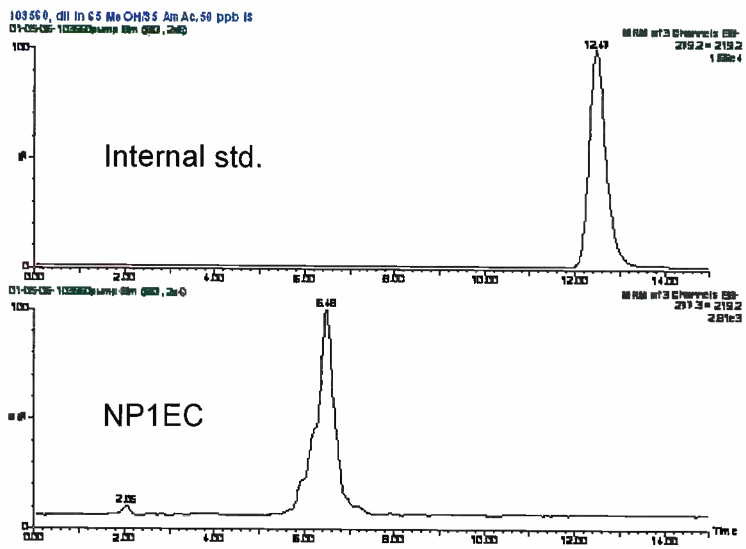


Figure 28. LC/MS/MS chromatogram of AP1EC (*m/z* 277→219) in a Livermore golf course groundwater sample. The effective concentration of the internal standard (*m/z* 279→219) is 1 µg/L.

Both pumped and bailed samples had low concentrations of herbicides but significant differences were observed between the pumped and bailed samples for both of these wells. Additional compounds, both target and non-target compounds, were detected in the bailed samples but these compounds are interpreted as contaminants introduced during the bailing process. Figure 29 shows the GC/MS TIC of sample 103559 (well 1P2). Three herbicides (simazine, oxadiazon and norflurazon) were detected in both the pumped and bailed samples. No additional target compounds were detected but a moderate amount of chromatographically unresolved compounds was present.

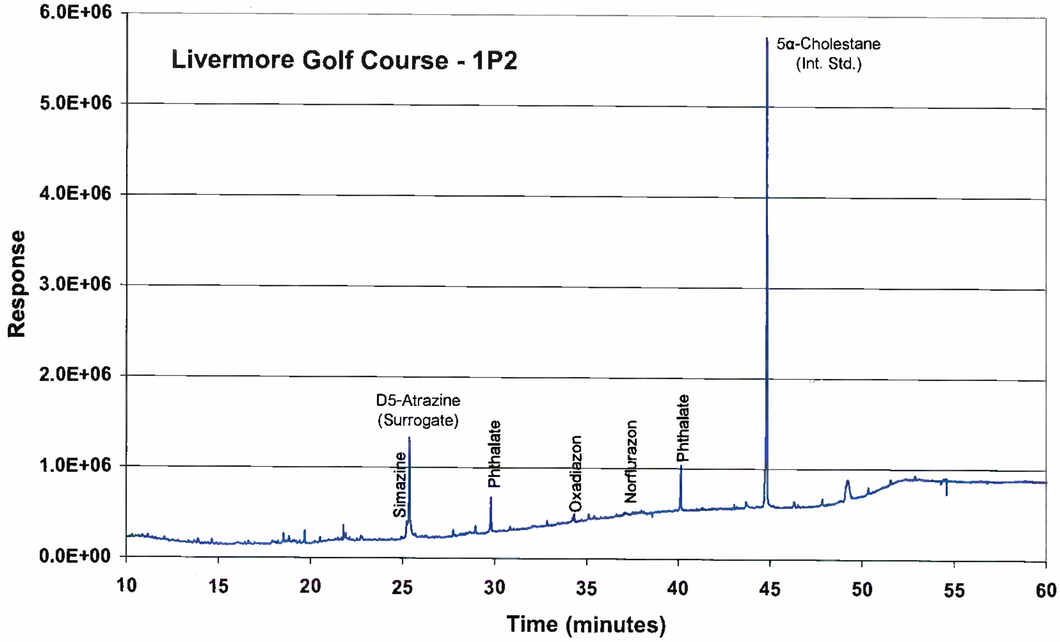


Figure 29. The GC/MS TIC of well 1P2 (sample 103559).

Figure 30 shows the GC/MS TIC of sample 103560 (well 2J2). Only one herbicide (simazine) and the triazine herbicide breakdown product desethylatrazine were detected in the pumped and bailed water samples. The source of the triazine herbicides in these samples is likely application of these compounds in the vicinity of the wells, as the compounds detected are in widespread use for pest and weed control. The herbicide compounds were not detected in full scans of the wastewater effluent. A trace amount of benzothiazole was also detected in both the pumped and bailed samples. Benzothiazole and structurally-related compounds have been identified as a relevant class of chemicals that survive municipal wastewater treatment and may be useful as organic tracers of municipal wastewater (Bester et al., 1997; Kloepfer et al., 2005). Numerous additional compounds were present in the bailed sample, including several fatty acids, fatty acid methyl esters, N-butylbenzene sulfonamide, and triallyl isocyanurate, a crosslinking agent. The bailed water sample also had a higher than normal amount of bis (2-ethylhexyl) phthalate and a high level of the herbicide oryzalin. The additional compounds found in the bailed sample are interpreted as sampling artifacts. The bailed water sample also had a higher amount of chromatographically unresolved compounds that resulted in an increase in the baseline signal during the GC/MS sample run.

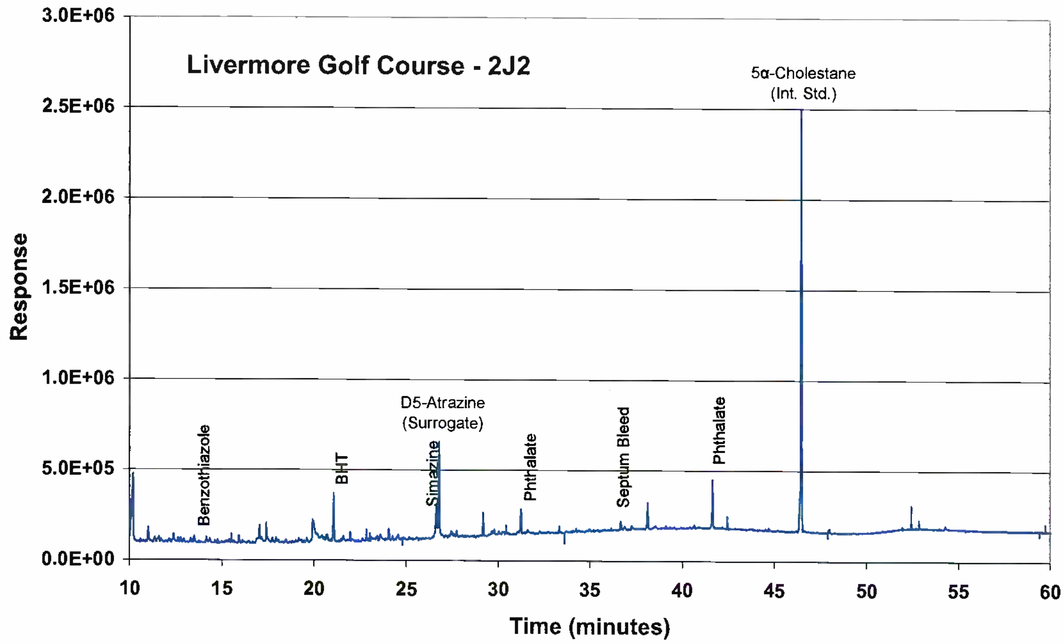


Figure 30. The GC/MS TIC of sample 103560 (Well 2J2).

COMPARING RESULTS FROM TWO AREAS OF RECYCLED WATER APPLICATION

Similarities between the Livermore and Gilroy sites include the relatively long time period that recycled water has been applied (10 to 25 years), the wastewater treatment methods (both the LWRP and SCRWA underwent upgrades that included enhanced treatment with a denitrification step), and the amount of water applied per acre per year (about 3 ft). The semi-arid climate of both settings leads to high evapotranspiration, and opportunity for volatilization of some organic compounds, during the time that recycled water is applied.

In both areas of recycled water application, groundwater quality is characterized by high chloride, sulfate, and sodium concentrations compared to ambient groundwater. Somewhat higher TOC concentrations and lower nitrate concentrations than ambient groundwater are also characteristic of groundwater with a significant wastewater component. With respect to isotopic abundances, stable isotopes of the water molecule are enriched due to evaporation in both locations. In Gilroy, $\delta^{18}O$ values of wastewater-influenced groundwater are about -5.0‰, compared to about -6.0‰ for other local groundwater sources (Figure 17), whereas in Livermore a similar shift of about 1‰ in oxygen isotope ratios is observed. Significantly, stable isotopes of nitrate show a large shift to values lighter than those recorded in ambient groundwater (Figures 18 and 26). Compared to other tracers of wastewater influence on groundwater, the shift in N and O isotopes of nitrate is robust and sensitive (i.e., a large signal relative to analytical uncertainty). The observed isotopic fractionation is due to denitrification, most of which likely occurs during wastewater treatment. Small amounts of dissolved excess nitrogen, equivalent to up to 12.5 mg/L as NO_3^- were observed in wastewater-influenced groundwater, indicating that a small amount of saturated zone denitrification takes place at both sites. Groundwater age in water showing a wastewater component ranges from 2 to 24 years; ages on the young end are prevalent in Gilroy.

In spite of the high fraction of wastewater recharge produced at monitoring wells, as evidenced by multiple geochemical and isotopic indicators described above, occurrence of trace organic compounds that originate in wastewater is quite limited at both sites (Table 4). Sampling and analytical reliability is extremely well controlled at these sites – samples were collected with Teflon bailers and Teflon-lined pump tubing (decontaminated between wells), multiple sampling, trip, and analytical blanks were examined, and sampling and analysis was repeated using the same techniques in 2003 and 2005. Results from the two sampling campaigns are nearly identical. Reliable, reproducible detections above 50 ng/L of the two NPEC compounds were found in two wells (2J2 at Las Positas golf course in Livermore and MW22 in Gilroy). The concentrations observed were 130 and 840 ng/L, respectively. Other geochemical and isotopic indicators of wastewater influence are readily observable at these two wells. Lower level detections of NPEC compounds occurred in one additional well in Livermore and two additional wells in Gilroy. Very low-level detections (<50 ng/L) of nonylphenol occurred in all of the Gilroy wells that showed evidence of wastewater recharge, but nonylphenol was not detected above the reporting limit in Livermore. Carbamazepine and primadone were detected in Gilroy in the same two wells that had detections of NPECs, and primadone was detected in one additional well in Gilroy.

Table 4. Key parameters for comparing results from the Livermore study area (shaded) and the Gilroy study area (unshaded). Wells in bold text are those most strongly influenced by a wastewater signature. (Fraction recycled water is calculated using the observed tritium concentration and a hydrologic model as described in the text for Livermore. For Gilroy wells, the recycled water fraction was determined via mixing ratios that are based on approximations for major ion concentrations in irrigation water and ambient groundwater end members.)

Location	Well	Depth to top perf (ftbgs)	GW age (yrs)	Fraction Recycled H_2O (%)	Target compounds detected (ng/L)
LPGC	**2J2**	**31**	**19**	**36-49**	**NPECs, herbicides, benzothiazole**
LPGC offiste	**1P2**	**40**	**5**	**50-67**	**NPECs, herbicides**
LPGC	2Q1	35	24	27-29	none
LPGC	2R1	21	7	39-48	none
LPGC	11C3	55	14	67	none
Gilroy farm	**MW-22**	**10**	**3**	**~75**	**NPECs, carbamazepine primadone**
Gilroy farm	**MW-24**	**20**	**15**	**~40**	**NPECs, carbamazepine primadone**
Gilroy farm offsite	Bloom-1	48	2	~30	primadone
Gilroy farm	MW-21	100	>50	0	none
Gilroy park	Bolsa-2	70	27	~10	none
Gilroy park	CH-1&2	29	<1	NC	none

Given that these compounds are present in typical municipal tertiary treated wastewater effluent at concentrations in the low μg/L range, their presence at the low concentrations observed (or, more frequently, their complete absence) in groundwater indicates substantial removal during recharge. Overall, concentrations of NP, NP1EC, NP2EC, and caffeine were from ~130- to 360-fold lower in LPGC groundwater than in irrigation water (i.e., LWRP effluent). Since hydrological modeling indicates that irrigation water was diluted only 33 to 73% with local precipitation in the aquifer, attenuation of these compounds during transport through the vadose zone and saturated zone (e.g., by sorption for the NPECs and NP, and by biodegradation for caffeine) must have been quite substantial. The detections of carbamazepine and primadone differ in that the concentrations typically observed in tertiary treated wastewater are of the same order of magnitude as the maximum concentrations observed in the groundwater samples, suggesting a low rate of removal during recharge and transport.

The occurrence of NPECs in groundwater from the two areas directly influenced by wastewater recharge sets those areas apart from ambient groundwater. Although groundwater from the two areas of wastewater recharge has distinctive major ion chemistry and isotopic signatures, with the exception of NPECs, it does not differ significantly from ambient groundwater with respect to occurrence of wastewater indicator compounds.

Findings on the fate of pharmaceuticals and PCPs from riverbank infiltration sites (Vogel et al., 2005, Schmidt et al., 2003), and from the well-studied Sweetwater soil-aquifer treatment site in Arizona (Fox et al., 2001, Drewes et al., 2002) indicate that significant attenuation and/or removal occurs for most compounds analyzed. Compared to those studies, the Livermore and Gilroy sites offer evidence for even more attenuation and/or removal. For example, the Schmidt et al. (2003) study shows that organophosphate esters persist in groundwater some distance from the recharge zone, while these compounds were not found in Livermore or Gilroy groundwater. Certain characteristics of the two sites likely contribute to the even greater attenuation rate observed in Livermore and Gilroy:

- In riverbank filtration sites, as well as at the Sweetwater SAT site, transport is predominantly by saturated flow, whereas the Livermore and Gilroy sites have well-established vadose zones. Vadose zone transport is likely important for removal of a number of compounds by biodegradation and sorption.
- Groundwater is initially oxygenated at the Livermore and Gilroy sites, but conditions become anaerobic at a shallow depth in the saturated zone, which likely promotes degradation of, e.g., sulfamethoxazole and other pharmaceuticals (Jekels and Gruenheid, 2005).
- Compared to the riverbank infiltration and Sweetwater sites, the groundwater examined in Livermore and Gilroy has had a longer residence time in the subsurface. Mean groundwater ages point to residence times of 2 to 27 years, while subsurface residence times at the riverbank infiltration and Sweetwater sites are measured in weeks to months. A longer subsurface residence time offers more opportunity for both degradation and for mixing with other water sources, including water that recharged at much earlier times.

This last factor may be the controlling one for the observed differences *between* the Livermore and Gilroy sites. For example, the pharmaceuticals that were observed in Gilroy (carbamazepine and primadone) may have been attenuated during the longer residence time for Livermore groundwater. Detecting even the most refractory compounds becomes quite unlikely at longer residence times and with greater dilution by ambient groundwater.

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James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT “H”

Brian Pacheco
20019 W. Belmont Avenue
Kerman, CA 93630

April 23, 2015

To Whom It May Concern:

I am writing this letter as a character reference for Jim Sweeney.

I am a 47 year-old dairyman and have known Jim for most of my life. I first became acquainted with Jim when I was a member of the Future Farmers of America. The Kerman FFA Chapter did not have a dairy cattle judging team and my instructor contacted another chapter and found out that Jim was coaching their team. At the time, Jim was the manager of a dairy in Fresno County and graciously let me participate with the other team.

Through hard work and perseverance, Jim has accomplished the American dream. He has worked his way up from a laborer to manager, to now a small business owner.

A short time ago, a mutual friend of ours committed suicide. I was asked to help run the family dairy until it could be sold. I immediately contacted Jim and asked for his help. Again, he generously accepted and helped me during this difficult time.

Jim Sweeney has an excellent reputation in the dairy industry. He is a man of integrity and is well respected among his peers. He is an honest, hardworking individual who will go the extra mile for those in need. I am glad to know Jim Sweeney and proud to call him my friend.

Sincerely,

Brian Pacheco

James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT "I"

OLD WEST RANCH COMPANY
Business Consulting – Receivership Support Services
4539 North Brawley Avenue, Ste 105
Fresno, California 93722
Tel (559) 275-9482 – Fax (559) 275-8786

April 24, 2015

Mr. Karl E. Longley
CVRWQCB
1685 E. Street
Fresno, CA 93706

RE: <u>Jim and Amelia Sweeney</u>

Dear Mr. Longley:

My name is John Van Curen. I am the President and owner of Old West Ranch Company, a company specializing in insolvency proceedings, both in State and federal courts in California. For over 30 years, I personally have served as a court-appointed Receiver in numerous state and federal court proceedings and as a Chapter 11 trustee in several federal court bankruptcy proceedings. My receivership work primarily involves agricultural enterprises, including numerous dairies in the Central Valley of California.

I have known Jim Sweeney as a friend and business associate for over 20 years.

My continuing business association with Mr. Sweeney involves utilizing his expertise as a dairyman and judgment as a businessman in analyzing and evaluating distressed dairy operations in fulfillment of my duties as a Receiver. In the many years that I have been involved with him, I have found Jim to be a man of unassailable character and integrity, who provides expert and honest evaluations and opinions that I can rely upon in the fulfillment of my duties.

During the time I have known Jim, he and his wife Amelia have owned and operated a 300 cow dairy near Visalia, California and raised a family of three children, all of whom have either completed or are pursuing college educations including in some cases post-graduate studies. Anyone who is acquainted with the family will observe that Jim and Amelia live by the highest principles and have inculcated those values into the lives of their children.

In conclusion, I unreservedly vouch for Jim's honesty and integrity and believe that whatever actions he takes in life will be guided by those principles.

Sincerely yours,

John Van Curen

John Van Curen

James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT "J"

University *of* California
Agriculture and Natural Resources

Cooperative Extension
Tulare County
UC
CE

4437B S Laspina St • Tulare CA 93274
Office (559) 684-3300 • (559) 685-3319
Website http://cetulare.ucanr.edu

April 29, 2015

To Whom It May Concern:

My name is Jim Sullins. I am the Director of Tulare/Kings County Cooperative Extension, University of California, Ag and Natural Resources.

I have known Jim Sweeney in a professional capacity for the last 15 years. I have visited Mr. Sweeney's operation with Regional Water Quality board member Soppy Tomkins and also attended meetings at his request with Regional Water Quality Executive Officer Pamela Creedon and staff member, Clay Rodgers at their office in Fresno.

Mr. Sweeney has attempted to resolve water quality permit issues with the Regional Quality Board with success and to my knowledge has been very professional and ethical in all of his actions.

Sincerely,

Jim Sullins
County Director
Tulare/Kings

James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

EXHIBIT "K"

April 10, 2015

Model for sustainability

If a country had among the Earth's highest output per acre for its food and feed crops and among the lowest input of pesticide and fertilizer per acre, would we say that country has a highly sustainable food production system?

Yes, we'd nearly all agree on that.

So which of these countries currently holds that status — New Zealand, Switzerland, Ireland, Brazil, or China? None of these hold that status. It is the United States of America.

In its most recent report, the World Bank shows that the U.S. ranked 63rd on amount of fertilizer applied per acre of arable land among all nations. The U.S. applied an average of 117 pounds per acre (131 kilograms per hectare) of total fertilizer per acre of arable land annually from 2010 to 2014. Meanwhile, the top 10 countries averaged 2,015 pounds per acre (2,300 kg/hectare) — about 18 times more than the amount applied by U.S. farmers. This data is available at http://data.worldbank.org/indicator/AG.CON.FERT.ZS/countries.

When it comes to application of pesticide, the U.S. ranked low as well. A 2012 report showed that the U.S. ranked 44th in pesticide use among 119 countries. The U.S. applied an average of 1.5 pounds of active ingredient per acre (1.7 kg/hectare) compared to 53 pounds per acre (63 kg/hectare) for the highest country. There were 13 European countries that used more per acre than the U.S. Among the world's highest income countries, 25 of 38 used more pesticide per acre than U.S. farmers. Pesticide use per acre continues to decline as American farmers adopt precision agriculture technologies. These data points are available at: Food Policy 37 (2012), pages 616 to 626.

Want to feed the world's growing population with sustainable food production? Look at farmers in the U.S. for the model of how to do this. They practice sustainability every day.

NORTH CAROLINA JACK BRITT

These columns are open to the readers of *Hoard's Dairyman* for the expression of their opinions on current issues of direct interest to dairy farmers. With the exception of letters promoting religious creeds, proprietary products, farm organizations, or political groups, the editors welcome readers' views on all subjects. Letters should be 250 words or less. The right is reserved to select and abstract letters to be published. Unsigned letters will not be printed, but names will be withheld on request. You may send letters to Hoard's Dairyman, P.O. Box 801, Fort Atkinson, WI 53538 or you may email them to editors@hoards.com.

James G. Sweeney and Amelia M. Sweeney
Submission of Evidence and Policy Statement Regarding Hearing
on Administrative Civil Liability Complaint R5-2015-506

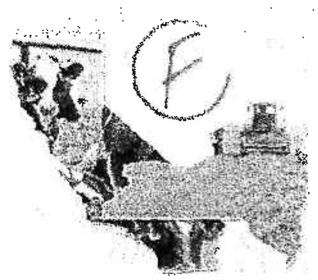
EXHIBIT "L"

HOARD'S DAIRYMAN

HOARD'S DAIRYMAN

Two major dairy states aren't ag friendly

By Corey Geiger, Managing Editor



When Colorado State University professors Greg Perry and James Pritchett set out to create the first-ever Agribusiness Friendliness Index, they didn't know how each of the nation's 50 states would eventually shake out on the list. However, in reviewing the final product, their first-ever ranking has two of our nation's top three dairy states ranked second from the bottom and dead last.

At number 49 on the Agribusiness Friendliness Index is the nation's third-largest dairy state, New York. The only state ranking lower was the nation's largest milk producer, California. Both states received a letter grade of F for working with agriculture. The only other top 10 dairy state to rank that low was New Mexico, coming in at 46 on the list.

In creating the ranking, the Colorado State University ag economists set out to mirror the popular State Business Tax Climate Index. In doing so, Perry and Pritchett included 38 variables representing regulatory and tax policy, government efficiency, impact of key government services and the overall business climate in each state.

"The Agribusiness Friendliness Index illustrates the different ways government influences the economic climate of agriculture and its allied businesses," said Perry.

Pritchett added, "Businesses are acutely aware of the role that state government plays in their success — a business friendly environment will encourage these enterprises to locate or expand operations while unfriendly policies shrink business and may even cause relocation."

How did other top 10 dairy states fare? The highest ranked was Wisconsin at No. 16. It was closely followed by Washington, Texas, Idaho, Minnesota, Michigan and Pennsylvania — each falling between No. 18 and No. 26, respectively.

For more details go to: www.news.colostate.edu/Release/7194

To comment, email your remarks to intel@hoards.com.

Subject=(Intel comment)

May 27, 2014

MEETING

STATE OF CALIFORNIA

CENTRAL VALLEY REGIONAL WATER QUALITY CONTROL BOARD

PARTIAL TRANSCRIPT

AGENDA ITEM NO. 8

CENTRAL VALLEY REGIONAL

WATER QUALITY CONTROL BOARD

11020 SUN CENTER DRIVE, SUITE 200

RANCHO CORDOVA, CALIFORNIA

June 4, 2015, 9:00 a.m.

Reported by:
Central Valley Water Board

Item 8. James G. and Amelia M. Sweeney, Sweeney Dairy, Tulare County - Consideration of Administrative Civil Liability Order

record of the Regional Board. We are going to be able to have transcripts produced by the court reporter based on the audio and video recordings. Kiran Lanfranchi-Rizzardi will provide any parties wishing to have a transcript of this proceeding with the contact information for the court reporter service that will do the transcribing.

Because we don't have a court reporter here today, I ask that all parties in attendance speak very distinctly into the microphones and announce who they are before they speak.

CHAIRMAN LONGLEY: We'll have to undoubtedly be interrupting folks asking them to identify themselves just so that it's clear on the record. And for the purposes of that, this is Karl Longley, member of the Board who is speaking.

So we're going to move now to Agenda Item 8. This is the time and place for public hearing to consider an Administrative Civil Liability Order issued by the Executive Officer to Sweeney Dairy in Tulare County.

Is there anyone present who is contesting the proposed actions and wishes to present evidence or testimony on this matter? Please stand if so.

P R O C E E D I N G S

June 4, 2015 2:42 P.M.

Item 8. James G. and Amelia M. Sweeney, Sweeney Dairy, Tulare County - Consideration of Administrative Civil Liability Order.

CHAIRMAN LONGLEY: Before we proceed I'm going to ask counsel to describe the situation we find ourselves without a court reporter once again for those who might not have been here previously.

COUNSEL: Okay. So there's a couple issues.

First, the Regional Water Board did meet in Closed Session and adopted a resolution authorizing the Executive Officer to sign a Settlement Agreement engaged with litigation mentioned in our agenda under litigation filed against the Central Valley Water Board, No. G, Administrative Civil Liability Order issued for storm water violations at Rocklin Crossings. That was the matter in Closed Session.

As for this afternoon, we do not have a court reporter here today. However, this Board meeting is being audio recorded and video recorded. The audio and video recordings of the Board meeting will be construed as the official

(Swearing in)

Do you swear the testimony you are about to give is the truth? If so, answer "I do."

Thank you.

Since there are persons wishing to contest this item we will proceed with the hearing.

The designated parties for this proceeding are as follows: the Board's Prosecution Team and Sweeney Dairy. All other persons are considered interested persons.

The Prosecution Team has a combined total of 30 minutes for direct testimony, cross examination, and a closing statement. Sweeney Dairy shall have a total of 30 minutes for the same. Interested persons should limit their comments to three minutes.

Pursuant to Government Code Section 11126(c)(3), please note that the Board may meet in closed session to deliberate on a decision to be reached based upon evidence introduced in the hearing.

At this time, evidence should be introduced on whether Sweeney Dairy should be assessed an Administrative Civil Liability Order in the amount of any liability.

The order of this hearing is as follows. First, testimony and cross examination of the Prosecution Team. Secondly, testimony and cross examination of Sweeney Dairy. Third, comments by interested persons. Finally, closing statement by Sweeney Dairy, followed by a closing statement by the Prosecution Team.

As has been emphasized before, please state your name, address, affiliation, and whether you have taken the oath before testifying. If you have not submitted a speaker card yet, now is the time to submit one to Ms. Lanfranchi-Rizzardi.

Does Regional Board Advisory Team Counsel have any legal issues to discuss at this time?

COUNSEL: Not at this time.

CHAIRMAN LONGLEY: Thank you.

Are there any procedural issues that the designated parties would like to raise?

Seeing none. Hearing none, we will proceed with the Prosecution Team's testimony.

MR. ESSARY: Good morning, Mr. Chairman and members of the Board. My name is Dale Essary. I am a Senior Engineer for the Dairy Compliance Unit in the Fresno Office, and I have taken the oath.

I am presenting for the Board's consideration today the recommended Administrative Civil Liability against James Sweeney and Amelia Sweeney for failure to comply with the Dairy General Order.

Throughout this presentation, we will refer to James and Amelia Sweeney collectively as the Discharger.

I will provide an overview of the penalty alleged by the Prosecution Team. Naomi Kaplowitz, Staff Counsel with the State Water Board Office of Enforcement, will provide the Prosecution Team's rebuttal to the Discharger's legal arguments.

FEMALE VOICE: Dale, since we are recording could you just say "next slide" every time you proceed.

MR. ESSARY: I will.

Next slide, please.

The Dairy General Order was adopted in May of 2007, following extensive interaction with the Dairy industry and other interested stakeholders. Care was taken during the preparation of the General Order to ensure that dairies would be protective of water quality and would have a cost-effective monitoring program to verify compliance.

The Board adopted the Reissued Dairy General Order in October of 2013, which replaces the 2007 General Order and accompanying this monitoring program.

Under the Dairy General Order, Annual Reports are due the first day of July of each year for activities conducted during the previous calendar year. Annual Reports are critical to confirm that monitoring has been conducted and that the Dairy is operated in compliance with the General Order.

Unlike other types of technical reports, monitoring data must be collected in a timely manner and cannot be recreated after the fact.

Next slide.

The Discharger owns and operates Sweeney Dairy located east and hydrologically upgradient of the City of Visalia in Tulare County. The facility is in an area with naturally occurring good groundwater quality at shallow depths.

A Report of Waste Discharge was received from the Discharger in October of 2005 and coverage under the Dairy General Order began in June of 2007 with the maximum allowable herd size of 334 mature cows.

Next slide.

I will now provide an overview of the Dischargers violation as alleged by the Prosecution Team. The Complaint alleges one violation, that the Discharger failed to submit the 2013 Annual Report.

On August 29 of 2014, Central Valley Water Board staff issued a Notice of Violation that urged the Discharger to submit the delinquent report as soon as possible to minimize the potential liability. To date the 2013 Annual Report has not been submitted for the facility.

On December 5 of 2014, Central Valley Water Board staff issued a pre-filing settlement letter notifying the Discharger that the Board was in the process of assessing Civil Liability for this alleged violation. The pre-filing letter included a calculation of the maximum penalty and a recommended penalty amount, and provided the Discharger with an opportunity to meet with the Central Valley Water Board staff to discuss the alleged violation.

On 26 February of 2015, the Prosecution Team retracted the pre-filing letter by issuing a letter to counsel for the Discharger. The

Retraction was based on a mistake of fact regarding the application of the Enforcement Policy factors.

Next slide.

The Prosecution Team issued an Administrative Civil Liability Complaint to the Discharger on March 11 of 2015 in the amount of $34,650 for failure to submit the 2013 Annual Report. The Complaint included a waiver form that provided the Discharger with an option to waive their right to a 90-day hearing and enter into settlement discussions with the Prosecution Team. The Discharger declined to submit the waiver.

Next slide.

The Monitoring and Reporting Program was issued under authority of the California Water Code, which allows the Central Valley Water Board to require the submission of technical reports including annual monitoring reports. Any person failing to furnish such a technical report may be civilly liable for a maximum amount of $1,000 for each day of violation. This would result in a maximum penalty of $157,000 in this case, based on using the pre-filing settlement letter issued to the Discharger on 5 December, 2014 as an end date.

This slide summarizes the scores developed using the State Water Board Enforcement Policy for the violation alleged in the Complaint.

Following the State Water Board Enforcement Policy, an initial per day liability factor of .35 was calculated based on the potential for harm and the deviation from requirements for non-discharge violations.

The potential for harm was determined to be minor because failing to submit the report hinders the Board's ability to detect and address noncompliance.

The deviation from requirements was deemed to be major because the requirement to submit an Annual Report has been rendered ineffective. The lack of information makes it impossible to determine the amount of nutrients applied to and removed from drop land, information that is necessary for the Board's efforts to prevent water quality degradation and implement the regulatory protective measures detailed in the Dairy General Order.

The penalty calculation methodology provides a process that reduces the number of days by using a multiple day approach for certain violations that occurred over an extended period of time.

Culpability was assessed a factor of 1.5 because the Discharger knowingly and willingly failed to submit the 2013 Annual Report. The Discharger has already been through enforcement actions for failure to file Annual Reports and therefore knows this requirement. The factor of 1.5 is appropriate where the Discharger's conduct amounts to intentional or negligent behavior falling well below what a reasonable and prudent person would have done in similar circumstances.

The Discharger was assessed a score of 1.5 for cleanup and cooperation because they did not cooperate with the Water Board to come back into compliance despite being sent notices for the need to do so.

The Discharger was assessed a score of 2 for history of violations because the Central Valley Water Board has adopted several Civil Liability Orders in the past. Details of these Orders will be provided later in this presentation by Ms. Kaplowitz.

Next slide.

In addition to the factors outlined in the preceding slide, under the Enforcement Policy this violation is eligible for a reduction in the number of days of violation because the Discharger's failure to submit an Annual Report results in no economic benefit that can be measured on a daily basis. The proposed liability amount has been adjusted by reducing the number of days of violation to 22 days, resulting in what the Prosecution Team believes is an appropriate penalty.

Regional Board staff believe that the Discharger has the ability to pay the total amount of liability because the Discharger owns the dairy property and thus has a significant asset and continues to operate a dairy business. The Discharger has not submitted any information for the record that demonstrates an inability to pay the proposed liability amount.

Board staff have also considered the economic benefit of noncompliance.

Next slide. I'm sorry, same slide.

Regional Board staff believe the proposed liability amount of $34,650 is appropriate.

Next slide.

BOARD MEMBER COSTANTINO: Dale, this is

Jon Constantino.

MR. ESSARY: Yes.

BOARD MEMBER COSTANTINO: You mention -- can you go back to the slide? You mentioned -- yeah, Slide 8. You mentioned the collapsed days, that the days were collapsed?

MR. ESSARY: Yes.

BOARD MEMBER COSTANTINO: And you believe that was valid. Can you provide any explanations to why, or what the rationale is for that, just so I have it?

MS. KAPLOWITZ: Can I ask for clarification? This is Naomi Kaplowitz, Counsel for the Prosecution Team, and I was just wondering if you could clarify the reason for collapsing at all or the reason for collapsing to 22.

What was your question?

BOARD MEMBER COSTANTINO: Either. Both, actually. Yeah, both. Thank you for clarifying my question. And I don't want to prejudice the answer; I just want to know the reason, not whether I'm for or against it, just why.

MR. RODGERS: Hi, this is Clay Rodgers, Assistant Executive Officer for the Fresno office.

Actually, we went through the Enforcement

Policy. If we had collapsed the days to the maximum amount allowed by the Enforcement Policy, We would have been at 11 days.

We actually felt that in this circumstance it should not be collapsed the maximum amount; therefore, we kept it at -- we put it at 22 days because we felt that this was an appropriate penalty based upon all of the conditions that we had had and built up over the past few years of getting where we are between culpability, all of those natures. The attempt to come back into compliance with the General Order.

The Orders have been petitioned, but we do -- you know, there was no stay issued by the State Board or anything during that time that said that he did not have an obligation to comply with the Order.

And we also -- the penalty needs to be enough to deter a similar type of activity. So it really was that deterrent factor that helped to use the 22 days. I mean, we didn't -- you know, it was a balancing act and so that's where we ended up.

BOARD MEMBER COSTANTINO: So why collapse at all? Is that a completely judgment discretionary act, or is there something that says that if A, then you can and should collapse?

MR. RODGERS: It was a discretionary act to collapse it. I mean, we're certainly not obligated and the Board certainly can readjust the collapsing of the days if they feel that that is appropriate.

What we felt was appropriate, you know, if we did not collapse the days, we would have 157 times, what, about 1.5 times $1,000, we would be up well over $200,000 penalty range. At least in my opinion, that was a very significant penalty. We felt comfortable coming to the Board, that the deterrent amount of just under $35,000 would attempt to drive the message that this is a serious issue that needs to be rectified.

Our goal is to convince Mr. Sweeney that he needs to comply with the Order, not to see just how large a penalty we can propose. And so it was judgmental on our end. We used our discretion in what to propose and came up with this amount.

BOARD MEMBER COSTANTINO: Thank you. And I think Dale said there was no economic benefit number that you could come up with. I'm not going to argue that, but what is the cost that was avoided?

MR. RODGERS: Yeah, I think the issue is there certainly is an economic benefit that Mr. Sweeney has achieved because he hasn't undertaken the analysis. He hasn't employed the people to do the work. He hasn't taken on the expense of reporting the work. So there certainly is an economic benefit. I mean, if you wanted to know what our calculated amount of economic benefit is, I'd have to refer you back to Dale.

You know, one of the things is that there's not a benefit on a day-to-day basis, and I think that's what Dale had mentioned here, and part of the argument for collapsing the days is that economic benefit is accrued over the course of the year and it's not an issue on a day-to-day basis. And if Naomi needs to re-explain that a little bit better to do it, I'll --

BOARD MEMBER COSTANTINO: No, I think that's fine -- this is Jon again -- The question is compared to what is the avoided cost; I guess that's my question, what is the avoided cost, just so I have a sense?

CHAIRMAN LONGLEY: This is Karl. Can you answer that question?

MR. RODGERS: This is Clay Rodgers again. I think just what was here was the avoided cost for preparing the report is just under $1,000, and then there's probably some additional analyses results that maybe Dale can clarify a little bit better.

MR. ESSARY: The estimate that the economist came up with was 964, and that's based on two cost estimates; the cost of doing the sampling and the cost of producing the report, and the sum of that is 964.

BOARD MEMBER COSTANTINO: Okay, thank you.

MR. ESSARY: Back to Slide 9.

This slide shows compliance rates for the submittal of the 2013 Annual Report relative to size of dairy as of March of 2015. Formal enforcement has or will be taken on four dairies out of the total of 1225 dairies regulated under the Dairy General Order. One of the four is Sweeney Dairy.

The Dairy General Order has been in effect for almost eight years. Board staff and the dairy industry have made a great effort to educate dairy owners and operators about their responsibilities under the Dairy General Order. As a result, the compliance rate for the submission of Annual Reports has improved significantly.

Dairies like the Sweeney Dairy that fail to submit Annual Reports are rare at this point in the program. Because the Sweeney Dairy has a repeated history of noncompliance with the Dairy General Order, the penalty proposed is higher to represent what the Prosecution Team believes is an appropriate deterrent.

I will now turn the presentation over to Prosecution Team Counsel, Naomi Kaplowitz.

CHAIRMAN LONGLEY: Before you leave the podium, how many cows is the Sweeney Dairy milking?

MR. ESSARY: We currently don't know how many cows he has because he hasn't submitted any Annual Reports, but the enrollment letter that was issued in '07 gave him a maximum allowable mature herd size of 334.

CHAIRMAN LONGLEY: Okay. So that's your basis. Obviously he's reflected somewhere in here, and it could only be in the middle category; is that correct?

MR. ESSARY: Correct.

CHAIRMAN LONGLEY: Thank you.

MS. KAPLOWITZ: Good afternoon, Mr. Chairman and members of the Board. My name is Naomi Kaplowitz and I'm counsel for the Prosecution Team. I will be presenting the Prosecution Team's legal arguments and responses. A copy of the Discharger's evidence and our rebuttal have been provided in your agenda materials.

Slide.

I'd like to remind the Board that the only alleged violation before you today is the Discharger's failure to submit the 2013 Annual Report. As Board members recall, this Board imposed Administrative Civil Liability in 2011, 2012, 2013, and 2014 for missing Annual Report violations in the amounts shown on the slide.

In addition to imposing liability for the missing Annual Reports, the 2011 Order imposed liability for failing to submit a Waste Management Plan, and the 2013 Order imposed liability for failing to submit a Groundwater Monitoring Well Installation and Sampling Plan.

The Discharger petitioned these Orders, but was not issued an order or stay granting a waiver from having to comply with the Reissued

General Order requirements.

As may be noted later on and as I'd like to bring up now, earlier this week the State Board dismissed the Discharger's petitions for each of the Orders shown above. They were dismissed for failing to raise substantial issues that are appropriate for review by the State Board.

I will now summarize some of the Prosecution Team's main points.

Slide.

The Discharger argues that the Reissued General Order is invalidated by a Writ of Mandate following the *Association de Gente Unida por el AGUA v. Central Valley Water Board Court* Decision, which I will hereafter refer to as the *AGUA* Decision.

The *AGUA* court held that the Central Valley Water Board violated the State Anti-Degradation Policy. Based on that ruling, a Writ of Mandate was issued to the Central Valley Water Board ordering the Board to set aside the Dairy General Order in accordance with the *AGUA* Decision.

In response, the Central Valley Water Board did set aside the Dairy General Order in

October 2013 when it adopted the reissued Dairy General Order, which readdresses the deficiencies that were raised in _AGUA_. A challenge to the Reissued General Order based on similar legal theories is currently pending before the State Board.

The _AGUA_ Court found the Dairy General Order deficient in regard to groundwater degradation prevention. The Discharger attempts to extrapolate from _AGUA_ that it is no longer required to monitor or otherwise comply with the requirements of the Dairy General Order or Reissued General Order.

By asserting this, the Discharger fails to recognize that the intent and effect of the _AGUA_ Decision was to strengthen the requirements imposed under the Dairy General Order, not eviscerate them.

The Discharger also argues that the Reissued General Order is unenforceable due to the fact that the Superior Court ordered that proceedings to determine the adequacy of the Central Valley Water Board's return to Writ of Mandate be stayed until the State Board has issued a decision or an Order of Dismissal on the

Petitioner's challenge to the Reissued General Order.

Sorry, that was wordy.

The Order to Stay Proceedings temporarily suspends the Superior Court's determinations regarding the Central Valley Water Board's return to the Writ of Mandate. It does not repeal the Central Valley Water Board's adoption of the Reissued General Order nor does it constrict the ability of the Central Valley Water Board to pursue enforcement under that Order.

Slide.

Next, the Discharger argues that the Reissued General Order is unlawful and unenforceable for a variety of other reasons. These arguments are virtually identical to those made by the Discharger before this Board in the previous proceedings. As such, they should be barred by collateral estoppels. They were rejected in the adoption of four Administrative Civil Liability Orders, yet the Discharger attempts to raise them again today and ask that you reach a contrary result.

This Board has already determined that the Discharger is required to submit Annual Reports.

We ask that you maintain consistency and reject these arguments today as you did in previous proceedings.

The window to challenge the Reissued General Order was the 30-day period following its adoption. The Reissued General Order is now final.

The Discharger filed a timely petition challenging the reissued General Order, but has not, as I pointed out before, received a stay or order excusing it from compliance.

In its response to rebuttal, the Discharger contends that because it timely filed a Petition it has the right to raise the same arguments again here today. However, challenging the propriety of the Reissued General Order in the context of an enforcement proceeding is not appropriate; it's a collateral attack on the Order and should be barred.

Slide.

In addition to the procedural bases I have discussed for dismissing the Discharger's arguments, the arguments lack merit.

First, the Discharger argues that the Reissued General Order is not supported by substantial evidence. The Discharger raises *AGUA* here again and argues that the case supports its assertions regarding a lack of substantial evidence.

Once again, this is a misconstruction of AGUA. The AGUA Court instead ruled that there was not enough substantial evidence to support the contention that the Reissued General Order complied with State Anti-Degradation policy. The AGUA Court did not hold, as the Discharger contends, that the Dairy General Order lacks substantial evidence to support the need for any monitoring and reporting.

Next, the Discharger argues that the Board failed to provide a written explanation regarding the need for monitoring reports and justifying the burden.

This requirement, however, is satisfied by the language in the Reissued General Order which describes why monitoring is needed, and has been detailed in the previous proceeding.

The Discharger raises arguments regarding economics. This Board has been sensitive to hardship faced by the Dairy industry and has acted to ameliorate it.

For example, reporting software provides dairies with a means to produce Annual Reports without consultants. In addition, revisions were made to the Dairy Program in 2009 and again in 2011, extending Waste Management Plan due dates and providing for groundwater monitoring coalitions.

The Discharger asserts that the Central Valley Water Board staff did not provide information regarding representative groundwater monitoring to the Discharger. This issue is not relevant to the subject complaint, which only alleges a violation for failure to submit the 2013 Annual Report.

Contrary to the Discharger's assertion, however, Central Valley Water Board staff does not have an obligation to convince dairies to join a coalition, only to provide information to be able to do so. Staff did, in fact, provide that information to the Discharger, which has been accounted for in detail in the previous proceedings.

Slide.

Next, the Discharger argues that because the attorneys for the Advisory and Prosecution Teams are both employed by the State Water Board, a conflict of interest exists.

The hearing procedures which were provided to the Discharger clearly state that the functions of those who will act in a prosecutorial role known as the Prosecution Team are separated from those who will provide legal and technical advice to the Board and are known as the Advisory Team.

Moreover, the hearing procedures provide further assurance of fairness and impartiality by forbidding designated parties and interested persons from engaging in ex parte communications regarding this matter.

Accordingly, the Discharger's accusation that the Advisory and Prosecution Teams have a conflict of interest is meritless and should be rejected.

I will now turn the presentation back over to Mr. Essary for our conclusion and recommendations.

Slide.

MR. ESSARY: The Discharger is asking you to treat his dairy differently from others in the Region. It does not believe that the Annual Report submittal requirement should apply.

The majority of dairies in the Central

Valley work hard to comply with environmental laws. The expend time and money to submit the reports required under the Reissued General Order.

Regarding submission of the 2013 Annual Report, the compliance rate exceeds 99 percent. Dairies that do not comply with these requirements receive an economic advantage over those that do. The Central Valley Water Board Prosecution Team pursues enforcement against noncompliers in part to ensure that people are treated fairly and consistently.

Slide.

By failing to provide the Annual Report, the Discharger violated Section 13267 of the California Water Code. The maximum penalty allowed under the Water Code is $157,000.

Based on the methodology for liability calculation defined in the Enforcement Policy, the Prosecution Team recommends that the Board make findings of fact and conclusions of law affirming Complaint No. R5-201500506 for a liability of $34,650.

A Proposed Administrative Civil Liability Order is included in your agenda package. We recommend the Board adopt this Order.

I would like to submit this presentation, the Agenda Package, and the Central Valley Water Board files referenced in the Agenda Package into the record.

This concludes our presentation and we are available to answer any questions.

CHAIRMAN LONGLEY: Any questions by members of the Board?

Seeing none, does the Sweeney Dairy wish to cross-examine?

MR. CARLSON: Yes, Mr. Chairman.

CHAIRMAN LONGLEY: Come forward, please.

MR. CARLSON: Thank you. My name is Ray Carlson. My address is 111 East Seventh Street, Hanford, California, 93230. I'm an attorney representing the Sweeney Dairy and I had just a couple questions here I'd like to follow-up -- excuse me.

I'd like to direct this to Mr. Essary who made most of the presentation.

MR. CARLSON: Was a report prepared for Mr. Sweeney in connection with Water Code Section 13267(B) which states, excuse me, again referring to Water Code Section 13267(B), states in part: "When reports are required, the burden, including costs of these reports, shall bear a reasonable relationship to the need for the reports and the benefits to be obtained from the reports."

It goes on to state that, "In requiring these reports, the Regional Board shall provide a person with a written explanation with regard to the need for the reports and shall identify the evidence that supports requiring that person to provide the report."

So my question is, was that done in the case of the Sweeney Dairy?

MS. KAPLOWITZ: Objection. Counsel is calling for a legal conclusion.

MR. CARLSON: I'm simply asking if a mandatory statutory duty under the Water Code was carried out in this case. This Code Section specifies the Discharger and the person, it does not say that a General Order, whatever it may say, satisfies the requirements of this section.

CHAIRMAN LONGLEY: I'll deny the objection and I'd like to hear an answer.

MR. RODGERS: Dr. Longley, this is Clay Rodgers. The actual answer to that is that it was not done specifically for the Sweeney Dairy, but detailed analyses, and that was considered very heavily when the General Order itself was adopted in 2007, and so those issues were addressed, they were addressed when the Order was originally adopted in 2007, it addressed it as far as individuals for everybody that would come under coverage from the General Order, and it has not been completed for each individual dairy, such as Mr. Sweeney's.

MR. CARLSON: Is it part of the public record?

MR. RODGERS: My understanding is that it is part of the record for when the Order was adopted.

MR. CARLSON: Thank you.

MR. PULUPA: I would interrupt. The violations that we're discussing here are actually violations, I believe the 2013 Reissued General Order. The Reissued General Order did have an extensive economics discussion about the consequences of imposing that Order. The Annual Reporting requirement is imposed under the General Order's MRP.

CHAIRMAN LONGLEY: You didn't state your name.

MR. PULUPA: And this is Patrick Pulupa,

attorney for the Board's Advisory Team.

CHAIRMAN LONGLEY: Thank you. Continue, sir.

MR. CARLSON: Thank you. Ray Carlson again. So I'm taking it that the answer was no in terms of there was no individual --

CHAIRMAN LONGLEY: Mr. Carlson, what I heard was that this was part of the General Order Proceedings when the Reissued General Order and the dissemination of that, the extent of the dissemination of that I'm hearing was certainly, it was evident to those who were being put under the General Order, but I don't know if each and every dairy was mailed a copy of that.

MS. KAPLOWITZ (Presumed): It's part of the General Order that each dairy received, Dr. Longley.

CHAIRMAN LONGLEY: So each dairy received a copy of that, is that correct? Of the General Order itself?

MS. KAPLOWITZ (Presumed): Yes, when it was adopted.

CHAIRMAN LONGLEY: Yes, thank you.

MR. CARLSON: As the rest of my inquiry on that point was a legal one, I have no further questions. Thank you.

CHAIRMAN LONGLEY: Thank you very much. Then it's your turn to present.

MR. CARLSON: Thank you. I'd like to call Mr. Sweeney, and then I guess I have my chance to make a closing? Is that correct, Mr. Chairman?

CHAIRMAN LONGLEY: That's correct.

MR. CARLSON: Thank you.

MR. SWEENEY: Okay, my name is Jim Sweeney of Sweeney Dairy, and I have taken the oath.

MR. CARLSON: Thank you. This is Ray Carlson again. I have a few questions I'm going to ask Mr. Sweeney, and then he'll be available for cross examination.

How old are you?

MR. SWEENEY: 56.

MR. CARLSON: And how long have you worked in the dairy industry?

MR. SWEENEY: 42 years.

MR. CARLSON: And during that time you've been a dairyman, in other words, working on a dairy?

MR. SWEENEY: Yes, I've been a dairy owner for about 25 years.

MR. CARLSON: Okay, and can you describe

where your dairy is located?

MR. SWEENEY: We're straight east of Visalia, California, between Woodlake and Exeter.

MR. CARLSON: And how many dairies are near you, let's go from north to east, where's the nearest dairy on the north?

MR. SWEENEY: Five miles.

MR. CARLSON: And on the west?

MR. SWEENEY: Two miles.

MR. CARLSON: South?

MR. SWEENEY: Five miles.

MR. CARLSON: And on the east?

MR. SWEENEY: Unknown, because it would be in Nevada.

MR. CARLSON: Do you own your dairy?

MR. SWEENEY: Me and the bank.

MR. CARLSON: Okay, so if you owe debt, you still owe debt on that dairy?

MR. SWEENEY: Correct.

MR. CARLSON: And how long have you owned the dairy?

MR. SWEENEY: Nine years.

MR. CARLSON: And how long has the dairy operated at your site?

MR. SWEENEY: Approximately 85 years.

MR. CARLSON: And how do you know that?

MR. SWEENEY: The guy that we bought it from, Joe Borgess, he was born on the dairy or, you know, his family owned the dairy when he was born.

MR. CARLSON: And did you work at that dairy before you owned it?

MR. SWEENEY: No, but we did lease it before we owned it.

MR. CARLSON: And when did you start leasing it?

MR. SWEENEY: 1990, I believe, or 1992.

MR. CARLSON: Okay. And then what year did you buy it?

MR. SWEENEY: Let's see, 2006.

MR. CARLSON: And how many cows do you milk at the present time?

MR. SWEENEY: A little under 300.

MR. CARLSON: And --

CHAIRMAN LONGLEY: If I may interrupt? And Mr. Sweeney, does that include your dry cows?

MR. SWEENEY: He asked how many I milk.

CHAIRMAN LONGLEY: I understand. So how many -

MR. SWEENEY: Probably no more than 320

including the dry cows.

CHAIRMAN LONGLEY: Okay, thank you.

MR. CARLSON: How many lagoons do you have?

MR. SWEENEY: Two.

MR. CARLSON: And what kind of water goes into those lagoons?

MR. SWEENEY: Just the wash water from the barn and the sprinkler pack. And none of it is recycled, we only use it once.

MR. CARLSON: Do you ever use that water in conjunction with well water to irrigate?

MR. SWEENEY: Yes, when we're irrigating we run them both together.

MR. CARLSON: How many irrigation wells do you have?

MR. SWEENEY: We have two wells on two separate pieces of property.

MR. CARLSON: And what's the depth of those wells?

MR. SWEENEY: Well, I don't know what it is today, but last year it was 55 feet.

MR. CARLSON: Excuse me --

MR. SWEENEY: I mean 55-feet with a pumping level. The depth of the wells is -- all our wells domestic and irrigation, they're between 100 and 120-feet.

MR. CARLSON: Do you know about what level your pumps are set in those wells?

MR. SWEENEY: Between 60 for the domestic wells and 90 for the irrigation wells.

MR. CARLSON: So the domestic wells are pumping at a shallower level than your irrigation wells?

MR. SWEENEY: True.

MR. CARLSON: Have you had any trouble at all with your domestic well in terms of the water quality that you know of?

MR. SWEENEY: Never.

MR. CARLSON: Is the milk from your cows tested?

MR. SWEENEY: Yes.

MR. CARLSON: And how often does that happen?

MR. SWEENEY: La Prima Foods tests it once a week. The Milk Inspector, which is Tulare County Health and Human Services, they test it at least twice a year, and if there's a problem they'll test it more, and then we also have milk sampling done by Tulare DHIA, which is a monthly thing.

MR. CARLSON: Now has any of this testing ever showed any nitrate?

MR. SWEENEY: Never.

MS. RAMIREZ [Presumed]: And just to make sure we're talking about the milk tested, right? Not water.

MR. SWEENEY: Right.

MR. CARLSON: Now is the water from your wells tested?

MR. SWEENEY: It has been.

MR. CARLSON: Can you describe for us when that happened and the circumstances that it happened?

MR. SWEENEY: Well, we have on the earlier for the reports for the Central Valley Regional Board, and then also it's done twice a year by the Tulare County Health Services.

MR. CARLSON: So when the Tulare County Health Human Services Agency or Tulare County Health Services has done this testing, have they ever noted a nitrate problem in the water?

MR. SWEENEY: Never.

MS. RAMIREZ: And I guess my question is what do you define as a nitrate problem?

MR. CARLSON: Well, I'm assuming - excuse me, this is Ray Carlson again --

MS. RAMIREZ: Sorry, and that was Carmen Ramirez asking.

MR. CARLSON: -- I'm assuming if it was above the MCL that that would be noted. I mean, I'm not the Tulare County agency, but I'm assuming that they would --

MS. RAMIREZ: I understand, I didn't ask for the number, I just want to make sure that when you said "problem" you meant MCL.

MR. CARLSON: Yes, yes. I mean, I'm assuming the MCL set a level so that there won't be a problem, and if it goes above it there will be a problem, or could be a problem.

Now, have you had any chance to check how much it would cost for you to do the report that the Board is requesting, including the sampling testing, the preparation of the report, and I'm presuming you would need to install monitoring wells?

MR. SWEENEY: Yes, I have. I have a quote here from Manual Avila of Dairy Monitoring Systems, and the quote, well, his quote would be for $6,172.00 a year, and then also the monitoring well fee, if I join the coalition without the membership fee, just the monthly fee, would be an additional $972.00. And then the fee from the State Water Resources Control Board is an additional $682.00 for the smallest dairy.

MR. CARLSON: So under the circumstance, you would have to drill one or more monitor wells on your property?

MR. SWEENEY: Well, if I didn't join the coalition I would have to.

MR. CARLSON: Okay. And you'd have to take samples?

MR. SWEENEY: True.

MR. CARLSON: And you'd have to hire somebody to produce the report?

MR. SWEENEY: Yes.

MR. CARLSON: I mean it would have to be prepared and stamped by a professional engineer. And so that is where the cost that you quote, that you got encompasses all of those things. Is that correct?

MR. SWEENEY: Correct.

BOARD MEMBER COSTANTINO: And this is Jon. I didn't do all the math in my head. Do you have a total number and an annual number?

MR. SWEENEY: $7,826.00. I don't know how broke down, that would exist for my dairy.

MR. CARLSON: And that's not for -- that doesn't include the drilling of monitoring wells.

MR. SWEENEY: No.

MR. CARLSON: And that is also if you did not join the Coalition. Is that correct?

MR. SWEENEY: No, that would be if I did joint the coalition, but that would just be the monthly fee, it wouldn't be the membership fee.

MR. CARLSON: Okay, thank you.

MR. SWEENEY: And I do have, you know, an itemized thing of how much it costs to sample each, like tissue samples, or water samples, if you're interested in that.

BOARD MEMBER COSTANTINO: Jon Constantino again. So the $7,826 is the annual total of being part of the coalition? Or does that also include --

MR. SWEENEY: No, no, to be -- I don't know because I didn't join it right away, so if I was to join it now, it would cost substantially more, but it's $81.00 a month to belong to the Monitoring Well Coalition. So the $7,826 does not include a membership fee and that's at least

$2,500.

BOARD MEMBER COSTANTINO: Okay.

MR. CARLSON: This is Ray Carlson again. When did you get that estimate?

MR. SWEENEY: September 23rd of 2014.

MR. CARLSON: Have you ever been provided a document that explains the need for you to do the report and, as it says in Water Code Section 13267(B), a written explanation with regard to the need for the reports and an identification of the evidence that supports requiring you to provide the report?

MR. SWEENEY: No, we haven't, and I specifically sent a letter asking for that.

MR. CARLSON: I have no other questions.

MS. KAPLOWITZ [Presumed]: I have two follow-up questions.

Were you ever provided a copy of the Revised General Order that you can recall?

MR. SWEENEY: Not that I can recall. I do have, you know, the little kind of peach colored book from the original Dairy General Order.

MS. KAPLOWITZ [Presumed]: Okay, and that's the 2007?

MR. SWEENEY: 2007.

MS. KAPLOWITZ [Presumed]: Okay, and so you can't recall having seen the revised one?

MR. SWEENEY: No.

MS. KAPLOWITZ [Presumed]: And when you said you sent a letter requesting it, do you recall who you sent that to and when you sent that?

MR. SWEENEY: Well, it was either Clay Rodgers or Dale Essary. And, you know, I don't have it physically with me, but I could provide it.

MS. KAPLOWITZ [Presumed]: Well, that's okay. You know, there's a couple ways to get testimony, and certainly your Declaration carries weight, as well. Do you know the approximate date you think you might have sent that? A year?

MR. SWEENEY: No, you know, that has been something that we've challenged on pretty much every Order, so it would have been early on that we challenged that.

MS. KAPLOWITZ [Presumed]: Okay, thank you.

CHAIRMAN LONGLEY: Any further testimony?

MR. CARLSON: No further testimony, Mr. Chairman.

CHAIRMAN LONGLEY: Thank you. Does the Prosecution Team wish to cross examine? If you could possibly do your cross examination from one of the chairs here in front of us?

MS. KAPLOWITZ: This is Naomi Kaplowitz for the Prosecution Team and I just have a couple of questions for cross, Mr. Sweeney.

Mr. Sweeney, in 2013 when you petitioned the Revised General Order, did you request a copy of the record?

MR. SWEENEY: Could you clarify what you mean as to record?

MS. KAPLOWITZ: Yeah, the record supporting the adoption of the Revised General Order, or Reissued General Order, excuse me.

MR. SWEENEY: To be honest, I don't know because my attorney would have been the one who would have done that, and it wouldn't have been Ray, it was a different attorney.

MS. KAPLOWITZ: Okay --

CHAIRMAN LONGLEY: Any further -

MS. KAPLOWITZ: I do have one more question.

And my second question is, have you submitted, or has your attorney on your behalf submitted any technical or monitoring reports in 2013 reflective of current conditions at the dairy to substantiate or support your testimony regarding water quality conditions?

MR. SWEENEY: No.

MS. KAPLOWITZ: That's all. Thank you.

CHAIRMAN LONGLEY: Thank you very much. Any questions from Members of the Board?

BOARD MEMBER KADARA: I just have one question for Mr. Sweeney. Denise Kadara. Staff has indicated that the compliance rate is 99 percent for all the active dairies, and I'm just curious as to why if all of the dairies are in compliance, why are you holding out in providing viable information concerning your operation, as required by this Board?

MR. SWEENEY: Okay, I think it's a little bit misleading as to -- is there any way that I could get one of the previous slides that they used to come up?

CHAIRMAN LONGLEY: Sure. If someone could assist Mr. Sweeney?

MR. SWEENEY: Okay, when the --

MALE VOICE: I'm sorry, this is slide 9 of the Prosecution's.

MR. SWEENEY: Okay, and this is Jim Sweeney again. Okay, when the Dairy General Order was first adopted, there were 1,651 dairies in the Central Region. And, you know, as you can see from that slide, right now there is approximately 1,200, but there's only one percent less cows. So, you know, the small dairies are the ones that paid the price. And also I'd like to point out that in February of 2009, I met with Sophie (ph) Tompkins, Scott Spears, and Jim Solens (ph) at our dairy and I explained to her why, you know, small dairies couldn't comply, because according to a report done by a guy that works for the State, it's a real Italian name, well, up until a couple years ago, the cost of compliance had been well over $100,000, and I do have that -- and you know, that's what's put most of the small dairies out of business. And in February of 2009, we also met with Clay Rodgers and Pamela Creedon at the Regional Board Office in Fresno, myself and two other small dairymen, and Jim Solins (ph), again, who is a U.C. Extension Director for Kings and Tulare County, and we pleaded with them, you know, that there's no way that small dairies can afford to comply with the things because it's just too much money. And the other Boards from the other Regions, including the North Coast and San Francisco Bay Regions, which have over 80 percent of their cows on dairies less than 700 cows, they exempted all the dairies under 700 cows because they did the economic analysis. The EPA also exempted all dairies in the whole United States under 700 cows, and the Air Board for the Central Region did the exact same thing. They exempted all the dairies under 700 cows. And we, you know, we're not like, you know, it would have been cheaper to comply than to hire attorneys and go through all this stuff. You know, I don't think that smaller dairies are being treated fairly and nobody is standing up for them. And you know, an example is Rosa Parks, you know, there was a lot of people that didn't think that she should stand up, but she did and all the other ones were doing what they were supposed to, but she did what was right. And you know, it took all the way to the Supreme Court before she got a favorable decision. So I'm just trying to stand up for what I believe is right. And, you know, I'm trying to teach my kids right from wrong, and I think that myself and my wife that we've done a good job because we have a Stanford graduate, we have a UCLA graduate, and my youngest daughter here is a senior at Cornell. You know, we try to teach them right from wrong and we try to teach them to stand up for what's right.

CHAIRMAN LONGLEY: Thank you.

BOARD MEMBER KADARA: I have no comments.

BOARD MEMBER COSTANTINO: This is Jon. So just to go along with what you just said, I'm not sure I got a direct answer to Denise's question. Is there a fundamental philosophical issue, or is it strictly you feel like the small dairies can't afford it --

MR. SWEENEY: Small dairies can't afford it, that's why all the dairies that are going out are small dairies. You know, because economically they can't afford it. And if the price was $960 some, you know, like they say, "I'll write you a check for 900 and something dollars. Okay, if that's really what it costs, I would be willing to pay that. Okay? But it costs at least 10 times that much, and most dairies it costs 20 or 30 times that much. You know, I had one of my friends who milks a little over 1,000 cows, he told me that it costs him $.15 per cow per day to comply with your stuff.

CHAIRMAN LONGLEY: Mr. Sweeney, the issue that you state is something that's happening in Ag, I grew up on a small farm and the reason I didn't become a farmer is I saw it coming. It's not just dairies, it's small Ag in general, and if you're small in this day and age, better have a second job. That's the unfortunate problem. The guy that sits across in the office from me, he farms oranges, he's moving into almonds like many of them are, but he has a full time job. It's unfortunate that that's what's happening to small Ag, but it's not just this Board, it's the general cost of being small that cannot be handled.

You know, our charge is water quality and there is a discharger out there, we are conscious of economic considerations, but what does trump economic considerations is possible impacts to the water quality, and that's why we have taken the particular stance that we've taken on the various General Orders that we put out, whether for Irrigated Ag or for the Dairy Order.

I see 147 dairies here that are apparently in compliance; as you rightly pointed out, that's much smaller than it was before, but dairies going out of business wasn't just our Board, the whole economic condition for dairies, it was very poor for a long period of time because of the price structure that was mandated on dairymen like yourself.

MR. SWEENEY: Right, but that has -

CHAIRMAN LONGLEY: And that means that you were not able to recoup costs because of a cap that was put on what you could get for your milk. And that's a whole different issue, that's not within the purview of this Board.

MAIL VOICE: But, Karl, and we'll get back to you whether or not we have a compliance issue and whether we want to adopt this order, but I'm seeing a big discrepancy between the claim costs and the question I asked earlier, and I don't know if we can resolve it today, but I certainly would like to get to the bottom of whose number is right. Or, I don't know if you've surveyed folks lately or whether your proof has been submitted to our staff, or our estimates have been submitted to stakeholders for cross-checking, but that's a big discrepancy, a ten-fold difference.

MR. SWEENEY: Right, and you know, I could give you my phone, I've got 20 or 30 dairymen on there, and you could pick any one to call and I'll bet they'll come back with my numbers. And, you know, I have a suggestion for the Board, too. To make it more fair, why don't you do something on a per animal basis, rather than -- or per pound of milk produced, rather than on how big the dairy is because the way the structure is right now, it's the small dairies and the big dairies, you know, it's not much difference.

CHAIRMAN LONGLEY: What you're saying "not much difference," you're talking about total cost?

MR. SWEENEY: Right. And you know, like just numbers out of the sky, let's just say a quarter a cow a year, you know, and I don't know that that would cover everything, but if a guy has got 10,000 cows, you know, he's got a hell of a lot more chance of discharging or causing a problem than a guy with 200 cows, and it would be more fair if there was something like that, rather than the way it is.

CHAIRMAN LONGLEY: Mr. Sweeney, the purpose of this hearing today, of course, is to get it while you're -- to take testimony on your not filing the report. I've allowed this discussion to go a little bit astray of that into issues which are really not pertinent from the standpoint of the alleged reasons for which this fine is being assessed, but I think we thank you very much for providing us the information you did provide us. Certainly, I think the Board was curious on why you were not filing your reports, it's obviously that you feel these beliefs very deeply, and for that I have to commend you for following up on your feelings, but quite frankly I cannot sympathize with not submitting your annual reports, so there's better ways to go at resolving your issues than, I think, the ones that you followed.

MR. SWEENEY: And what would they be? Can I just ask that?

CHAIRMAN LONGLEY: Well, certainly you could be part of the program and separately work with Legislators and others to change the rules as they are, but it could be that you're mistaken in your beliefs and others don't go along with you. I see 147 dairies here that apparently are not on board with you, they may sympathize with you, but they're paying their dues, they're doing the monitoring. And you know, I have some issues with the numbers I hear, I think those numbers have to be validated and I think they have to be validated by a third party. I'm not that confident that what I'm hearing of any numbers that is necessarily correct.

Any further questions or comments?

FEMALE VOICE: Well, just to make sure, I thought I heard you raise two issues, one was certainly the economic issue that you just talked about, and secondly was whether or not the Board's second Order was compliance. So the second part of sort of not the protest, but the reason that you object, is a legal compliance issue. Is that right? Is it those two?

MR. SWEENEY: Can you explain that again?

FEMALE VOICE: So in the Prosecution Team's slides, I think there was a couple slides that said that you felt that even the reissued order did not comply with what the Court had originally ordered in the Agua case. Is that a position that you've taken? You can disregard it. I want to make sure --

MR. SWEENEY: I'm not sure I understand the question.

CHAIRMAN LONGLEY: Well, maybe Mr. Carlson understands the question.

MR. CARLSON: I understand the question. This is Ray Carlson speaking. I was going to address that in my closing.

FEMALE VOICE: All right, thank you Mr. Sweeney.

MR. SWEENEY: But I have written Legislators and they just don't answer. They don't respond. And I did talk to Connie Conway who was our Assemblywoman and she said because we live in the middle of the Republican part that she can't do anything.

CHAIRPERSON LONGLEY: Any further testimony?

MR. CARLSON: No. This is Ray Carlson. No, Mr. Chairman.

CHAIRPERSON LONGLEY: Thank you very much. Very good. I guess what I need to ask for right now is comments by interested persons. I don't see -- I have no cards, I don't see anybody wishing to testify, so I think that's it. I believe that was your closing statement, or no, you were going to give me your closing statement, I'm sorry. So go ahead and give me your closing statement now and then we'll go to the Prosecution Team for closing.

MR. CARLSON: Mr. Chairman, Members of the Board, Ray Carlson again. This is my closing for the matter of the Sweeney Dairy. I don't want to go over all the ground that we've gone over, there's a lot of it in the papers, in fact, it's all in the papers, so I'm just going to highlight a couple of points.

One is getting back to the point I made earlier about Water Code Section 13267(B) and the obligations under that. I know that not everybody here is going to agree, but I'm just going to state that our position is that it requires what it says it does under the normal rules of statutory construction, and I don't know that a General Order can meet those requirements.

As for the status of the Orders, I think it's pretty clear from the Courts, and by that I mean the trial court's Order of April 17, 2013, that the 2007 Order was set aside. Paragraph 1 of that Order says: "Set aside the waste discharge requirements General Order for existing milk cow dairies, Order No. R5-2007-0035, and reissue the permit only after the application of and compliance with the State's Anti-Degradation Policy Resolution No. 68-16, etc." So as of that date, which was October 17, 2013, and the adoption of the reissued General Order, there was no General Order, period.

The Reissued General Order was issued on April 3rd, 2013. It was proffered to the trial court as a return on the Writ of Mandate issued by the trial court in the April Decision. It was proffered as a return or filed as a return on October 11, 2013, the Regional Board filed a return to the Writ of Mandate, indicated it had rescinded the permit and adopted the General Order. So in other words, the General Order was meant to be the return on the Writ of Mandate and if the Court found that it satisfied the Court's condition, it would discharge the Writ and the Court's role in this matter would be over with. Instead, that is not the case and for presumably other reasons the trial court issued a stay with the agreement of the parties that any issues relating to the sufficiency of the 2013 Reissued Order vis a vis the Court's Writ of Mandate would be stayed pending the outcome of the Petition that the Petitioners in the Agua case had filed with respect to the 2013 General Order.

And the Sweeney's themselves had also

filed a Petition challenging that Order, and it was well within the timeframe, or it was within the timeframe within which such a Petition had to be filed.

So the bottom line is that the efficacy of the 2013 Order does not exist. You have to have an Order that is free of any court mandate and the fact that it isn't is not the fault of Mr. Sweeney or anybody else. The Board or the staff of the Board could simply make vigorous efforts to make sure that the Order complies with the Writ of Mandate, and the Writ of Mandate is discharged. That hasn't happened yet. Thank you.

CHAIRMAN LONGLEY: Thank you very much. Closing arguments from the Prosecution Team.

MR. RODGERS: Hi, this is Clay Rodgers, Assistant Executive Officer for the Central Valley Water Board. And I'll try to touch on just a few of the issues here, there were probably a few more.

I'll not touch much on the legal issues other than, you know, we have over 1,200 dairies in the Central Valley. And all of them, but four, actually submitted the Annual Report this past year and complied with the requirements. We've been here over and over and over with Mr. Sweeney, you know, for repeated years. For the last several years, he didn't do a number of things that he was required to do in addition to the annual report.

So, you know, we get comments like, "We have really good quality water, we don't have any problems, everything is great," but we don't know. None of that data has been submitted. We have severe nitrate problems on the east side of Tulare County, where we have disadvantaged communities, we have people whose water quality has been impaired, and dairies are part of the issue associated with that, those findings are clear within the Annual Report. That's part of the issue that we had with when we lost the lawsuit from Agua, and we had to rewrite the Annual Report to address that. It certainly wasn't because our Order was too tough because we were requiring people to do enough that we got our Order remanded back, it was because it didn't comply with the law and we actually needed to go the other way.

Mr. Sweeney argues that, you know, he was never supplied any of this information. I will tell you when Mr. Sweeney petitioned the 2013

Order, he requested from us and was provided a copy of the entire record, all several thousand pages of it. So he has been provided the information. I don't know whether he read every page, I don't know what he did with it after he received it, but we did provide that to him. He says small dairies can't comply, but clearly as you can see from the compliance on the chart here, they do.

You know, small dairies have gone out of business the last decade or so, there's a lot of reasons for that, I won't tell you that complying with the Order is free, but I also know that we had depressed milk prices, we had extremely high commodity prices for feed and whatnot that made the dairy industry economically challenged, and in fact this Board took steps to offset some of those costs by delaying preparation of the Waste Management plan, we've allowed options other than having to install individual groundwater monitoring wells at every dairy, we had rewritten the Monitoring and Reporting Program to allow a coalition to do the monitoring on a representative site of dairy so that not every dairy would have to install wells to answer the questions.

CHAIRMAN LONGLEY: I'd like to ask you a question there because I heard Mr. Sweeney's testimony, he was siting the cost of constructing and operating monitoring wells. Is that what is required of each and every dairy?

MR. RODGERS: The Order itself originally required that the Executive Officer could require every individual dairy to do groundwater monitoring. What we did was we provided an option to Mr. Sweeney and every other dairyman to say you can join a coalition so you can answer the questions of what are the appropriate management practices, what works, and what doesn't, as a group, instead of to do it individually at every dairy, that that would be a far less of an economic burden in order to do that as a group, and join the coalition. Most of the dairymen joined. Some folks decided not to join because they didn't want to pay a fee. And that's also part of the issue here. That's a complete separate issue from the Annual Report. Mr. Sweeney is part of the cost up here that he talks about, says that all of these costs are included, but he's using like the fees that he would pay to that group to do the representative monitoring.

But those costs are not associated with preparation of the Annual Report, so we're comparing a little bit of apples and oranges. He also used the annual fees that he pays to the State Water Resources Control Board, were included in his calculation here, which were not included in our calculation because our fees were simply to prepare the Annual Report itself, not to do all this other stuff that is ancillary to the economic burden to do the Annual Report.

And along that note, I'll add that because of the severe groundwater problems that we have, and they bring up the issues with 13267 of the Water Code and the economic burden, is that while it's not free to comply with the Order, it does cost money, the argument is the economic burden is too great. The economic burden to fix groundwater after it's become impaired is far more significant than the cost we're talking about here to do the annual reports. And that really is the economic burden, is that, you know, the benefit provided by this to make sure that appropriate steps are being made to know that we're being protective of groundwater quality is very important because the problem is, when the balance tips the other way, and then we have problems with groundwater that then have to be fixed, those costs are extraordinarily high, as we see with disadvantaged communities, individual homeowners that really can't drink the water that they pump.

So our belief is the economic burden and the reissued 2013 Annual Report certainly points those things out that they are there. And that information has been provided.

You know, there's a lot of costs, things about ability to pay. Mr. Sweeney argues that small dairies can't afford it. Every one of these Administrative Civil Liabilities that we've had with Mr. Sweeney, he's been asked to provide information whether he has the inability to pay. And no information has ever been submitted about the economic hardship that would be placed upon him to pay the Administrative Civil Liabilities. He makes the claim that it's too expensive to comply with the Order, he can't do it, and it would drive him out of business. We ask him for the demonstration that he has the inability to pay, and to date we have not received any information other than just their reiterated comment that it's too expensive to comply, and therefore I'm going to stand up and say no, that I won't do this.

The unfortunate thing is that we continue to ramp up the costs on these because obviously we have not provided a penalty sufficient to provide a deterrence. He says he has the legal arguments that he's not obligated to comply, but he discharges; discharge is a privilege in this state, not a right. If he's going to discharge, he needs to comply with the Water Code. And with that, I recommend that the Administrative Civil Liability in the amount of $34,650 be adopted by the Board, and I'll add that, you know, I'm not completely convinced the penalty is sufficient, but I'll leave that in the hands of the Board. Thank you.

CHAIRMAN LONGLEY: Thank you, Mr. Rodgers. Any questions for Mr. Rodgers? Then I'll close the hearing and the discussion will be limited to Board members and members of the Advisory Team. What is your pleasure?

BOARD MEMBER CONSTANTINE: So I guess I'll look at Patrick just to -- is there a brief answer to the legal question that was in the close?

MR. PULUPA: I think there was a few --

this is Patrick Pulupa, counsel to the Advisory Team. We've got a lot of issues that were discussed in the course of this proceeding, the 2007 Order, Economic Benefit, Economic Cost of Compliance, I think it boils down to really just a couple very clear issues. But before we get into that, I would note for the record that the Board has complied with the separation of functions requirement, I have not had any communications with the Prosecution Team with respect to any matters on the Board's consideration today, neither has any other member of the Board's Advisory Team, and that's to satisfy the separation of functions requirements for adjudicative matters such as this.

In terms of what we're talking about right here today, it's compliance with the 2013 Order. That 2013 Order is valid and enforceable. The 2013 Order is still under the purview of the Superior Court, Sacramento Superior Court, due to the fact that there is a Petition pending at the State Water Board. We did take judicial notice of the fact that a number of Mr. Sweeney's Petitions have been dismissed, the one petition that he does still have in place is a petition of the validity of that 2013 Order, as does the environmental petitioners, the Environmental Justice Petitioners, I should say, and that's the *Agua* Coalition that was mentioned earlier. Both of those parties have very different considerations over the validity of that Order, one wanting it one way, the other wanting it the other way.

But the fact of the matter is there was an Administrative remedy available to Mr. Sweeney and any other affected dairy if they wanted the State Water Board to nullify the enforcement of the Board's 2013 Order. That is a stay, and that is in the Regional Board's Regulation and the State Board's Regulations pertaining to petitions. If MR. Sweeney had requested a stay of that Order, then the 2013 Order would not be enforceable today. There is no stay in place of that Order. Second, they could also get an injunction, there is no injunctive relief granted.

Lastly, with respect to the validity of the Orders, the proceeding itself was a Writ of Mandate proceeding. The Court itself did not invalidate the Board's Order; what the Court did was command the Regional Board to do certain actions, it commanded us to rescind the Order, to set it aside, and it commanded us to not replace that Order before we had gone through the steps required in 6816. We did that on the same day in 2013 when we reissued the Dairy General Order.

So again, my legal comment is we have a fully enforceable 2013 Order and that's why we're here today.

The last matter is the matter that was talked about in a handful of different contexts, and that is the economic benefit of noncompliance. As Clay mentioned, there are two ways of complying with the General Order, and one way of complying with the Board's directive is it's not a part of the General Order. Under the General Order you can either deploy your own monitoring well network and pay the cost of drilling those wells, of monitoring those wells, of sampling those wells on a regular basis, or you can participate in the Regional Monitoring Coalition that the Dairy Industry has set up. That is a pooled resource that basically says you don't have to monitor every single dairy, we've got a few monitoring wells installed at a few dairies, we think that's representative of the broad swath of practices that are employed at dairies throughout the

Central Valley, and if you pay into that pool, and that's that $900 and some amount, the Annual Reporting requirements won't require you to drill your own monitoring wells and sample those wells. That is where the economic benefit of noncompliance, and that's really the nexus with this Order.

The other issues raised were the general cost of compliance for small dairies, really the Board was trying to give a hand out to a lot of dairies, to offer them that compliance route. We still will be requiring some dairies where problems are noted to do that individual monitoring because some small dairies are causing a problem and it merits further investigation.

And then the other option, of course, is to do that separate investigation all on your own, not paying into the pooled fund that does the monitoring. And that's another means of compliance and I think that's the ten-fold increased number that Mr. Sweeney was talking about.

There is of course another avenue for compliance. You could get your own individual Order with the Regional Board, that is an extraordinarily expensive way to go about it, and that frankly is something that the Agua Petitioners have been asking for because that is so expensive and it applies a lot of regulatory requirements that we're gradually easing in over the course of the life of the General Order. And that's it from a legal standpoint. I will see if Pamela has any additions to that from a policy perspective.

MS. CREEDON: Thank you, Patrick. This is Pamela Creedon. There are two issues, one that's really not relevant to the item, but I'll address it because they keep asking about it, but in 2007 during the hearing for the original Order, the Board seriously deliberated and considered a different standard for smaller dairies and it was rejected. That also was available to the Board in 2013 and again the Board did not opt to do something different for smaller dairies. So it was something as a deliberative act by the Board, there's discretion to do so, and they elected to keep the standards the same for all sized dairies. So that's really -- I know Mr. Sweeney does not agree with it, but it's not a point to question it now, it's been enforced on both Orders, it's not before the Board now to decide whether to change that Order. He needed to comply with the Order and he has elected to not comply with the Order for any requirement. So this is just for reporting. I'm certain Mr. Sweeney is not complying with any other directive of the Order if he's not complying with reporting. And we do have known data and information that suggests dairies are contributing nitrates to groundwater from their activities. So that's not the point here, and the point here is for the Board to consider this ACL, and whether it's an appropriate amount that would be sufficient to stop this behavior of Mr. Sweeney and compel him to start complying with the Order. And I would suggest or recommend to the Board that you seriously consider those factors and how it was assessed because I personally do not think it's sufficient to deter him in the future.

CHAIRMAN LONGLEY: So back to members of the Board. Your pleasure. Carmen, you're on.

BOARD MEMBER RAMIREZ: I'm on. I think that, you know, Mr. Sweeney, he knows that I appreciate him standing on principle, I don't agree with him, but I understand that he's rolling the dice on whether or not the court is going to rule in his favor, and so I understand why he's holding out, and so I don't know what the appropriate thing to say about that is, but I mean, the court is going to rule. At this point, I'm inclined to support the penalty as it is proposed by staff.

CHAIRMAN LONGLEY: Denise.

BOARD MEMBER KADARA: It's a little bit frustrating to hear Mr. Sweeney speak about the issues that he's facing, and I do understand it, but to not be in compliance, there have been many avenues of how this issue might have been addressed over the past years since 2009, and not submitting the documentation as staff has said, Mr. Rodgers, it is affecting the groundwater. There's no reporting. That's what we're here for, to make sure that those businesses that will have some impact on the groundwater, that the reporting, the monitoring, all of those things are in place to make sure that the water quality is protected. And to just neglect to do that because of the cost, there are options, as Legal staff has said, to join the Coalition, find a way to work out -- you said it yourself that it was cheaper to go with the Coalition, but you fought it because of your own personal position, and I understand that, but I'm in agreement that we need compliance for the dairies, and if 100 percent of the small ones, less than 300, are complying, and the medium 300, 700, 98 percent of them are complying, we think that's the role that Mr. Sweeney should be playing with his dairy. That's my comment.

CHAIRMAN LONGLEY: Thank you. Jon.

BOARD MEMBER COSTANTINO: Thank you. This is Jon. So I've got a couple of notes. One, I appreciate the legal answer, that's helpful, I appreciate the position, Mr. Sweeney, you're taking and I appreciate your daughters showing up to listen to Government in action. And you know, the question is, is the regulation fair and is it just, and to me fair means if it's out there and it's in effect, everybody should do what's required. And so from an enforcement point of view, you certainly have to comply if it's out there. Is it just? That's a question where, is it on the small dairies, is the cost reasonable? And I know we have estimates, but when I asked today about the number, it was kind of a soft thousand dollars number, and I think Karl even alluded that that wasn't sort of given with a whole lot of confidence. And we heard if you're in the Coalition, if you're not in the Coalition, if you do it yourself, there's fees, there's this, I basically don't need it now, but I would like to see, now that this thing has been in place for a while, what is the cost of compliance? I don't think that's something that should be outside of our knowledge base and if we can get something back to the Board maybe it's an average, or what, but what does it cost to comply with this? I think I would be in favor of that.

But as far as the item in front of us, I'd be supportive of the number because as far as I know it's 35 times what the compliance cost is, and that's at least a reasonable disincentive to not comply. So I would move the Order.

CHAIRMAN LONGLEY: So did I hear you say that you're moving the motion? You're making the motion to approve the ACL? Am I correct?

BOARD MEMBER COSTANTINO: Yes.

CHAIRMAN LONGLEY: And do I have a second?

BOARD MEMBER KADARA: I so move.

CHAIRMAN LONGLEY: Denise seconded it. I think my position is pretty clear, my comments during this hearing. The cost of farming today are certainly much greater than they were in the past, a lot more regulation, but in our particular case we're concerned about our groundwater basin, and the eastern part of Tulare County that has soils which have a very close connection to a shallow groundwater, the impacts can be pretty quick. And we know that in that same area we have a lot of disadvantaged communities that have had to drill mobile wells and sometimes they can't even find good water because of nitrate contamination. There's testimony to how fragile that aquifer is and how closely connected it is to actions that take place on the surface, the offset of that, of course, would be many parts of the west side of the valley where there are clays, and there is good isolation from the groundwater. But it's nice to have dairies on the east side, you want your animals to not be standing in mud and in clay, certainly. Good drainage is important.

So I too support the Order, and with that I will ask the roll to be called.

MALE VOICE: Ms. Kadara - Yes; Dr. Longley - Aye; Board member Costantino - Aye; Board member Ramirez - Yes.

Motion carries.

CHAIRMAN LONGLEY: Thank you very much. Let's have you back here at a quarter to three, and we'll move on to Item 9.

TRANSCRIBER'S CERTIFICATE

I do hereby certify that the testimony in the foregoing hearing was taken at the time and place therein stated; that the testimony of said witnesses were transcribed by me, a certified transcriber and a disinterested person, and was under my supervision thereafter transcribed into typewriting.

And I further certify that I am not of counsel or attorney for either or any of the parties to said hearing nor in any way interested in the outcome of the cause named in said caption.

IN WITNESS WHEREOF, I have hereunto set my hand this 23rd day of June, 2015.

Karen Cutler

Karen Cutler
Certified Transcriber
AAERT No. CET**D-723

CA.GOV

Home » Water Issues » Programs » Nitrate Project » Nitrate Tool

Is My Property Near a Nitrate-Impacted Water Well?

Over 95% of Californians receive safe drinking water from their public water system. This interactive tool is intended for private domestic well owners to evaluate if their well is near a nitrate-impacted well.

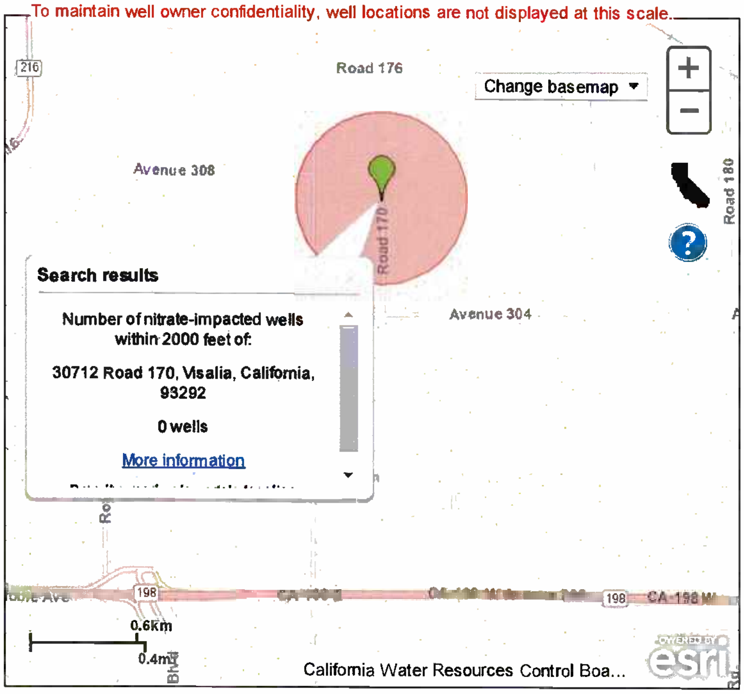
If your location is not within 2,000 feet of a nitrate-impacted well, the State Water Board still recommends that you test your domestic well annually by a certified drinking water laboratory. Since the availability of groundwater data is limited, and domestic wells are not regulated, domestic well water quality is largely unknown.

Nitrate in Groundwater Frequently Asked Questions

☐ Show all sampled wells

Zoom to an address

To maintain well owner confidentiality, well locations are not displayed at this scale.



(Updated 12/8/14)

Water Boards
Enforcement News

Central Valley Regional Water Quality Control Board
http://www.waterboards.ca.gov/centralvalley/

Visalia Dairy Fined $34,650 for Failing to Provide Annual Report to Assess the Impacts of Dairy Operations on Water Quality

For Immediate Release
June 12, 2015

Contact: Doug Patteson
Phone: (559) 445-5116

SACRAMENTO - The Central Valley Regional Water Quality Control Board adopted an Administrative Civil Liability Order imposing a penalty of $34,650 against the Sweeney Dairy located near the City of Visalia for failure to file an annual report. This amount is an increase over previous penalties imposed on the Sweeney Dairy for failure to submit annual reports in prior years.

The Administrative Civil Liability Order states that James and Amelia Sweeney, owners of the Sweeney Dairy, failed to file a 2013 annual report. All dairies regulated by the Reissued Waste Discharge Requirements General Order for Existing Milk Cow Dairies (Dairy General Order) are required to submit annual reports. These reports contain information the Central Valley Water Board needs to assess potential impacts on water quality from dairy operations.

The Dairy General Order, first adopted by the Regional Board in 2007, requires dairies to handle waste in ways that preserve water quality. The Dairy General Order contains a number of requirements, including standards for manure and dairy wastewater storage, and criteria for the application of manure and dairy wastewater to cropland as fertilizer. The Dairy General Order also contains reporting requirements for regulated dairies, including the submission of an annual report. Failure to submit the required report is a violation of the Dairy General Order.

"Annual reports are the cornerstone of our Dairy General Order. Annual reports are one of the primary tools we use to ensure that water quality is protected" said Clay Rodgers, Assistant Executive Officer for the Central Valley Water Board. "In assessing this penalty our Board recognized that running a dairy comes with the responsibility of complying with waste discharge requirements, including submitting the required documents."

The Central Valley Regional Water Quality Board is a California state agency responsible for the preservation and enhancement of water quality. For more information on the Central Valley Water Board, visit the homepage at: http://www.waterboards.ca.gov/centralvalley

The State Water Boards are now on Twitter! *Follow us at: https://twitter.com/CaWaterBoards*

###

THE SENTINEL

BREAKING: Leprino milk supplier fined $34,650

[illegible] • STAFF REPORTS

A Tulare County dairy that supplies milk to Leprino Foods in Lemoore has been fined $34,650 for allegedly violating water quality reporting requirements.

The Central Valley Regional Water Quality Control Board said in a written statement that the amount imposed on Sweeney Dairy was an increase over previous fines levied against the business for failing to submit reports in previous years.

A rule adopted in 2007 requires dairies to apply water quality standards to manure, dairy waste water storage and the application of manure fertilizer to cropland. The rule also requires dairies to submit annual reports to the board.

"In assessing this penalty, our board recognized that running a dairy comes with the responsibility of complying with waste discharge requirements, including submitting the required documents," said Clay Rodgers, the board's assistant executive officer, in a written statement.

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IN BRIEF

Tulare County dairies fined $34,650

A dairy north of Farmersville has been fined $34,650 by a state agency after being accused of failing to file an annual report on the potential effects the dairy operation may have on groundwater and surface water in the area.

The Central Valley Regional Water Quality Control Board levied the fine through an administrative civil liability order against Sweeney Dairy. Officials from the agency said the amount is an increase over prior penalties imposed on the Sweeney Dairy for failing to submit annual reports in prior years.

In the latest matter, dairy owners James and Amelia Sweeney are accused of failing to file their 2013 annual report, as all dairies regulated by the Reissued Waste Discharge Requirements General Order for Existing Milk Cow Dairies are required to submit these reports.

The general order was adopted by the regional board in 2007, requiring dairies to handle waste in ways that preserves water quality in the areas around them. This includes standards for manure and dairy wastewater storage, along with setting criteria for the application of manure and dairy wastewater used as fertilizer on crops grown by dairy operations.

Other regulations are in the order, including requirements for regulated dairies to submit annual reports.

"Annual reports are the cornerstone of our Dairy General Order. Annual reports are one of the primary tools we use to ensure that water quality is protected" Clay Rodgers, assistant executive officer for the Central Valley Water Board, said in a written statement.

"In assessing this penalty, our board recognized that running a dairy comes with the responsibility of complying with waste discharge requirements, including submitting the required documents," it continues.

See BRIEFS, Page 5A

Briefs

Continued from Page 3A

For more information on the Central Valley Water Board, go online to *www.waterboards.ca.gov/centralvalley* or follow the agency on Twitter.

—David Castellon

Meeting will be held in close session to discuss assignment

The Visalia Unified School District will hold a special closed-session meeting Tuesday night.

An agenda for the meeting that was released Friday states only that the school board members will discuss an employee assignment or reassignment, but the identity of that employee wasn't disclosed, nor was the nature of the job.

Public agencies aren't required to disclosed such information about employment issues, nor do the meetings have to occur in public.

The meeting is scheduled to begin at 6 p.m. at the district's board room, 5000 W. Cypress Ave. See the agenda online at *http://bit.ly/1ScghMy*.

— David Castellon

Dairy fined for missing report

The Central Valley Regional Water Quality Control Board has issued an administrative penalty of $34,650 against Sweeney Dairy in Visalia.

The dairy was fined for failing to file a 2013 annual report on how it handles its waste water. The report is required by law and is designed to preserve the state's water quality. State officials said it has issued penalties against the dairy before for failing to submit annual reports.

The Central Valley Regional Water Quality Contol Board is a state agency responsible for the preservation and enhancement of water quality.

Subject: Fwd: Sweeney Dair A Req re 2013 Order

---------- Forwarded message ----------
From: **Japlus3** <japlus3@aol.com>
Date: Fri, Oct 11, 2013 at 5:21 PM
Subject: Sweeney Dairy
To: crodgers@waterboards.ca.gov

Clay Rodgers,

I would like to make a public records request for all material considered in the new /revised dairy general order that was adopted on October 3, 2013. I would appreciate it as soon as possible. Thank you.

Jim Sweeney

Subject: Fwd: Sweeney Dai :A 2013 Order

---------- Forwarded message ----------
From: **Japlus3** <japlus3@aol.com>
Date: Thu, Oct 24, 2013 at 10:20 AM
Subject: Fwd: Sweeney Dairy
To: lasallem@lightspeed.net

-----Original Message-----
From: Patteson, Doug@Waterboards <Doug.Patteson@waterboards.ca.gov>
To: Japlus3 <japlus3@aol.com>
Cc: Sholes, David@Waterboards <David.Sholes@waterboards.ca.gov>; Cregan, Alan@Waterboards <Alan.Cregan@waterboards.ca.gov>; Pulupa, Patrick@Waterboards <Patrick.Pulupa@waterboards.ca.gov>; Mayer, Alex@Waterboards <Alex.Mayer@waterboards.ca.gov>; Rodgers, Clay@Waterboards <Clay.Rodgers@waterboards.ca.gov>
Sent: Sat, Oct 12, 2013 3:46 pm
Subject: Re: Sweeney Dairy

Mr. Sweeney

We have previously provided you with the administrative record for adoption of Order R5-2007-0035. So, I assume you are requesting the record only for adoption of the reissued Dairy General Order adopted on 3 October 2013. Could you please confirm that? We will calculate the cost of providing that and get back to you as soon as possible. Thanks.

Doug Patteson

Sent from my iPhone

On Oct 12, 2013, at 10:32 AM, "Rodgers, Clay@Waterboards" <Clay.Rodgers@waterboards.ca.gov> wrote:

> **From:** Japlus3 [mailto:japlus3@aol.com]
> **Sent:** Friday, October 11, 2013 5:21 PM
> **To:** Rodgers, Clay@Waterboards
> **Subject:** Sweeney Dairy
>
> Clay Rodgers,
>
> I would like to make a public records request for all material considered in the new /revised dairy general order that was adopted on October 3, 2013. I would appreciate it as soon as possible. Thank you.
>
> Jim Sweeney