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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.

¹The 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 an 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

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

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.

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.

¹⁰Hoard'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 showing¹¹ 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.

¹¹Information 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 liability¹² of "at least" \$12,012.00, then adjusted this amount upward to \$34,650.00 based upon the Sweeneys' failure to file the earlier Annual Reports required under the 2013 "Reissued" Order¹³ 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

¹²Letter 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."

¹³At 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 or 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.

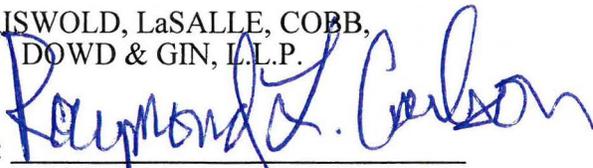
I. CONCLUSION.

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:


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

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

¹⁵The 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

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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.

(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.

(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.

(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.


KATIE ASKINS

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SERVICE LIST
ADMINISTRATIVE CIVIL LIABILITY COMPLAINT R5-2015-0506

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E-mail: patrick.pulupa@waterboards.ca.gov

Prosecution Team

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11020 Sun Center Drive, Suite 200
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Clay Rodgers, Assistant Executive Officer
Central Valley Regional
Water Quality Control Board
1685 E Street
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Doug Patteson, Supervising WRC Engineer
Central Valley Regional
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Dale Essary, Senior WRC Engineer
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Central Valley Regional
Water Quality Control Board
April 30, 2015
Page 27

Naomi Kaplowitz, Staff Counsel
State Water Resources Control Board
Office of Enforcement
Physical Address:
1001 I Street
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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
- 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

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"

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FILED
ENDORSED
APR 17 2013
Frank Timmerman
By **FRANK TIMMERMAN**
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 17 2013
39
CIVIL

[Proposed] Writ of Mandate

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

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

3 1. 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
5 compliance with, the State's anti-degradation policy (Resolution No. 68-16), as interpreted by the
6 Court of Appeal in its opinion, including, without limitation, adequate findings that any allowed
7 discharges to high quality water:

- 8 a. Will be consistent with maximum benefit to the people of the State;
9 b. Will not unreasonably affect present and anticipated beneficial use of
10 the affected waters;
11 c. Will not result in water quality less than that prescribed in applicable
12 water quality objectives; and
13 d. That waste-discharging activities will be required to use the best
14 practicable treatment or control of the discharge necessary to assure that:
15 i. A pollution or nuisance will not occur, and
16 ii. The highest water quality consistent with the maximum benefit
17 to the people of the State will be maintained.

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

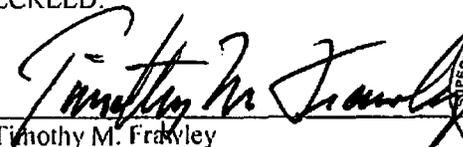
20 3. Plaintiffs/Petitioners shall recover their costs on appeal in the amount of
21 \$3,485.63, as reflected in the Notice of Amended Costs on Appeal, filed February 22, 2013.

22 4. The Court retains jurisdiction to consider any motions for an award of
23 attorneys' fees.
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IT IS SO ORDERED, ADJUDGED, AND DECREED.

Dated: April 17, 2013


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

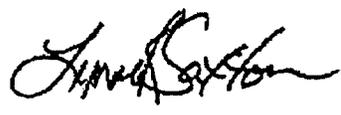


APPROVED AS TO FORM:

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

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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: _____

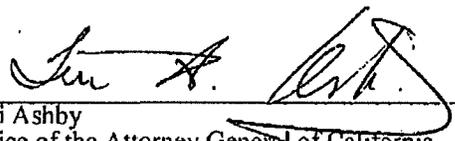
Laurel Firestone
Community Water Center
Attorney for Petitioners Asociacion De Gente Unida
El Agua and Environmental Law Foundation

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.

Lynne Saxton, Esq.
Re: AGUA v. RWQCB
April 9, 2013
Page 2

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

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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

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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.



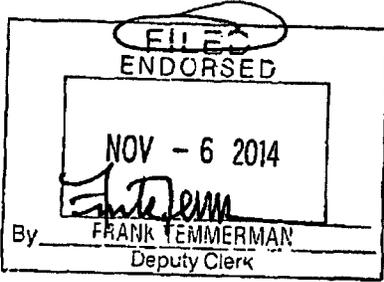
Nicole Feliciano
DECLARANT

Service List

<p>1 2 3 4 5 6</p> <p>Lynne Saxton Saxton & Associates 912 Cole Street, #140 San Francisco, California 94117 Telephone: (415) 317-6713 Email: lynne@saxtonlegal.com</p>	<p><i>Attorney for Petitioners AGUA, ELF</i></p>
<p>7 8 9 10 11</p> <p>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</p>	<p><i>Attorney for Respondent California Regional Water Quality Control Board, Central Valley Region</i></p>
<p>12 13 14 15 16 17 18</p> <p>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</p>	<p><i>Attorney for Intervenor CARES</i></p>
<p>19 20 21 22</p> <p>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</p>	<p><i>Attorney for Intervenor CARES</i></p>
<p>23 24 25 26 27 28</p> <p>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</p>	<p><i>Attorneys for Petitioners AGUA</i></p>

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"



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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:

1 Lynne R. Saxton (State Bar No. 226210)
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4 San Francisco, CA 94117
5 Tel: (415) 317-6713
6 Email: lynne@saxtonlegal.com
7 Attorneys for Petitioners Environmental Law Foundation and
8 Asociacion de Gente Unida por el Agua

6 Laurel Firestone (State Bar No. 234236)
7 COMMUNITY WATER CENTER
8 909 12th Street, Suite 200
9 Sacramento, CA 95814
10 Tel. (559) 789-7245
11 Fax (916) 706-2731
12 E-mail: laurel.firestone@communitywatercenter.org
13 Attorney for Petitioner Asociacion de Gente Unida por el Agua

11 Phoebe Seaton (State Bar No. 238273)
12 LEADERSHIP COUNSEL FOR JUSTICE AND ACCOUNTABILITY
13 764 P Street, Suite 12
14 Fresno, CA 93721
15 Telephone: (559) 369-2790
16 Email: pseaton@leadershipcounsel.org
17 Attorney for Petitioner Asociacion de Gente Unida por el Agua

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

5
6 WHEREAS, the Writ of Mandate directed the Regional Board to reissue the Permit only after
7 application of, and compliance with, the State's anti-degradation policy as interpreted by the Court
8 of Appeal in its decision in *Asociacion de Gente Unida por el Agua v. Central Valley Regional*
9 *Water Quality Control Board* (2012) 20 Cal.App.4th 1244, and

10
11 WHEREAS, the Court directed the Regional Board to reissue the permit only after including,
12 without limitation, adequate findings that any allowed discharges to high quality water (1) will be
13 consistent with the maximum benefit to the people of the State, (2) will not unreasonably affect
14 present and anticipated beneficial use of the affected waters, (3) will not result in water quality
15 less than that prescribed in applicable water quality objectives, (4) that waste-discharging
16 activities will be required to use the best practicable treatment or control of the discharge
17 necessary to assure that (a) a pollution or nuisance will not occur, and (b) the highest water quality
18 consistent with the maximum benefit to the people of the State will be maintained, and

19
20 WHEREAS, the Writ of Mandate further commanded the Regional Board to file a Return within
21 180 days, and

22
23 WHEREAS, on October 3, 2013, the Regional Board rescinded the Permit and issued Order R5-
24 2013-0122, Reissued Waste Discharge Requirements General Order For Existing Milk Cow
25 Dairies ("General Order"), and

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

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

14
15 WHEREAS, on November 5, 2013, Petitioners filed a petition to the State Water Resources
16 Control Board (“State Board”) under Water Code § 13320 and California Code of Regulations,
17 title 23, §§ 2050-68 challenging the General Order as adopted by the Respondents, which included
18 among other issues, the three issues raised above, and

19
20 WHEREAS, Petitioners’ Response to the Return to the Writ of Mandate asked the Court to stay
21 any further action on the Regional Board’s return until the completion of administrative
22 procedures before the State Board, and

23
24 WHEREAS, Petitioners stated that if the State Board corrected the perceived deficiencies,
25 Petitioners would so inform the Court and the case could be terminated and further stated that if
26 the State Board does not correct the perceived deficiencies in the General Order, the Petitioners

27
28

1 would seek a further order from the Court, and

2

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

6

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

9

10 WHEREAS, on October 10, 2014, the Court held a Case Management Conference in Department
11 29, having heard argument from all parties and good cause appearing,

12

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

17

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

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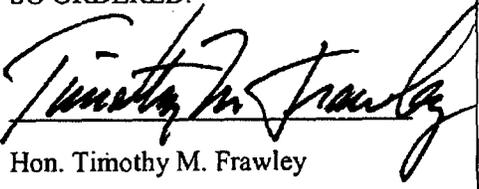
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Dated: Nov. 6, 2014

SO ORDERED:



Hon. Timothy M. Frawley

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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

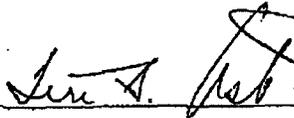
Theresa A. Dunham
Somach Simmons & Dunn
Attorneys for Intervenor CARES

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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

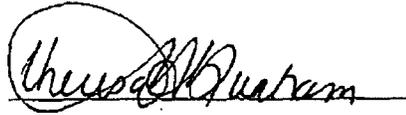
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Approved as to form:



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

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PROOF OF SERVICE

I, Nicole Feliciano, hereby declare:

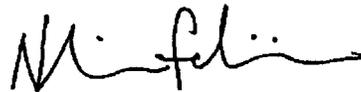
I am over the age of 18 years and am not a party to this action. I am employed in the county of Alameda. My business address is 1736 Franklin Street, Ninth Floor, Oakland, CA 94612.

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

1 2 3 4	Lynne Saxton Saxton & Associates 912 Cole Street, #140 San Francisco, California 94117 Telephone: (415) 317-6713 lynne@saxtonlegal.com	<i>Attorney for Petitioners AGUA, ELF</i>
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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 "C"

1-1-2008

When Does Nitrate Become a Risk for Humans?

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When Does Nitrate Become a Risk for Humans?

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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.

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

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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 haemoglobin 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 thyroid 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 than 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 (Dyckhuizen 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 carcinogenicity 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 contradictory 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 N₂ 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 N₂-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"

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

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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 $\delta^{15}\text{N}$ values (4.3–61‰), and $\delta^{18}\text{O}$ values (–4.5–24.5‰) that plot with $\delta^{18}\text{O}/\delta^{15}\text{N}$ 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 herd 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 ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) 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 $\delta^{15}\text{N}$ at the University of Waterloo. Analytical uncertainty (1 σ) is 0.3‰ for $\delta^{15}\text{N}$ of nitrate and 0.5‰ for $\delta^{18}\text{O}$ 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

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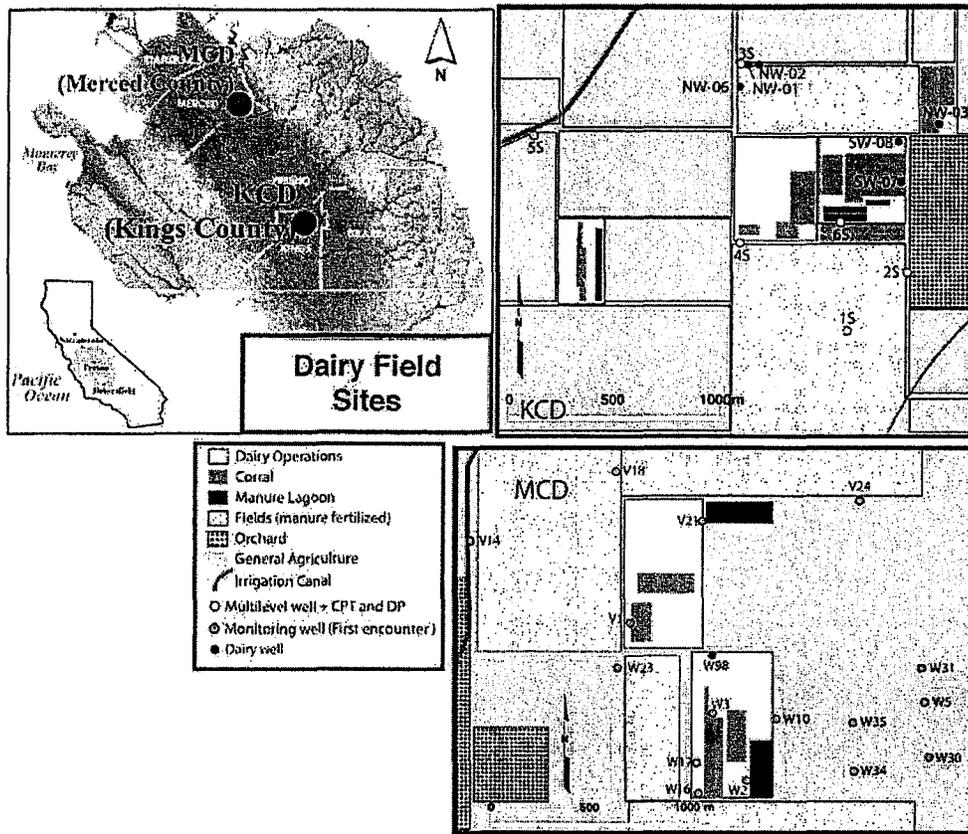


FIGURE 1. Location of dairy study sites, and generalized maps of each dairy showing sample locations relative to lagoons and dairy operations.

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

Noble Gases and $^3\text{H}/^3\text{He}$ 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 tritogenic helium ($^3\text{He}_{\text{trit}}$):

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

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

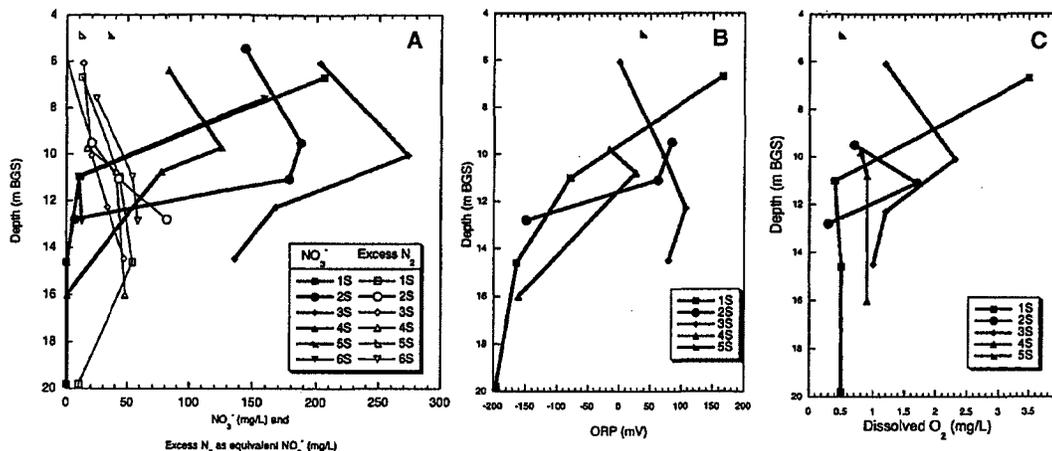


FIGURE 2. (A) Average excess N_2 and nitrate concentrations, (B) oxidation-reduction potential (ORP), and (C) dissolved oxygen in multilevel monitoring wells at the KCD site.

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:

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

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

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

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} cm³(STP)/g H₂O for KCD and 1.7×10^{-3} cm³(STP)/g H₂O 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

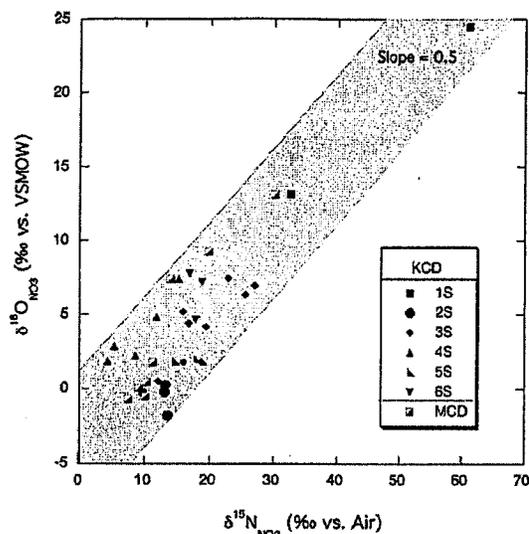


FIGURE 3. Oxygen and nitrogen isotopic composition of nitrate in dairy groundwater from multilevel monitoring wells at KCD and first encounter wells at MCD. The shaded region indicates a slope of 0.5 for a range of starting compositions. Calculated slopes for linear fits to multilevel wells at KCD and 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 $\delta^{15}\text{N}$ value close to 5‰, but is enriched in ^{15}N to varying degrees due to volatile loss of ammonia, resulting in $\delta^{15}\text{N}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values for nitrate at the two dairies based on the average values for $\delta^{18}\text{O}$ of groundwater at each site (–12.6‰ at KCD and –9.9‰ at MCD). Based on this approach, the predicted initial values for $\delta^{18}\text{O}$ in nitrate are –0.7‰ at KCD and 1.1‰ at MCD. Samples with the lowest nitrate $\delta^{15}\text{N}$ values have $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$ values (0–5‰) and $\delta^{18}\text{O}$ values around 23‰ (39).

Denitrification drives the isotopic composition of the residual nitrate to higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ vs $\delta^{15}\text{N}$ diagram (34). Nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 ($f = C/C_{\text{initial}}$), the initial $\delta^{15}\text{N}$, and the fractionation factor (α) for denitrification:

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

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

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

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^- :

$$f = C_{\text{NO}_3^-} / (C_{\text{NO}_3^-} + C_{\text{excess N}_2})$$

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 $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ 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.

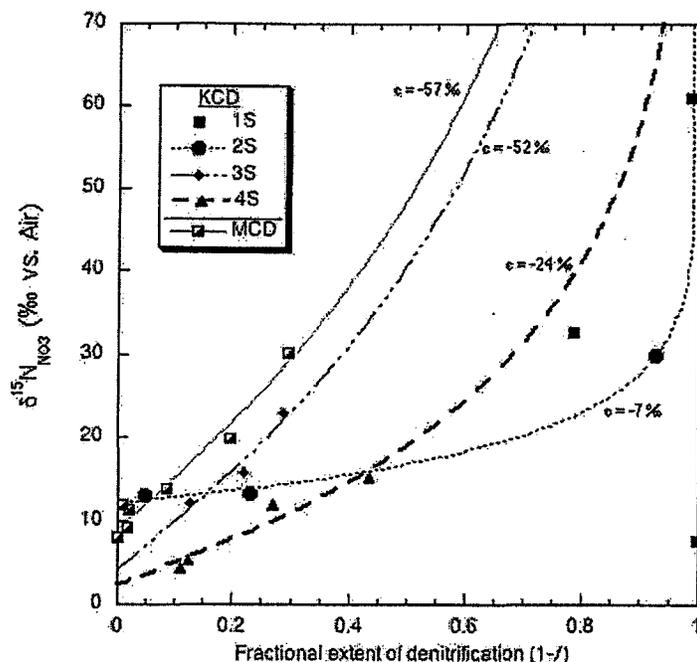


FIGURE 4. Nitrate $\delta^{15}\text{N}$ values plotted against the fractional extent of denitrification ($1 - f$) based on excess N_2 and residual nitrate. Enrichment factors (ϵ) are calculated by fitting the Rayleigh fractionation equation to data from three multilevel well sites at KCD and wells at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

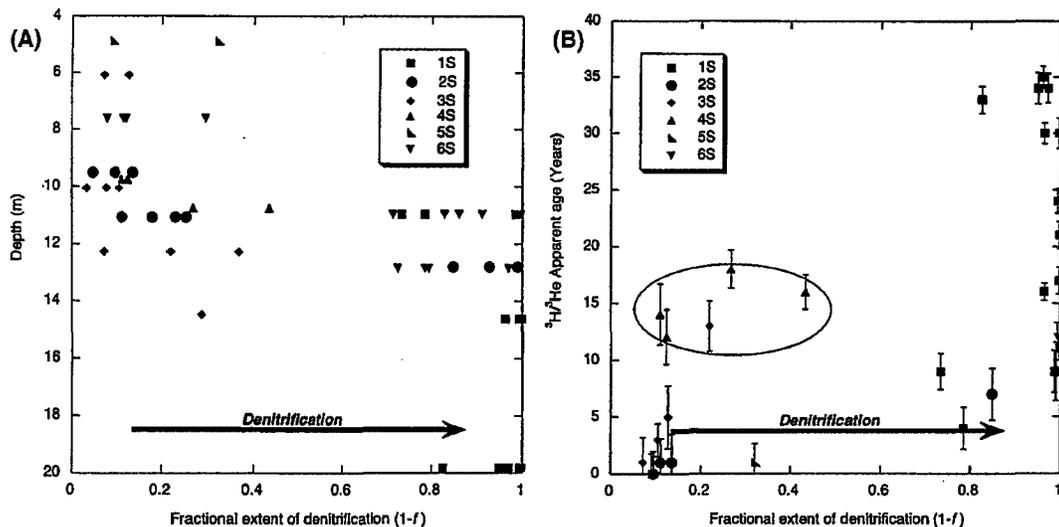


FIGURE 5. Sample depth (A) and $^3\text{H}/^3\text{He}$ apparent age (B) plotted against the fractional extent of denitrification ($1 - f$). Samples at two sites have experienced less denitrification than is typical for samples with $^3\text{H}/^3\text{He}$ apparent age > 8 years (circled, see text).

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 $^3\text{H}/^3\text{He}$ 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 $^3\text{H}/^3\text{He}$ 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 $^3\text{H}/^3\text{He}$ 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 $^3\text{H}/^3\text{He}$ 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 $^3\text{H}/^3\text{He}$ 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

Singleton et al, Saturated Zone Denitrification....

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. Esser¹, J. E. Moran¹, G. B. Hudson¹, W. W. McNab², and T. Harter³

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.

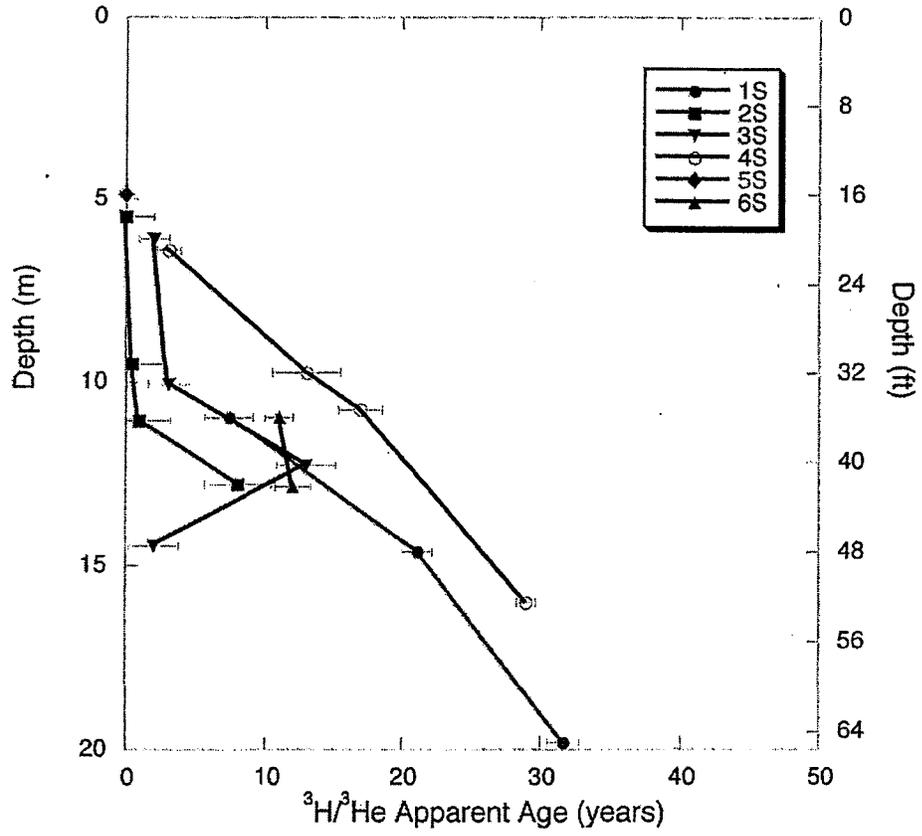


Figure S1. Groundwater $^3\text{H}/^3\text{He}$ apparent ages from multilevel monitoring wells at KCD. Error bars show analytical error.

Table S1. Chemical, dissolved gas, and isotopic compositions for multilevel groundwater monitoring wells and lagoons. Average values are given for wells sampled more than once. Excess N₂ 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)	δ ¹⁸ O H ₂ O (‰ SMOW)	δ ¹⁵ N NO ₃ ⁻ (‰ Air)	δ ¹⁸ O NO ₃ ⁻ (‰ SMOW)	³ H/ ⁴ He age (yr)	+/- (yr)	Excess air determined from Ne (cc STP/g)	Recharge Temp. from Xe (°C)	+/- (°C)	³ H 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	102	
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	
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			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	121
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	134
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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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

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November 2010

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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.

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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 | Upgrades to dairy
- Annual fees paid to RB5

A. Monthly Inspections/Service 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 fertilizer 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. CDFM 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 Pollution 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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California GAMA Program: Impact of Dairy Operations on Groundwater Quality

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Prepared in cooperation with the
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

**August 8, 2006 (Draft)
August 17, 2009 (Final)**

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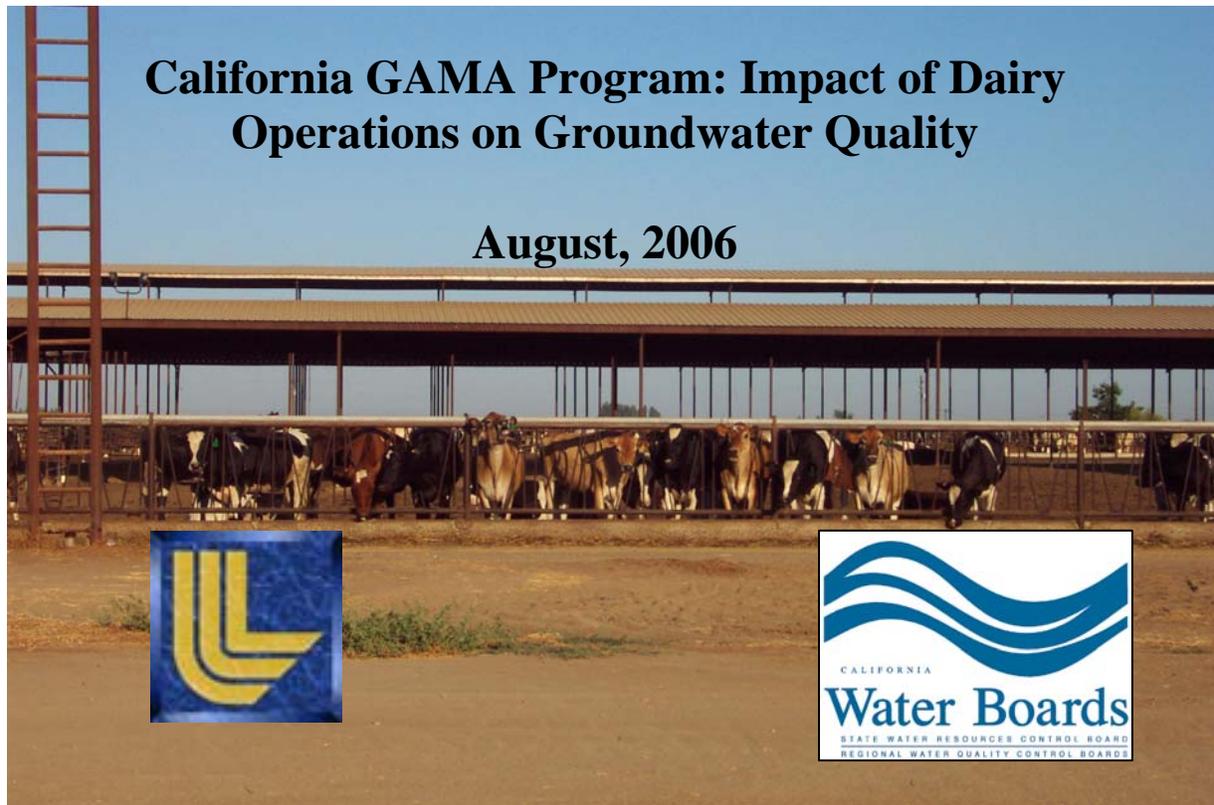
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LAWRENCE LIVERMORE NATIONAL LABORATORY

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California GAMA Program: Impact of Dairy Operations on Groundwater Quality

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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.

Appendix B: 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**, 753-758.

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 2×10^{-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 $\mu\text{S}/\text{cm}$) surface water from the Sierra Nevada is the main source of irrigation water.

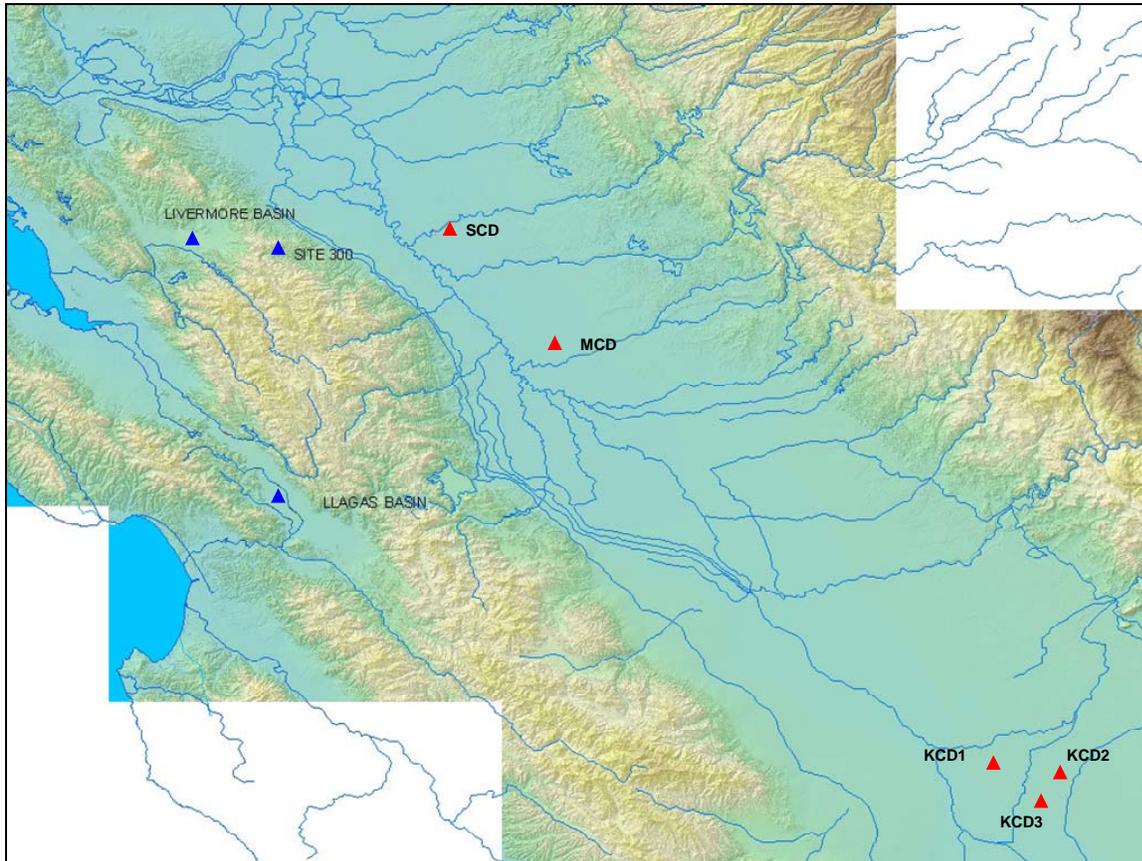


Figure 1. Dairy Field Sites in the Central Valley.

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 of 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.

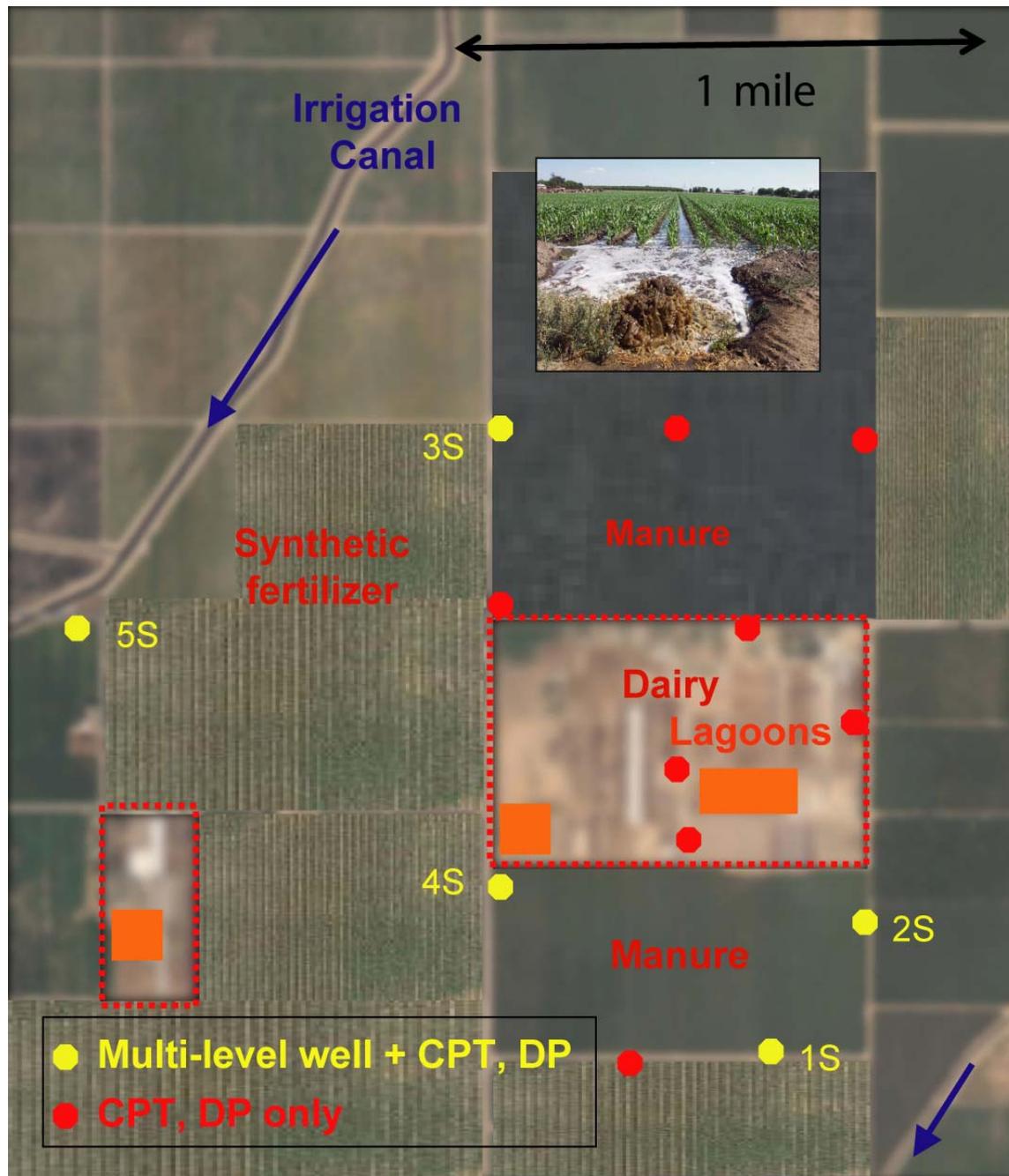


Figure 2. KCD1 Dairy Field Site.

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.

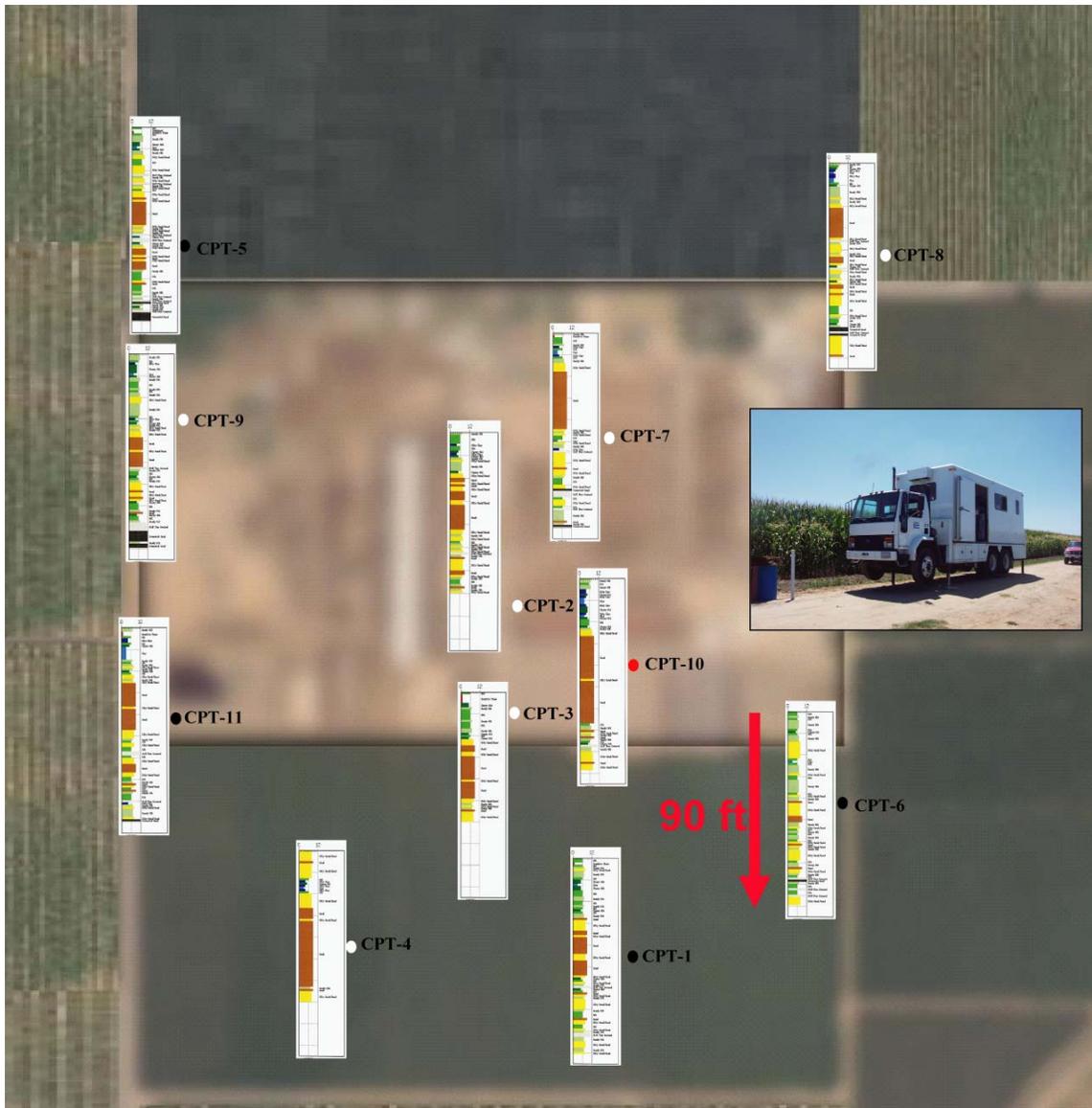


Figure 3. KCD1 field site with CPT/DP locations.

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.

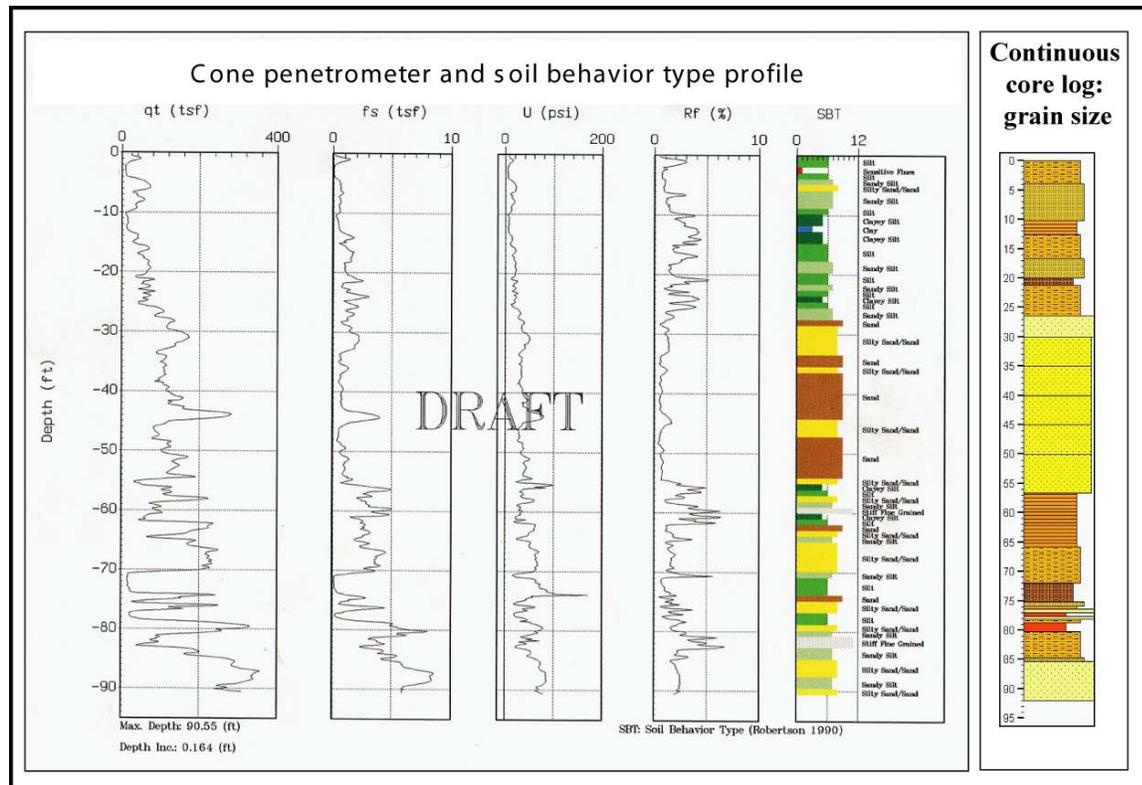


Figure 4. KCD Field Site CPT Logs.

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, electromagnetic 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 ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) 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 $\delta^{15}\text{N}$ at the University of Waterloo. Analytical uncertainty is 0.3 ‰ for $\delta^{15}\text{N}$ of nitrate and 0.5‰ for $\delta^{18}\text{O}$ of nitrate.

Isotopic compositions of hydrogen and oxygen in water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) 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 CO₂ 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 N₂)

Previous studies have used gas chromatography and/or mass spectrometry to measure dissolved N₂ 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 N₂ from denitrification in groundwater systems (BELLER et al., 2004).

Samples for N₂, O₂, Ar, CO₂ and CH₄ 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 CO₂ at mass 28 (N₂) is corrected based on calibration with CO₂-rich waters with known dissolved N₂, 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}):

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

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 redoxcline 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.

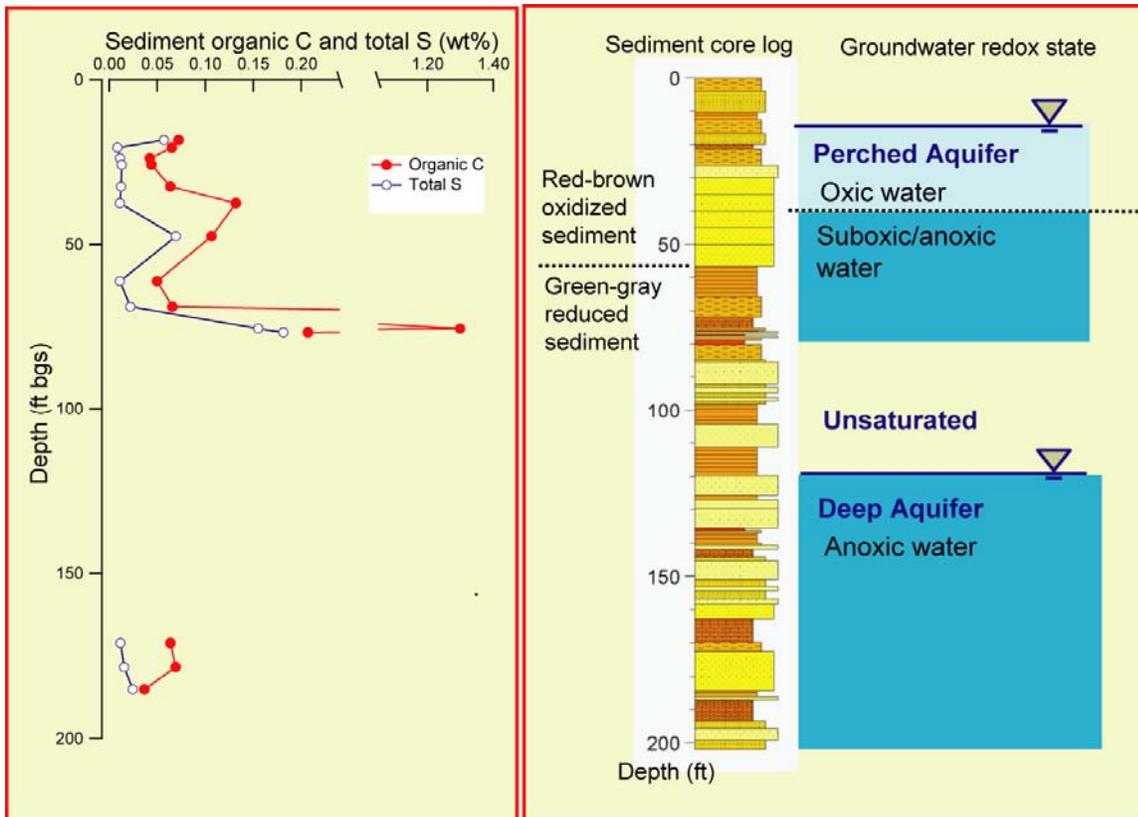


Figure 5. KCD1 Well Cluster 1 sediment composition, texture & groundwater oxidation state

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).

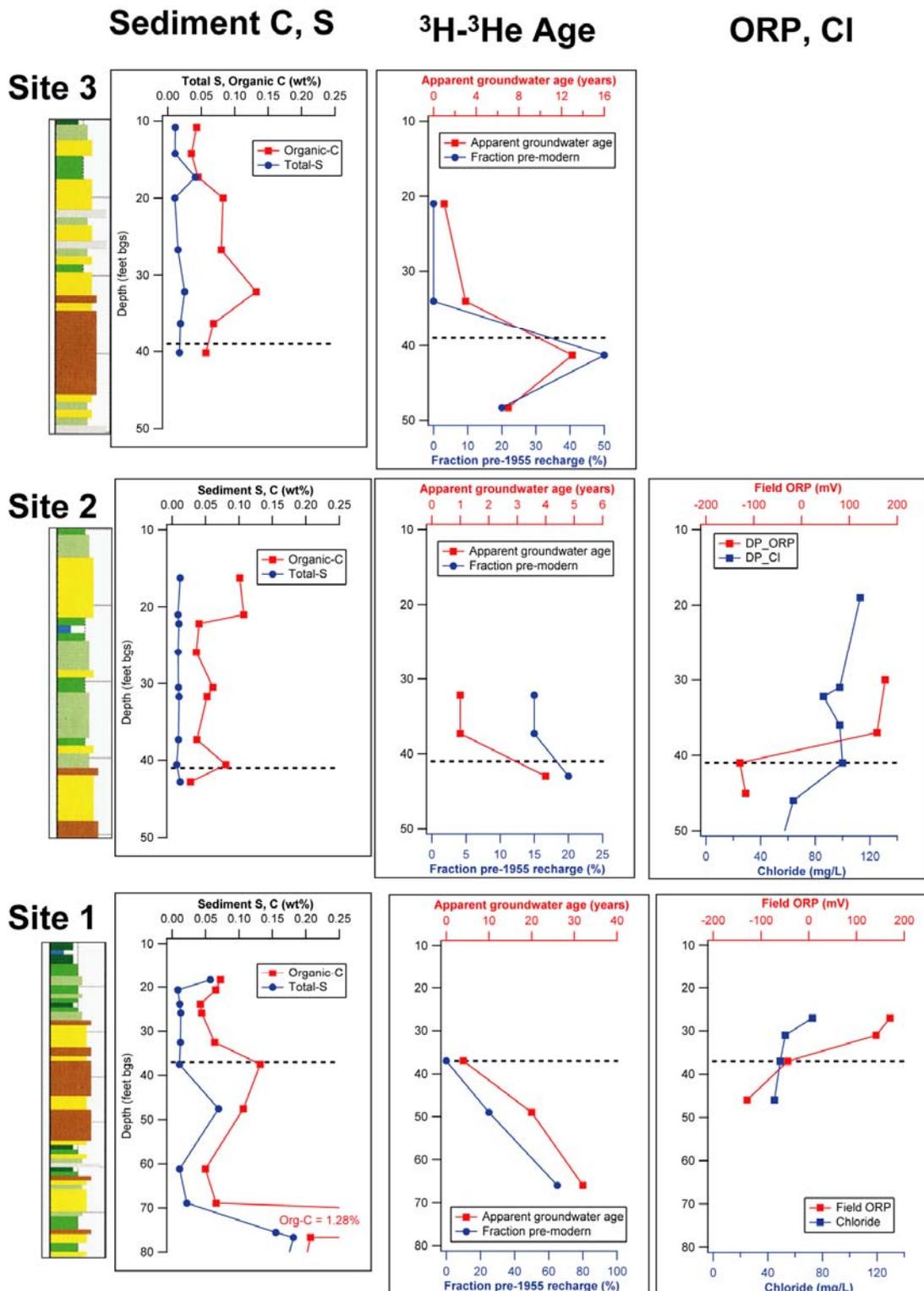


Figure 6. KCD1 depth profiles of sediment and water properties.

KCD1 soil behavior type, sediment organic carbon and total sulfur, ^3H - ^3He 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.

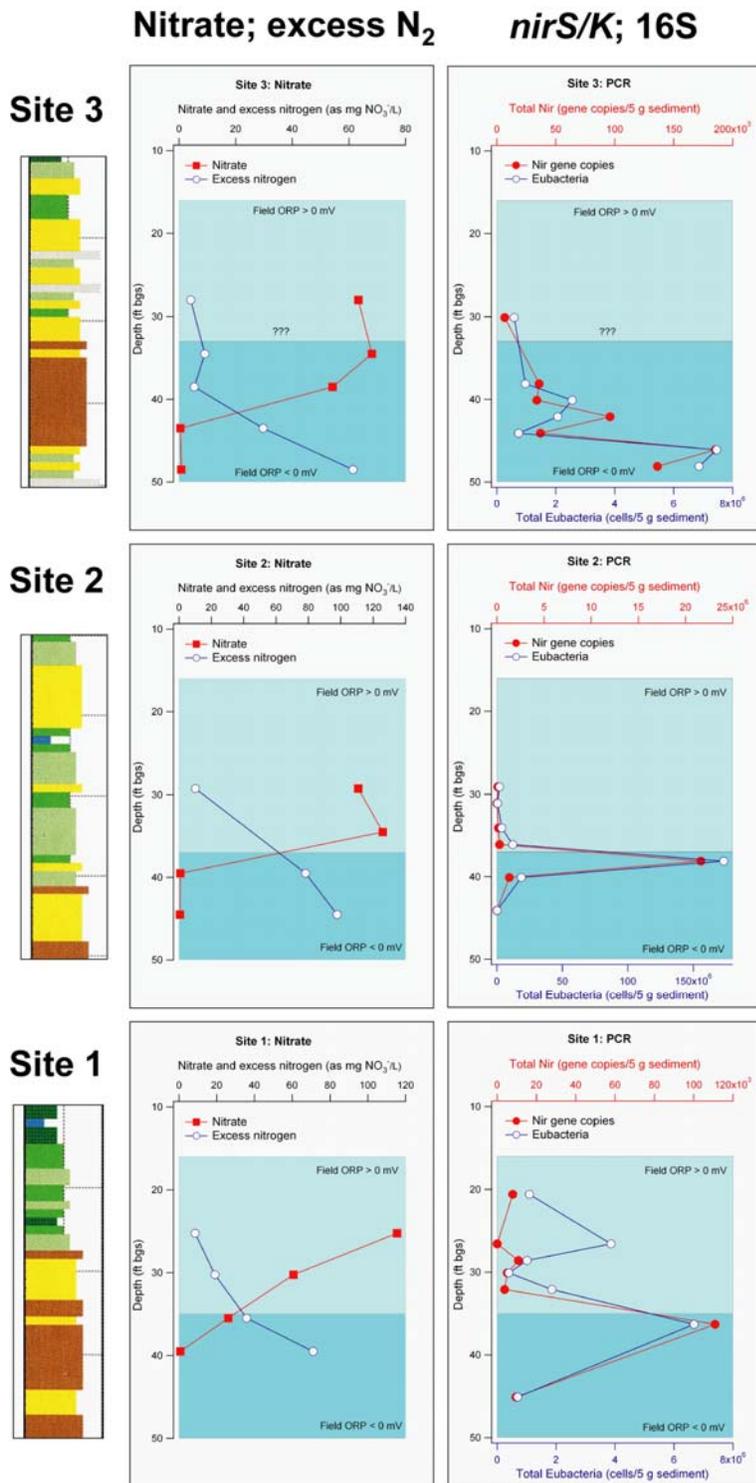


Figure 7. KCD1 depth profiles of nitrogen speciation and bacterial populations.

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 $^3\text{H}/^3\text{He}$ 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 $\delta^{15}\text{N}$ values (4.3–61 ‰), and $\delta^{18}\text{O}$ values (-4.5–24.5 ‰) that plot with a $\delta^{18}\text{O}/\delta^{15}\text{N}$ 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 ($\epsilon_{\text{N}} \approx -10\text{‰}$; $\epsilon_{\text{O}} \approx -5\text{‰}$) 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 ($\epsilon_{\text{N}} \approx -50\text{‰}$; $\epsilon_{\text{O}} \approx -25\text{‰}$).

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- $\delta^{15}\text{N}$ and $-\delta^{18}\text{O}$ (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 ($R^2 \sim 0.19$ 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.

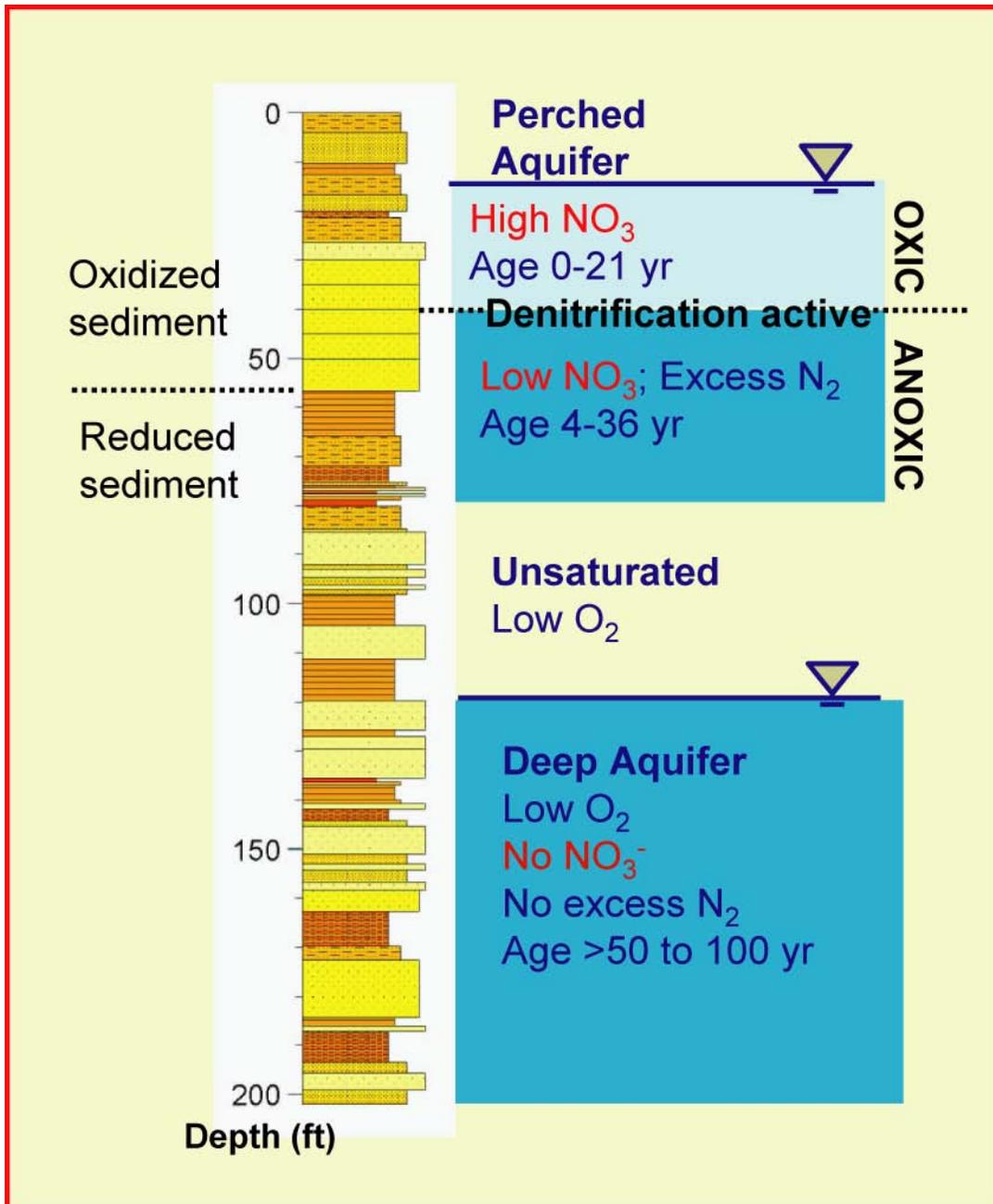


Figure 8. KCD1 site saturated-zone denitrification.

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 N₂ 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 be 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 (CO₂, CH₄, N₂, Ar, Ne). Modeling of geochemical processes occurring within the dairy site manure lagoons suggests substantial off-gassing of CO₂ and CH₄ 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.

Atmospheric Gas in Dairy Lagoon Water

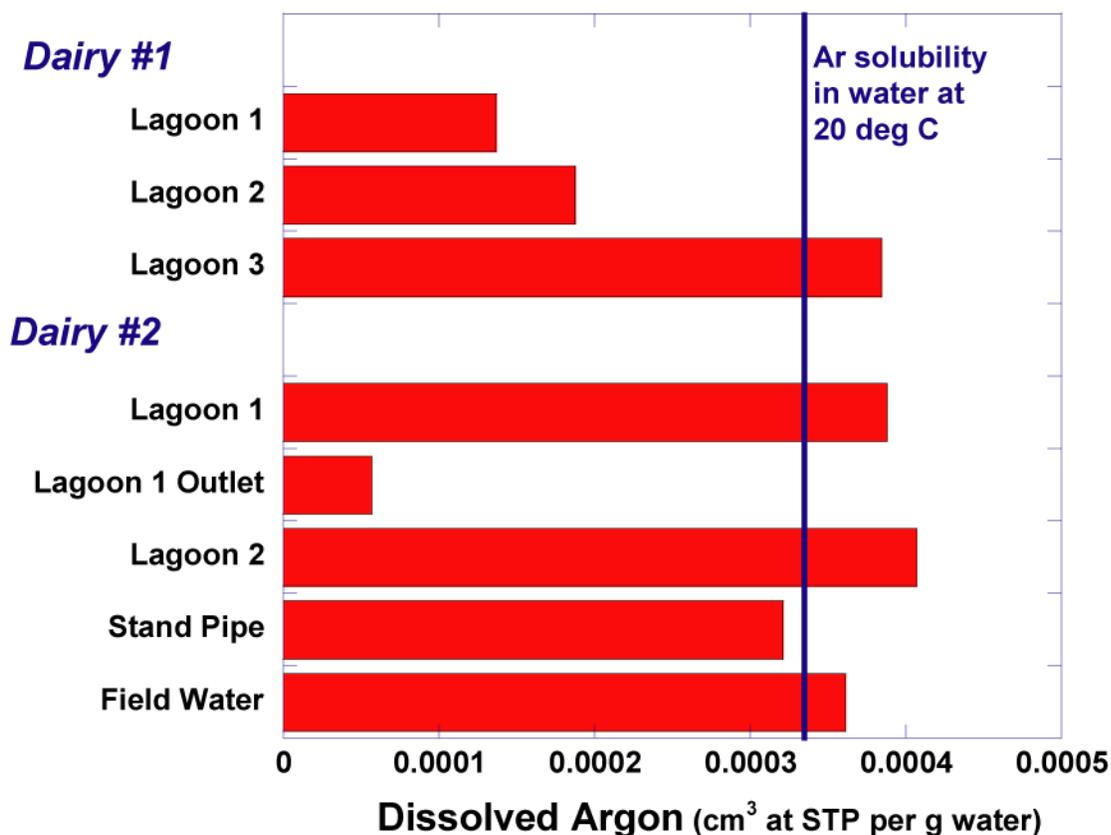


Figure 9. KCD1 and KCD2 manure lagoon dissolved argon content.

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.

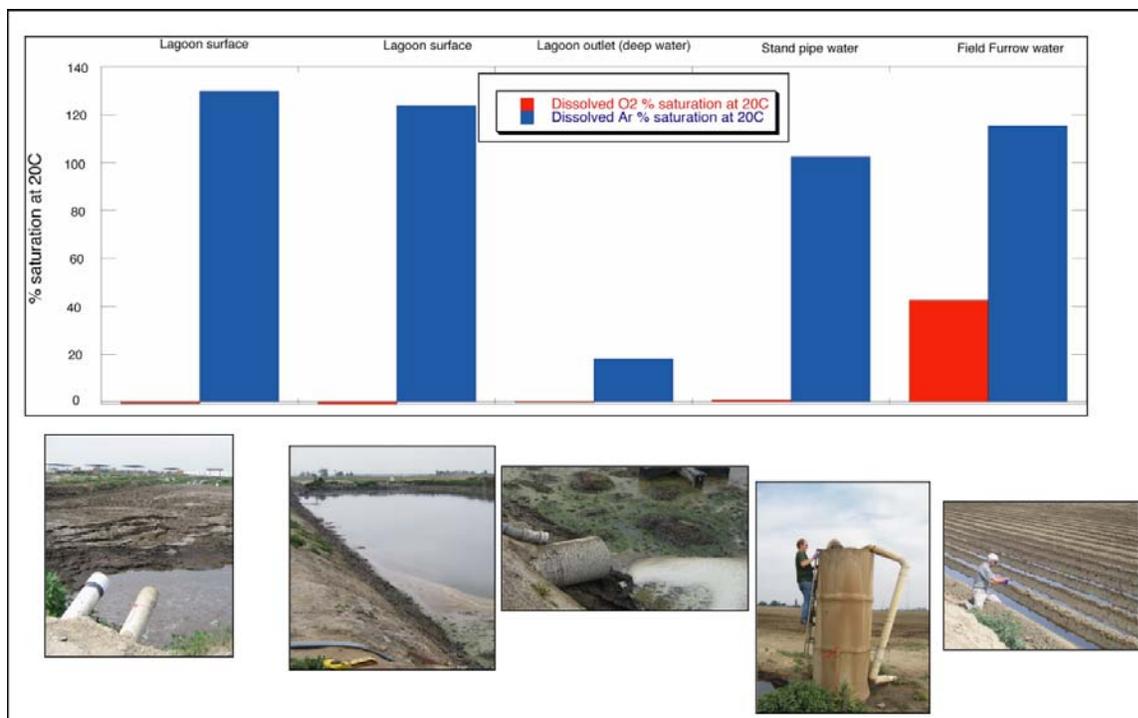


Figure 10. Dissolved argon and oxygen at KCD2.

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 ratios 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).

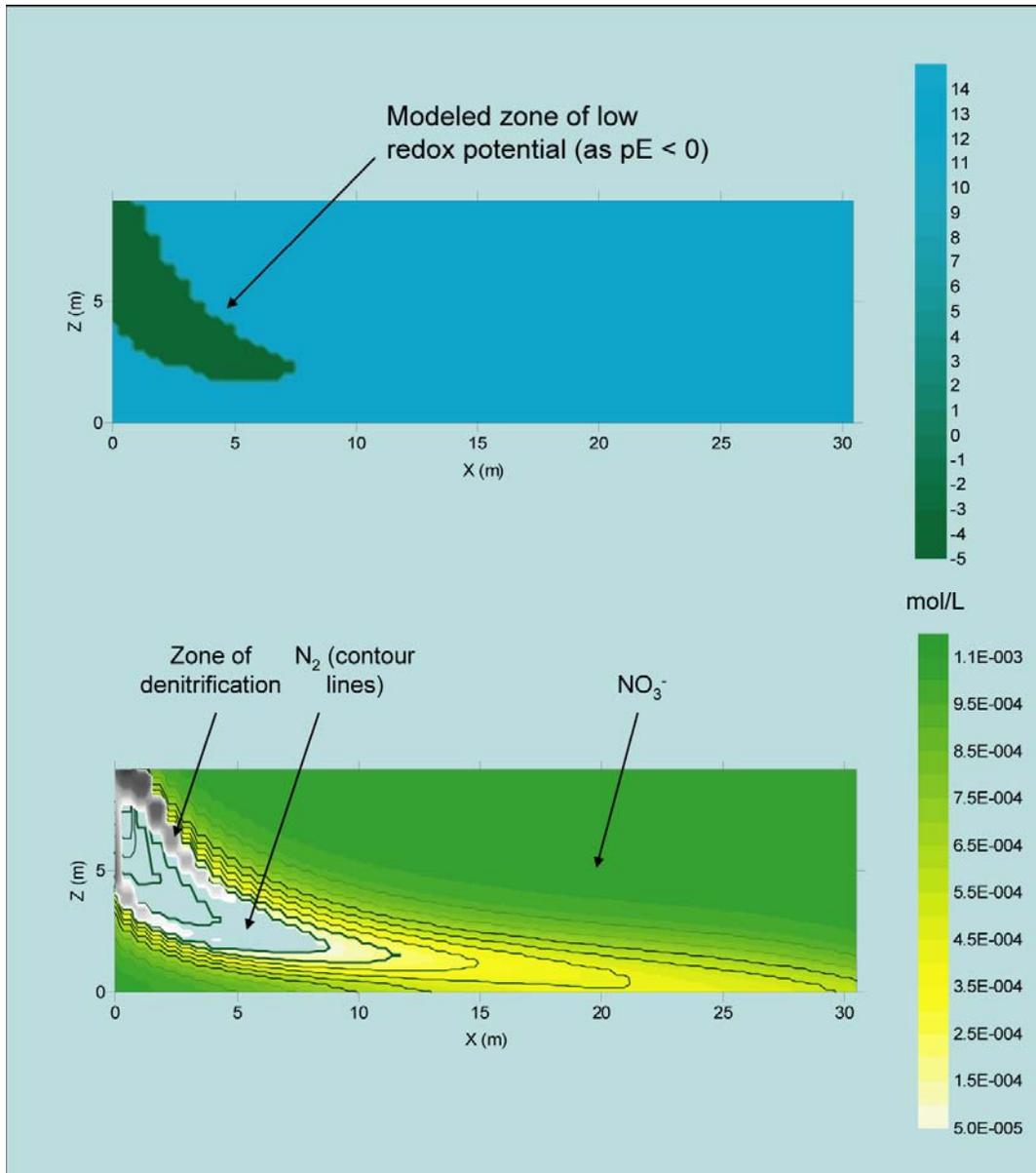


Figure 11. Simulation of transport of lagoon seepage through groundwater.

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 appear 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 NH_4^+ ; ~ 0.01 M K^+) – agricultural well water.
- Allow equilibration with calcite, ion exchanger, and HFO surface.

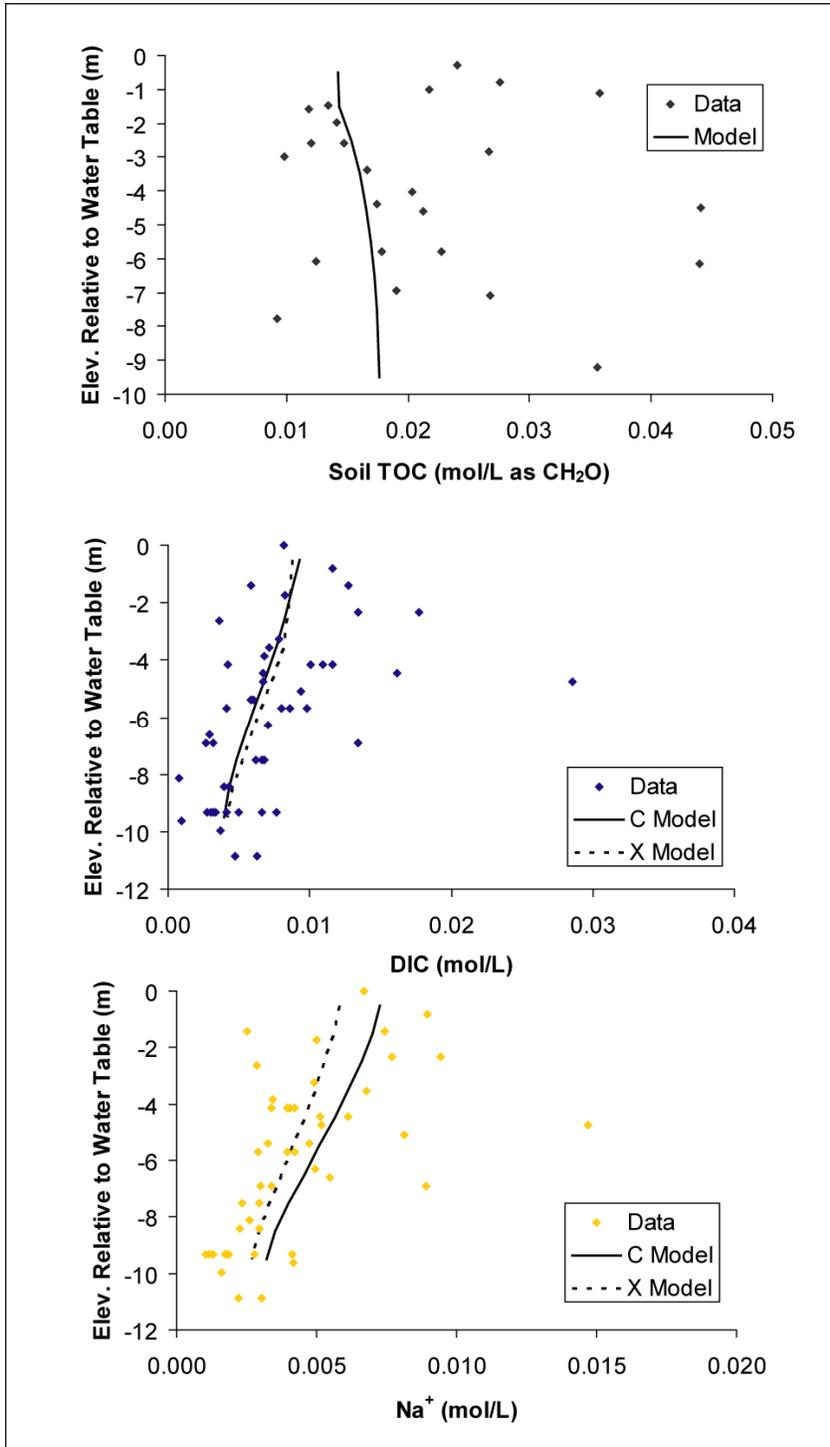


Figure 12. Simulation of dairy wastewater percolation through sediment.

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.

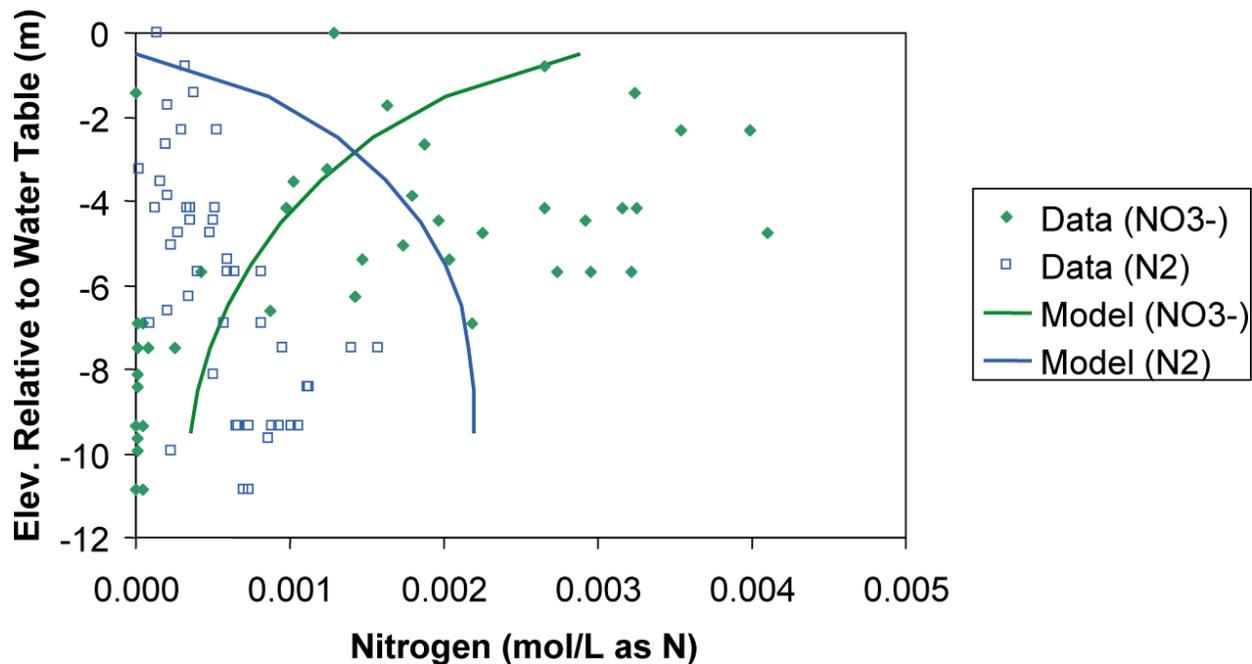


Figure 13. Simulation of denitrification associated with dairy wastewater percolation.

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 ^4He 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 un-

impacted 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.

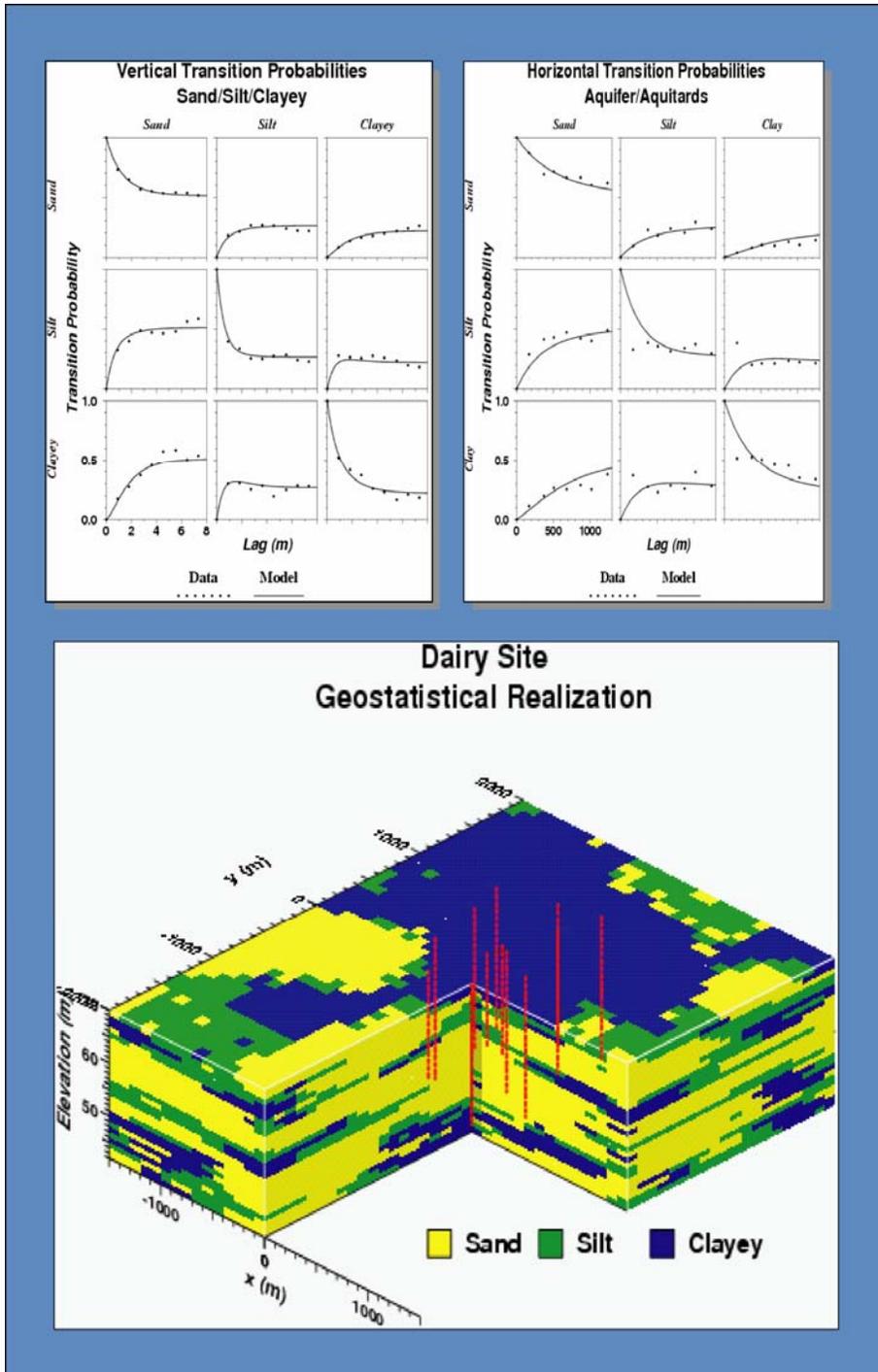


Figure 14. Geostatistical representation of the subsurface at KCD1.

Transition probability matrices and geostatistical representation of hydrofacies architecture for the KCD1 site. See text for explanation.

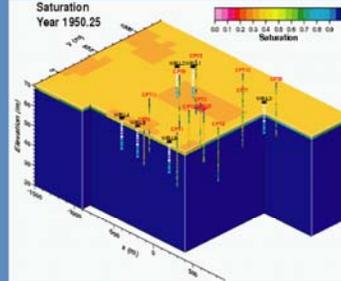
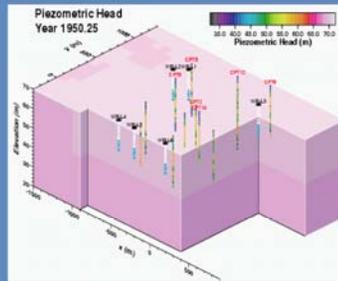
Flow and transport simulation (Figure 15 and 16). We used LLNL's NUFT code to simulate variably saturated **flow** according to the Richards equation (Figure 15). The simulation runs from late 1949 through 2001. Initial conditions are equilibrated to local head measurements and rainfall recharge of 1 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.

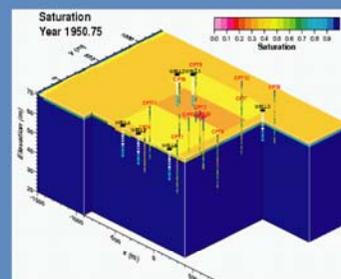
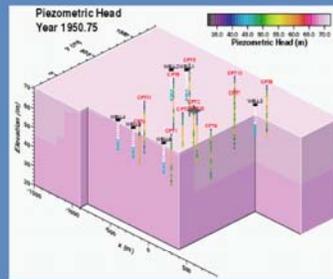
We used LLNL's NUFT code to simulate tracer **transport** from different recharge sources (Figure 16). The three primary recharge sources near the dairy site are canal, dairy crop irrigation, and irrigation from surrounding areas. The transport simulation results indicate that nitrate entering the saturated 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

Piezometric Head Saturation

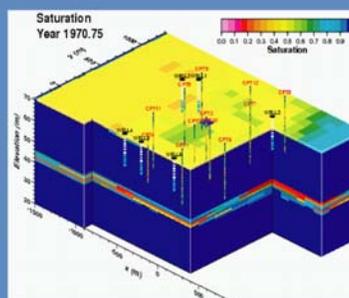
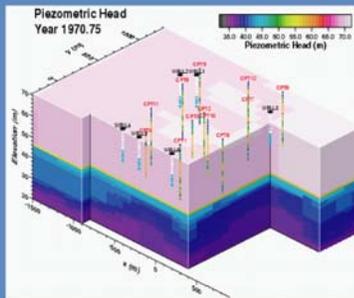
April 1
1950



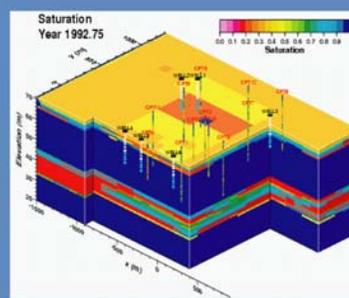
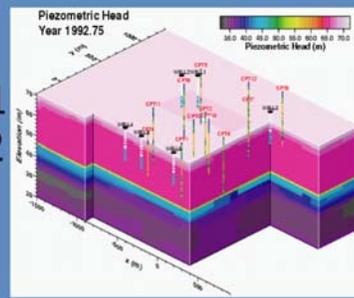
Oct 1
1950



Oct 1
1970



Oct 1
1992



Oct 1
1999

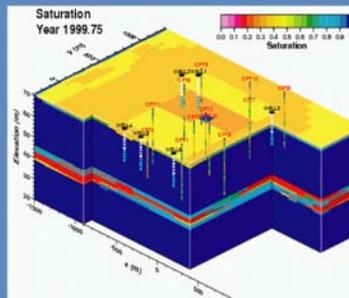
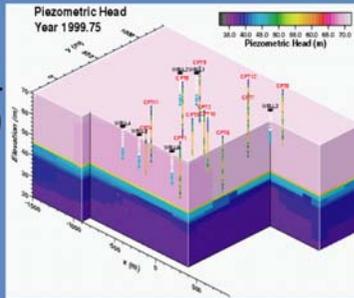


Figure 15. Simulation of groundwater flow at KCD1.

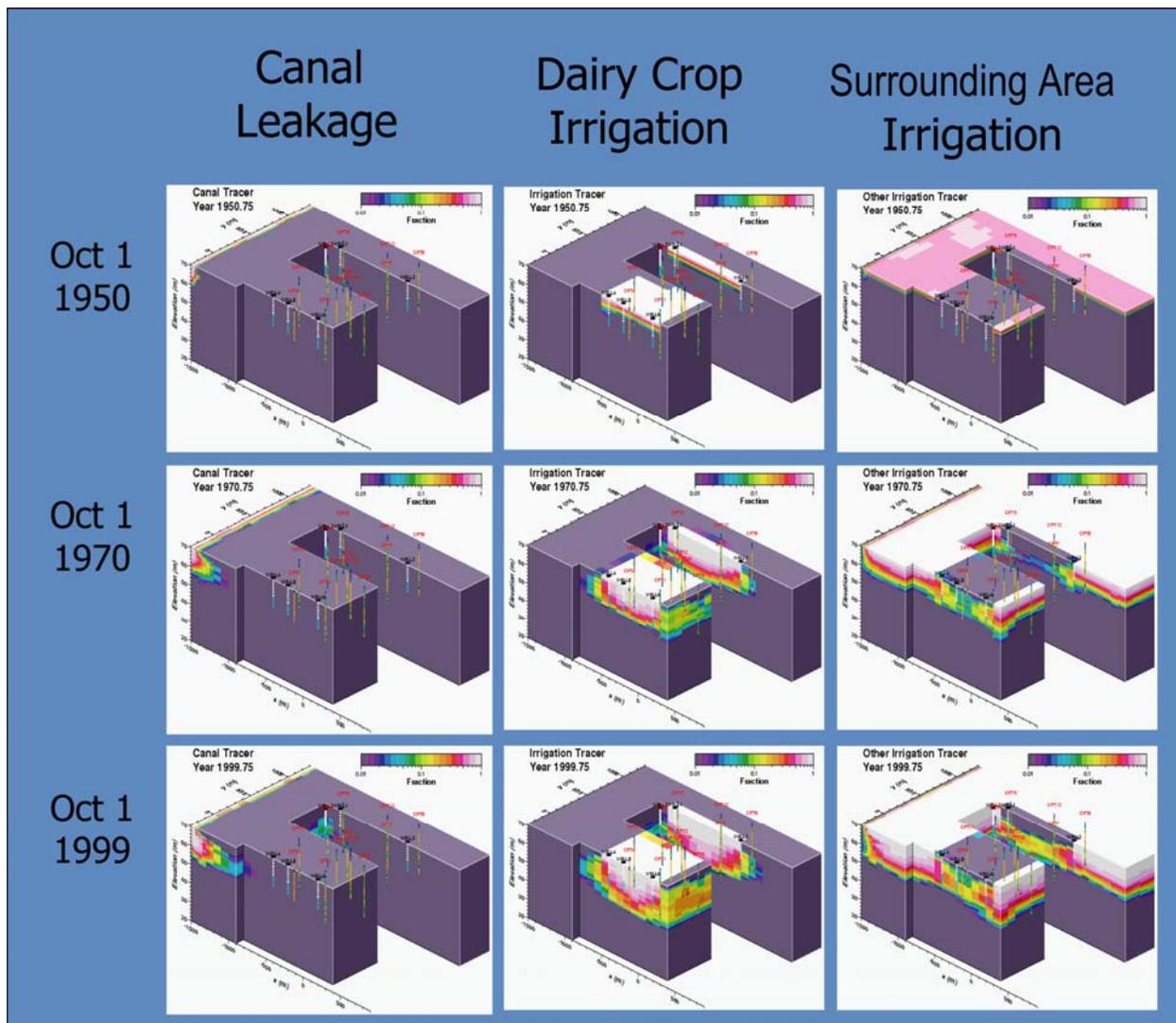


Figure 16. Simulation of transport at KCD1.

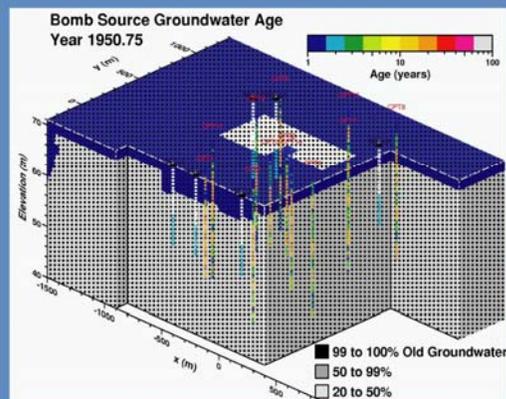
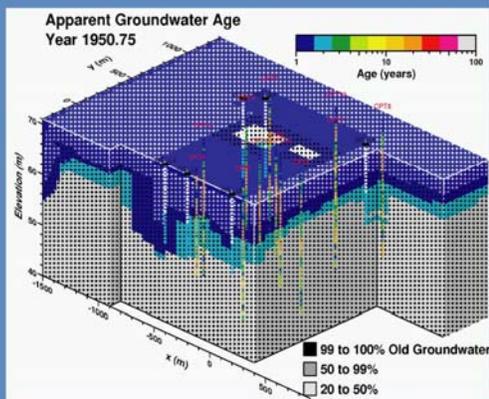
Model validation. To validate the groundwater flow and transport model, we used the model to simulate ^3H - ^3He groundwater ages in the aquifer and compared the results of the simulation to measured values. Groundwater ages determined using the ^3H - ^3He method are apparent age estimates of the average 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.

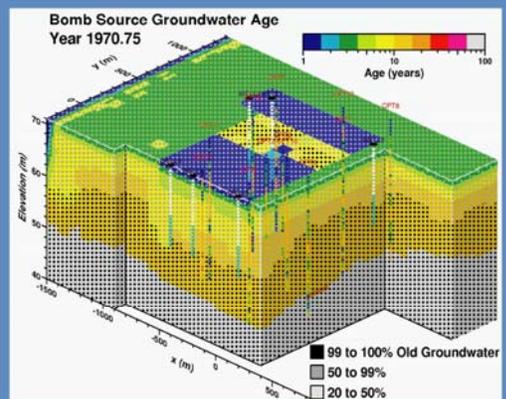
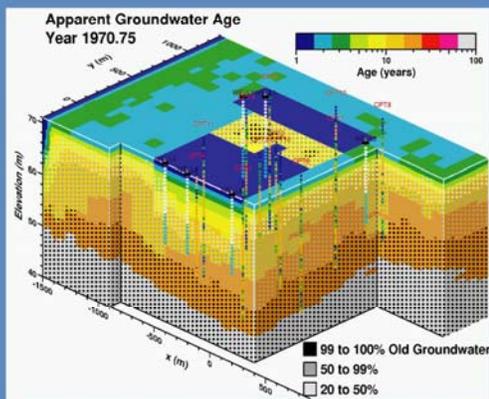
Ideal Source

Bomb Source

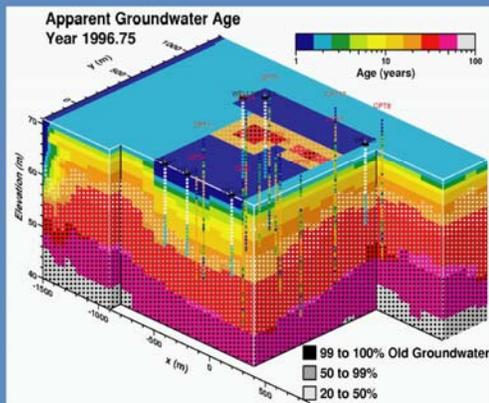
Oct 1
1950



Oct 1
1970



Oct 1
1996



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.

Figure 17. Simulation of apparent groundwater age at KCD1.

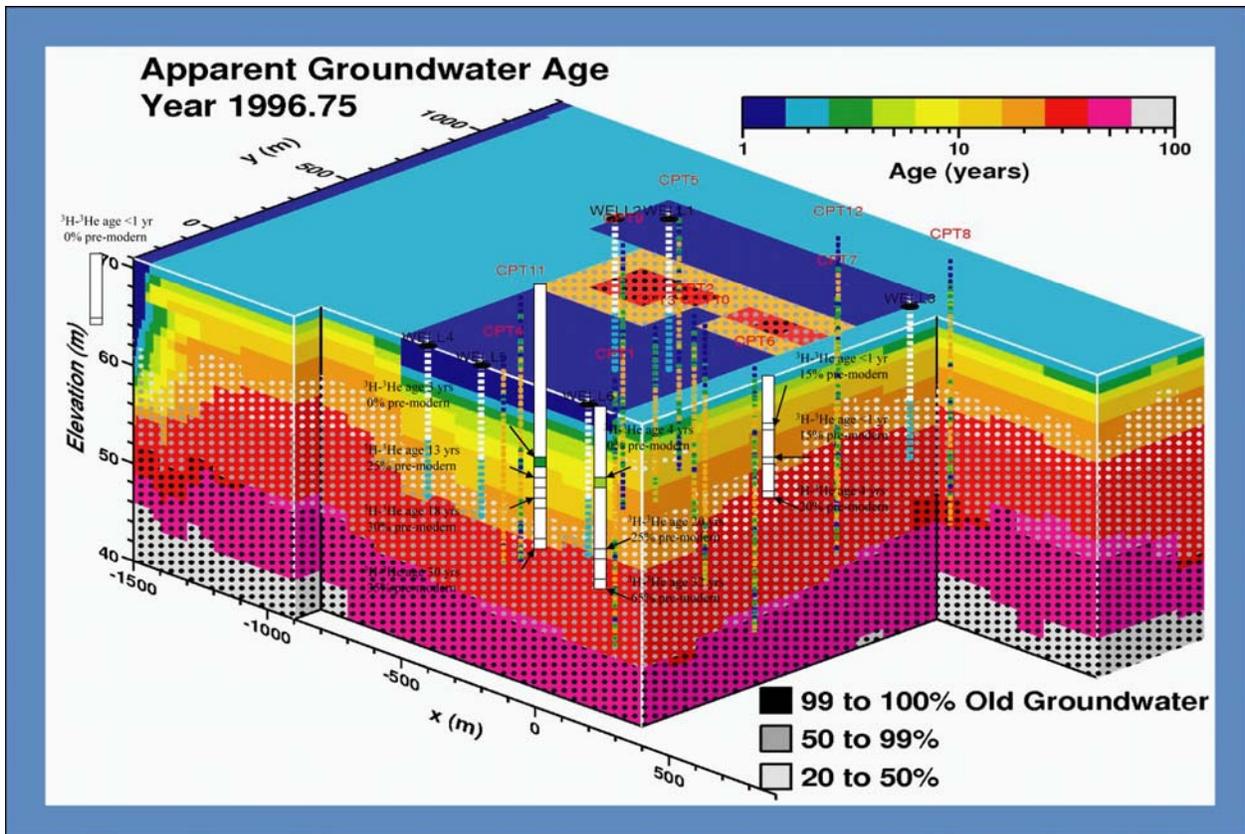


Figure 18. Comparison of measured and simulated groundwater ages at KCD1.

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 ${}^3\text{He}$ 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 ⁴He 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 ($\text{NO}_3 + \text{NO}_2 + \text{excess N}_2$) 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 lateral 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. The 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).
- Esser B. K., Beller H. R., Carle S. F., Hudson G. B., Kane S. R., LeTain T. E., McNab W. W., Moran J. E., and Singleton M. J. (2005) Characterization of saturated-zone denitrification in a heterogeneous aquifer underlying a California dairy (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., Letain T. E., Singleton M. J., Beller H. R., Kane S. R., Balser L. M., and Moran J. E. (2005) Molecular and geochemical evidence of *in-situ* denitrification at a dairy field site in the Central Valley of California (abstr.). *Eos, Transactions, American Geophysical Union* **86**(52), Abstract B31A-0972. 2005 AGU Fall Meeting (San Francisco, December 5-9, 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)*.

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Table 1: KCD2, KCD3, & SCD Site Data

Field Parameters, chemical composition, 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 ⁻	³ H/ ³ He age (yr)	Recharge T (°C)	Excess air (cc STP/g)	H ₂ O-δ ¹⁸ O (‰ SMOW)	NO ₃ ⁻ -δ ¹⁵ N (‰ Air)	NO ₃ ⁻ -δ 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 Tot C (wt%) (2sd)	Carb C Carb C (wt%) (2sd)	Org C Org C (wt%) (2sd)	Total S Total S (wt%) (2sd)	Sulfate S Sulfate S (wt%) (2sd)	Reduced S Reduced S (wt%) (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 <i>Nir</i> (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

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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 N₂ and residual NO₃⁻ concentrations. Nitrate in dairy groundwater from this study has δ¹⁵N values (4.3–61‰), and δ¹⁸O values (–4.5–24.5‰) that plot with δ¹⁸O/δ¹⁵N slopes of 0.47–0.66, consistent with denitrification. Noble gas mass spectrometry is used to quantify recharge temperature and excess air content. Dissolved N₂ is found at concentrations well above those expected for equilibrium with air or incorporation of excess air, consistent with reduction of nitrate to N₂. 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 NO₃⁻ (all nitrate concentrations are hereafter given as NO₃⁻). 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 herd size of 1.7 million milking cows (5).

Denitrification is the microbially mediated reduction of nitrate to gaseous N₂, and can occur in both unsaturated soils and below the water table where the presence of NO₃⁻, denitrifying bacteria, low O₂ 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 (δ¹⁵N and δ¹⁸O) 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 δ¹⁵N at the University of Waterloo. Analytical uncertainty (1σ) is 0.3‰ for δ¹⁵N of nitrate and 0.5‰ for δ¹⁸O 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 CO₂ 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 N₂ gas in groundwater samples (16–19). Dissolved concentrations of N₂ 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 CO₂ at mass 28 (N₂) is corrected based on calibration with CO₂-rich waters with known dissolved N₂, but is negligible for most samples. Samples are collected for MIMS analysis in 40 mL amber

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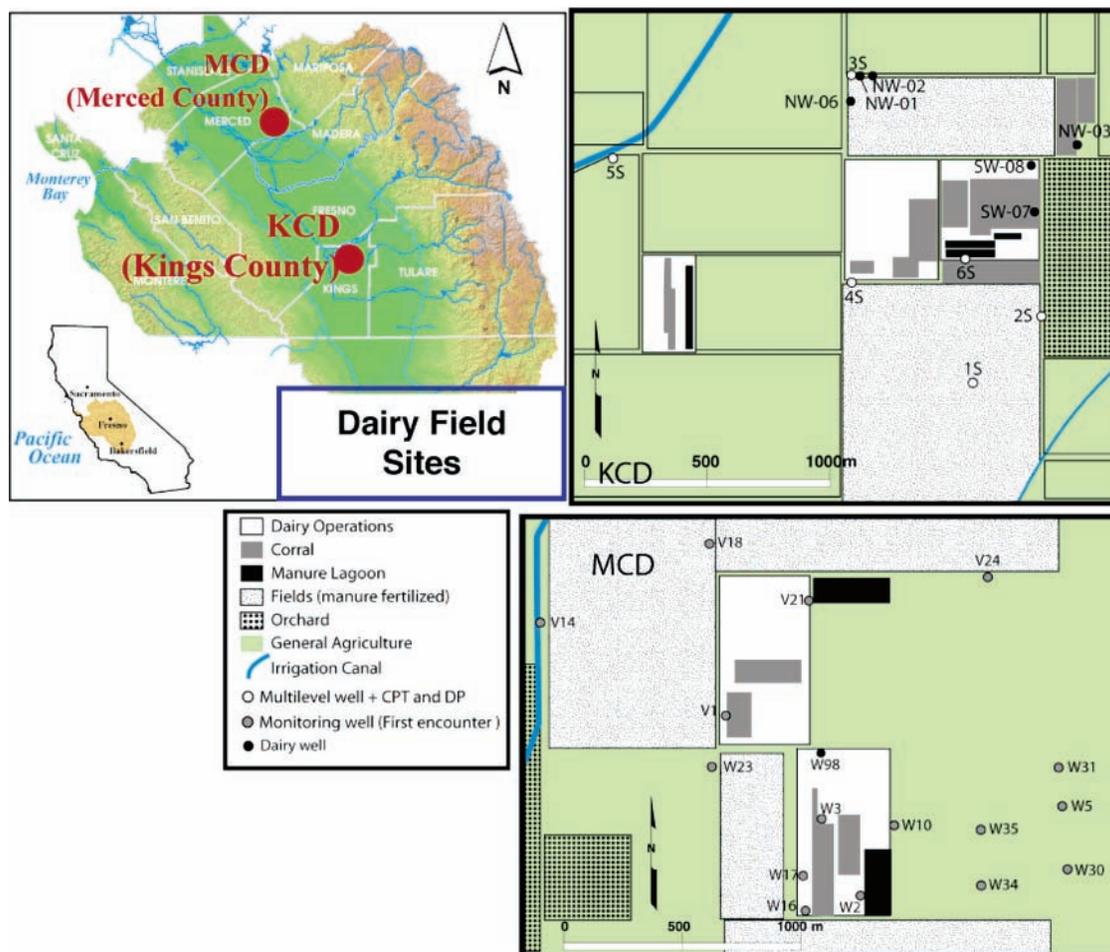


FIGURE 1. Location of dairy study sites, and generalized maps of each dairy showing sample locations relative to lagoons and dairy operations.

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

Noble Gases and $^3\text{H}/^3\text{He}$ 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 ($^3\text{He}_{\text{trit}}$):

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

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

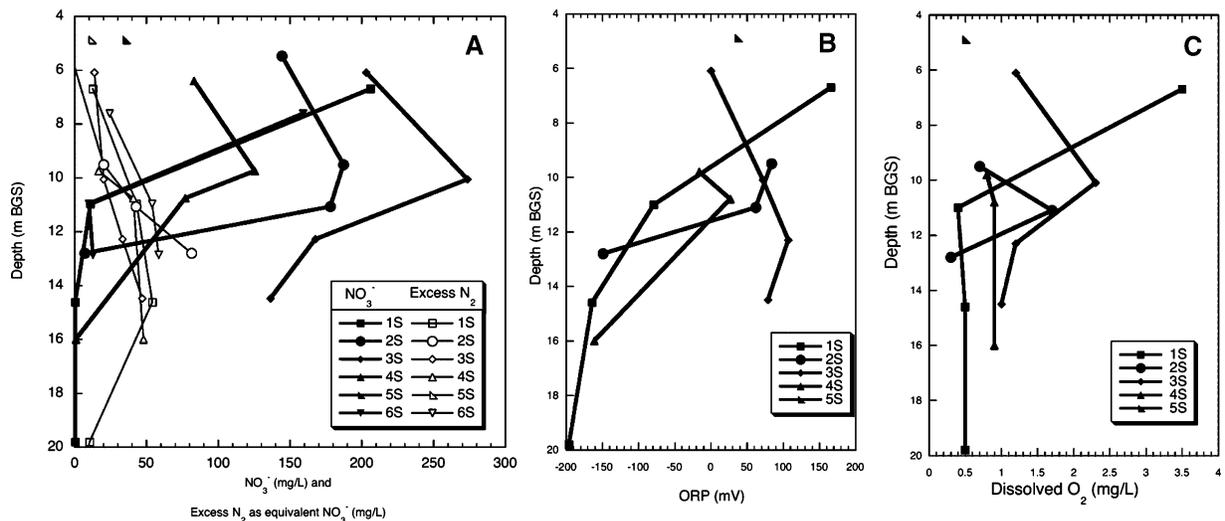


FIGURE 2. (A) Average excess N₂ and nitrate concentrations, (B) oxidation–reduction potential (ORP), and (C) dissolved oxygen in multilevel monitoring wells at the KCD site.

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 N₂ 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 N₂ is a sum of these three sources:

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

By normalizing the measured dissolved concentrations as N₂/Ar ratios, the amount of excess N₂ from denitrification can be calculated as

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

where the N₂ and Ar terms for equilibrium are calculated from equilibrium concentrations determined by gas solubility. The N₂/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 N₂ based on the N₂/Ar ratio assume that any excess air entrapped during recharge has the ratio of N₂/Ar in the atmosphere (83.5). Any partial dissolution of air bubbles would lower the N₂/Ar ratio (30, 31), thus decreasing the apparent amount of excess N₂.

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 N₂ 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} cm³(STP)/g H₂O for KCD and 1.7×10^{-3} cm³(STP)/g H₂O for MCD. From these parameters, we estimate the site representative initial N₂/Ar ratios including excess air to be 41.2 for KCD and 40.6 for MCD. Measured N₂/Ar ratios greater than these values are attributed to production of N₂ by denitrification.

The excess N₂ concentration can be expressed in terms of the equivalent reduced nitrate that it represents in mg/L NO₃⁻ based on the stoichiometry of denitrification. Considering excess N₂ in terms of equivalent NO₃⁻ provides a simple test to determine whether there is a mass balance between nitrate concentrations and excess N₂. From Figure 2, there does not appear to be a balance between nitrate concentrations and excess N₂ in KCD groundwater, since nitrate concentrations in the shallow wells are more than twice that of equivalent excess N₂ concentrations in the anoxic zone. There are multiple possible causes of the discrepancy between NO₃⁻ concentrations and excess N₂ concentrations including (1) the NO₃⁻ 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 NO₃⁻ waters has diluted both the NO₃⁻ and excess N₂ concentrations, or (3) some dissolved N₂ 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

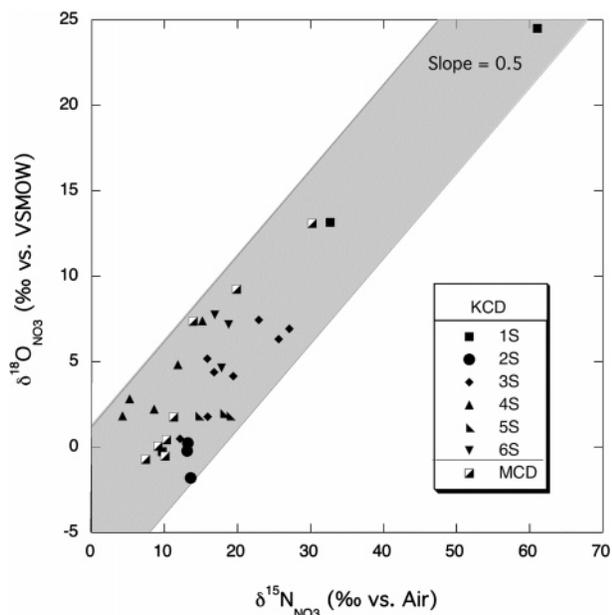


FIGURE 3. Oxygen and nitrogen isotopic composition of nitrate in dairy groundwater from multilevel monitoring wells at KCD and first encounter wells at MCD. The shaded region indicates a slope of 0.5 for a range of starting compositions. Calculated slopes for linear fits to multilevel wells at KCD and 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 $\delta^{15}\text{N}$ value close to 5‰, but is enriched in ^{15}N to varying degrees due to volatile loss of ammonia, resulting in $\delta^{15}\text{N}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values for nitrate at the two dairies based on the average values for $\delta^{18}\text{O}$ of groundwater at each site (–12.6‰ at KCD and –9.9‰ at MCD). Based on this approach, the predicted initial values for $\delta^{18}\text{O}$ in nitrate are –0.7‰ at KCD and 1.1‰ at MCD. Samples with the lowest nitrate $\delta^{15}\text{N}$ values have $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$ values (0–5‰) and $\delta^{18}\text{O}$ values around 23‰ (39).

Denitrification drives the isotopic composition of the residual nitrate to higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ vs $\delta^{15}\text{N}$ diagram (34). Nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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 ($f = C/C_{\text{initial}}$), the initial $\delta^{15}\text{N}$, and the fractionation factor (α) for denitrification:

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

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

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

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^- :

$$f = C_{\text{NO}_3^-} / (C_{\text{NO}_3^-} + C_{\text{excess N}_2})$$

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 $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ 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.

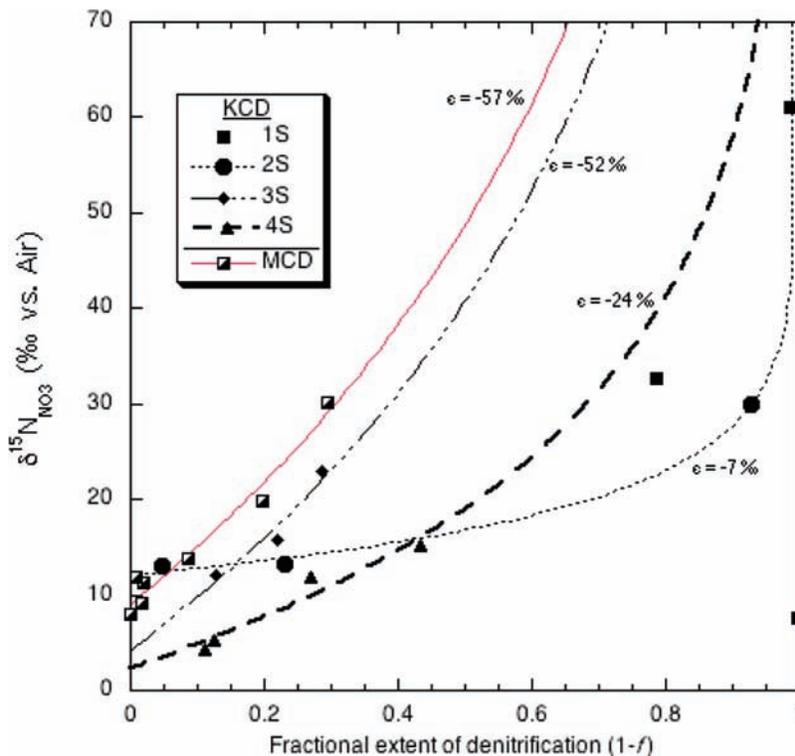


FIGURE 4. Nitrate $\delta^{15}\text{N}$ values plotted against the fractional extent of denitrification ($1 - f$) based on excess N_2 and residual nitrate. Enrichment factors (ϵ) are calculated by fitting the Rayleigh fractionation equation to data from three multilevel well sites at KCD and wells at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

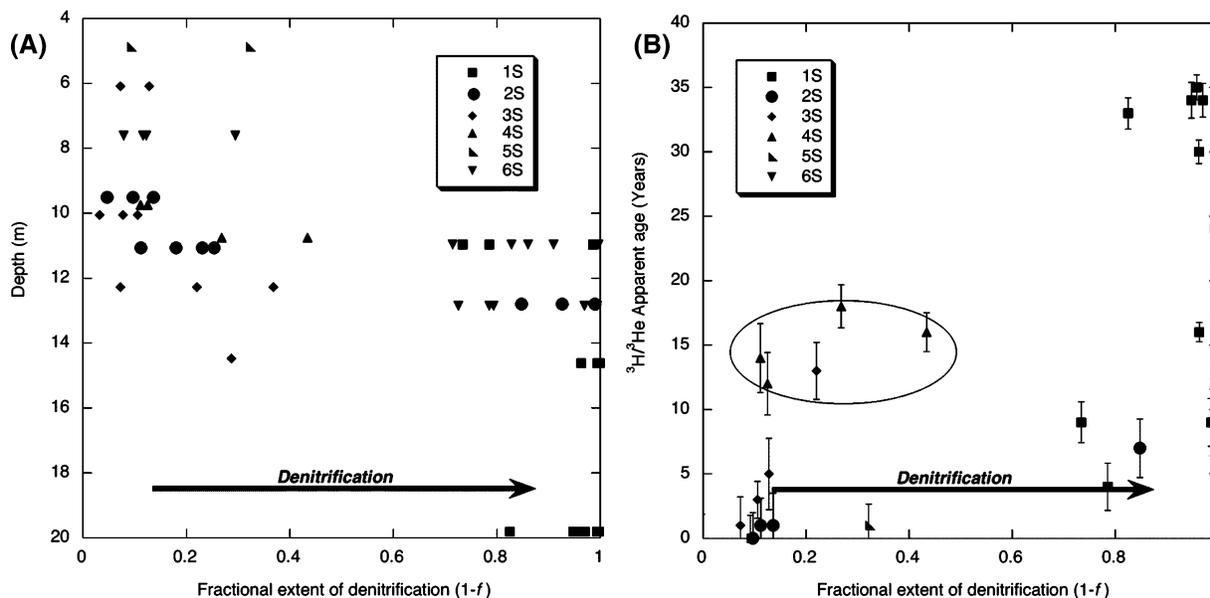


FIGURE 5. Sample depth (A) and $^3\text{H}/^3\text{He}$ apparent age (B) plotted against the fractional extent of denitrification ($1 - f$). Samples at two sites have experienced less denitrification than is typical for samples with $^3\text{H}/^3\text{He}$ apparent age > 8 years (circled, see text).

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 $^3\text{H}/^3\text{He}$ 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 $^3\text{H}/^3\text{He}$ 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 $^3\text{H}/^3\text{He}$ 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 $^3\text{H}/^3\text{He}$ 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 $^3\text{H}/^3\text{He}$ 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.

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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. Esser¹, J. E. Moran¹, G. B. Hudson¹, W. W. McNab², and T. Harter³

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.

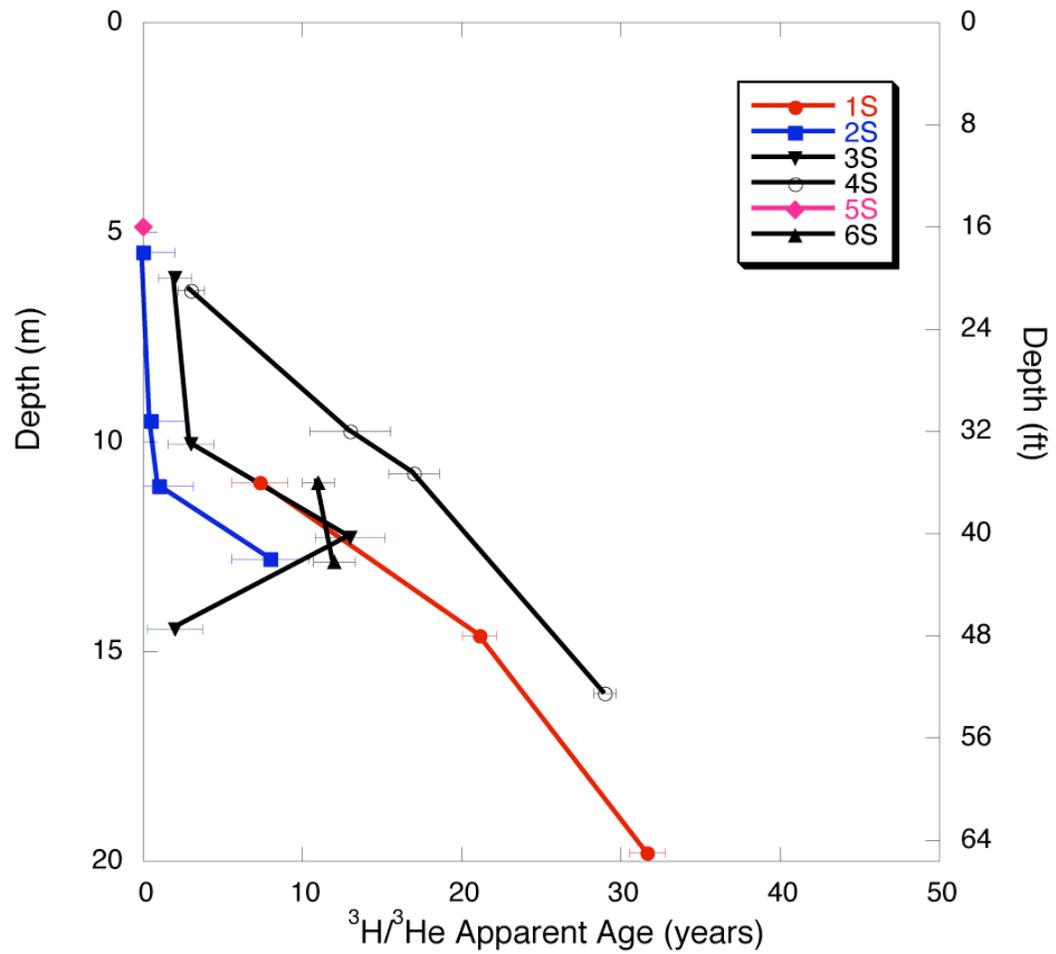


Figure S1. Groundwater $^3\text{H}/^3\text{He}$ apparent ages from multilevel monitoring wells at KCD. Error bars show analytical error.

Table S1. Chemical, dissolved gas, and isotopic compositions for multilevel groundwater monitoring wells and lagoons. Average values are given for wells sampled more than once. Excess N₂ 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)	δ ¹⁸ O H ₂ O (‰ SMOW)	δ ¹⁵ N NO ₃ ⁻ (‰ Air)	δ ¹⁸ O NO ₃ ⁻ (‰ SMOW)	³ H/ ² He age (yr)	+/- (yr)	Excess air determined from Ne (cc STP/g)	Recharge Temp. from Xe (°C)	+/- (°C)	³ H 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	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	100
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
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	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		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	120
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	130
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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Assessing the Impact of Animal Waste Lagoon Seepage on the Geochemistry of an Underlying Shallow Aquifer

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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 \times 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

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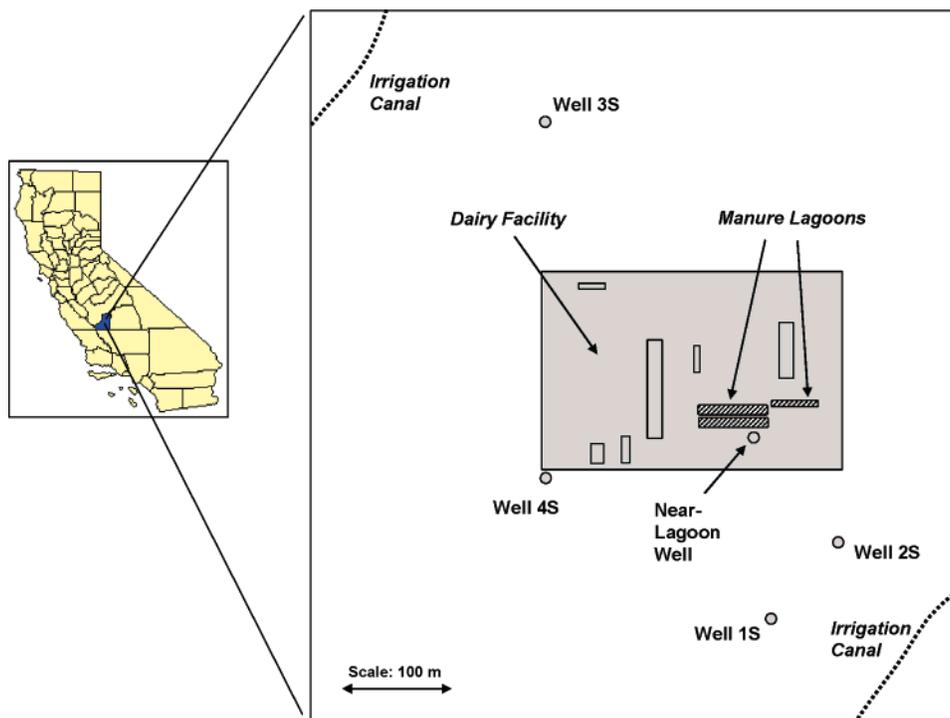


FIGURE 1. Dairy facility map, Kings County, CA. Water quality data from the lagoons and all five monitoring wells were included in the study.

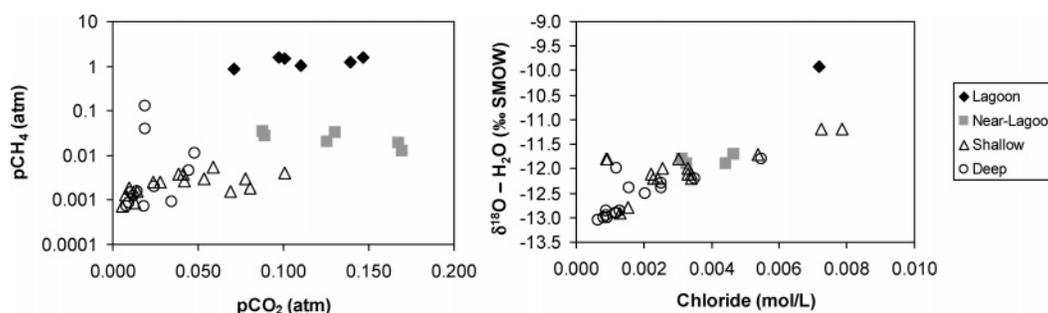


FIGURE 2. Partial pressures of CH_4 and CO_2 in the dairy facility lagoon and groundwater samples (left) and $\delta^{18}\text{O}$ and Cl^- (right). SMOW = standard mean ocean water.

quantified in a subset of samples as CO_2 gas pressure after acidification with orthophosphoric acid. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ 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, $\delta^{18}\text{O}$ 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

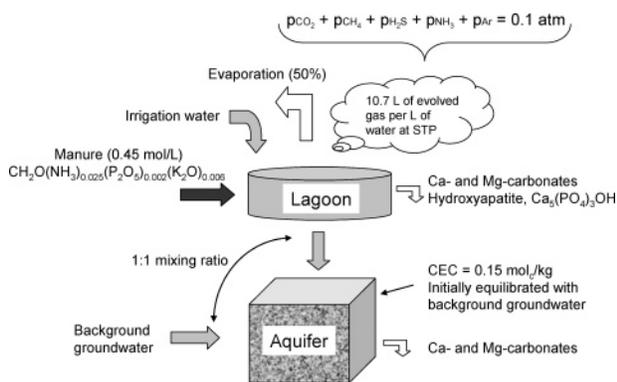


FIGURE 3. Geochemical process model of lagoon water formation and seepage.

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 $\text{CH}_2\text{O}(\text{NH}_3)_{0.025}(\text{P}_2\text{O}_5)_{0.002}(\text{K}_2\text{O})_{0.006}$, 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, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, 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). $\delta^{13}\text{C}$ –DIC, quantified in a subset

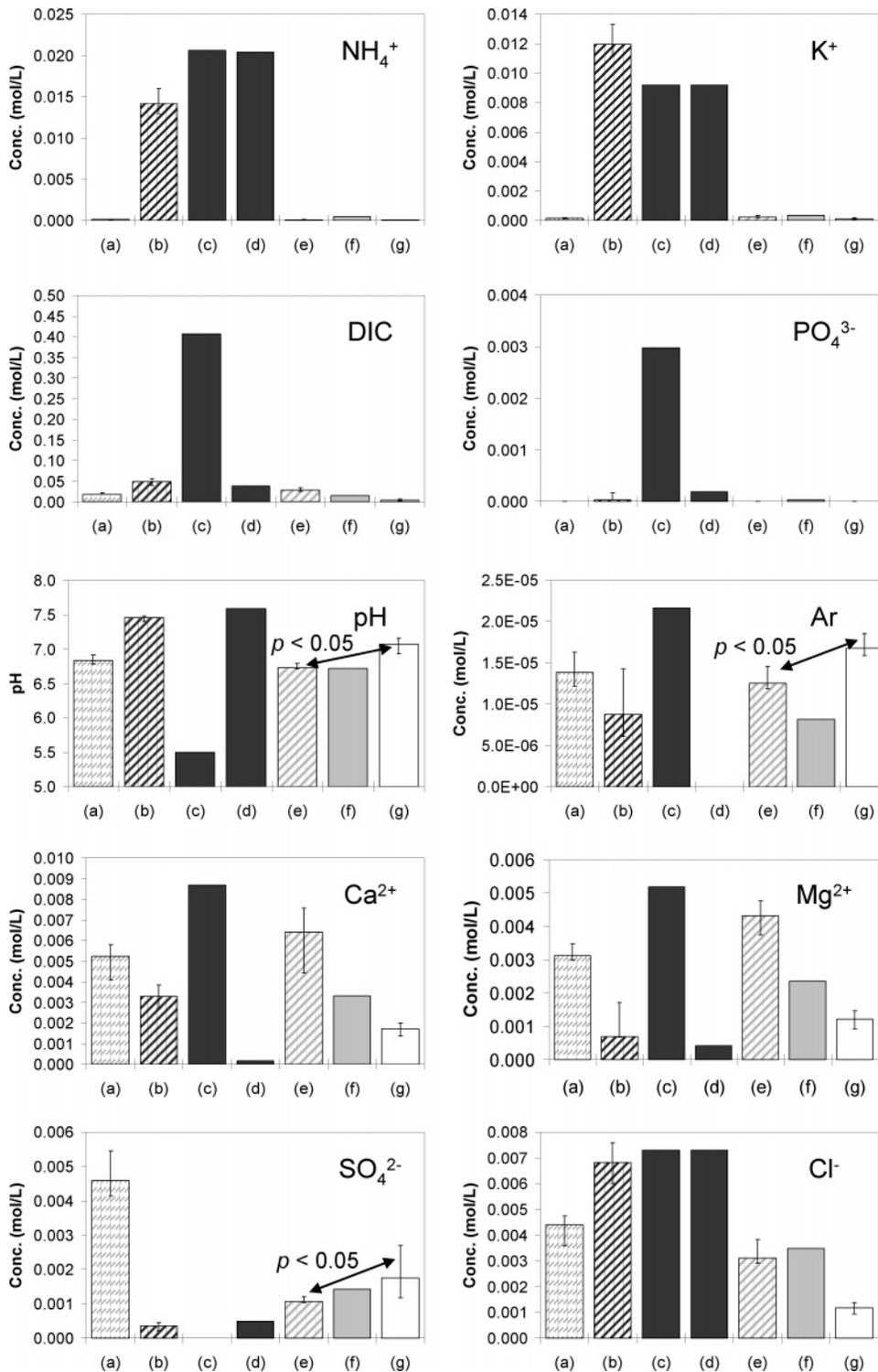


FIGURE 4. Modeling results and dairy site median water characteristics: (a) agricultural water samples, (b) lagoon water samples, (c) lagoon water modeled without any heterogeneous reactions, (d) lagoon water modeled with mineral precipitation and gas evolution, (e) Near-Lagoon Well samples, (f) modeled Near-Lagoon water impacted by seepage, and (g) 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 $\delta^{13}\text{C}$ 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.

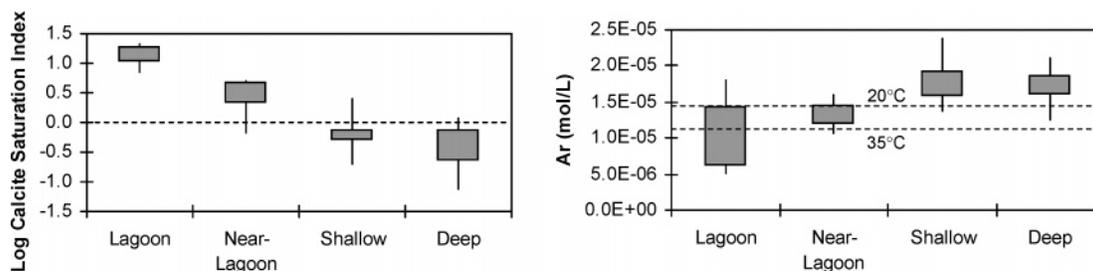


FIGURE 5. Thermodynamic saturation indices for calcite in site water samples, calculated with PHREEQC (left) and Ar concentrations and solubility (22) (right). The box-whisker marks correspond to the minimum, maximum, median, lower quartile, and upper quartile values for each group. Deep samples exclude groundwater samples from Well 2S.

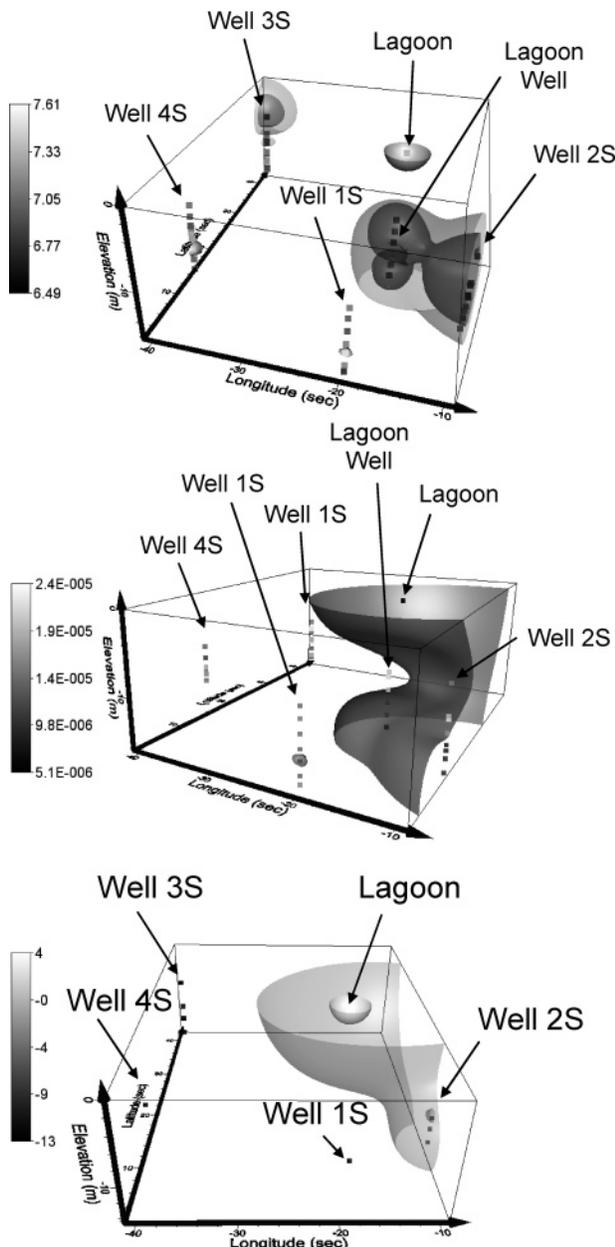


FIGURE 6. Distributions of pH (top), Ar (middle), and $\delta^{13}\text{C}$ (bottom) in site groundwater, each consistent with lagoon seepage that may have impacted Well 2S at depths greater than 11 m. Isosurface values for pH correspond to 6.75, 6.8, and 7.3. The isosurface value for Ar corresponds to 3.6×10^{-4} mol/L. The isosurface values for $\delta^{13}\text{C}$ 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 $19 \text{ mol m}^{-2} \text{ day}^{-1}$) 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 ground-

water. 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

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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

$\text{CH}_2\text{O}(\text{NH}_3)0.025(\text{P}_2\text{O}_5)0.002(\text{K}_2\text{O})0.006 + \text{O}_2 = \text{HCO}_3^- + 0.025\text{NH}_4^+ + 0.004\text{PO}_4^{3-} + 0.012\text{K}^+ + 0.975\text{H}^+$

log_k 100

Magnesite

$\text{MgCO}_3 + \text{H}^+ = \text{HCO}_3^- + \text{Mg}^{+2}$

log_k 2.2936

Ar(g)

Ar = Ar

log_k -2.854

SOLUTION_SPECIES

$2 \text{NO}_3^- + 12 \text{H}^+ + 10 \text{e}^- = \text{N}_2 + 6 \text{H}_2\text{O}$

#log_k 207.080

log_k 203.

delta_h -312.130 kcal

$\text{CO}_3^{2-} + 10 \text{H}^+ + 8 \text{e}^- = \text{CH}_4 + 3 \text{H}_2\text{O}$

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 NO_3^-

S(6) 440.52 as SO_4^{2-}

S(-2) $1\text{e}-010$ as SO_4^{2-}

P 0.02 as PO_4^{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"

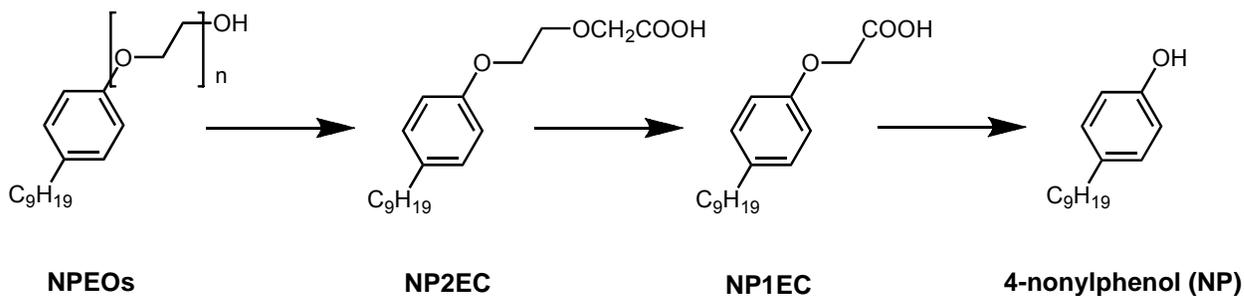
LAWRENCE LIVERMORE NATIONAL LABORATORY



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



June, 2006

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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 alkylbenzene sulfonates (LAS), and N, N-diethyl-*m*-toluamide (DEET). These compounds are frequently detected in treated wastewater at concentrations in the microgram per liter ($\mu\text{g/L}$) 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, Stamatelatos et al., 2003, Bryns, 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 $\mu\text{g/L}$ 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 Waldo, 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 17 β -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 1.8×10^9 kg/yr (Karsa, 1998). Commercial North American formulations are actually mixtures composed of homologs of different alkyl chain lengths (C₁₀ – C₁₄) 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).

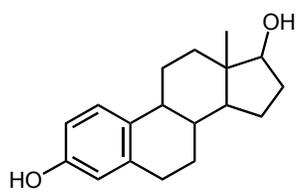
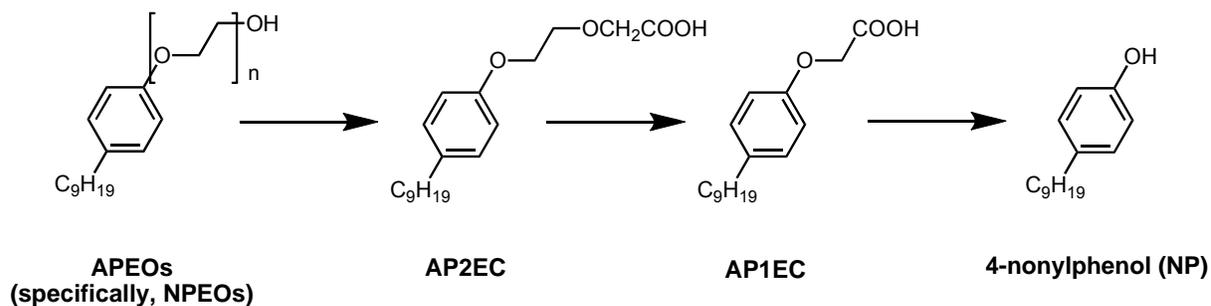
Fecal Sterols

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 McGillivray, 1979; Teshima and Kanazawa, 1978). The desire to distinguish between human and animal (e.g., herbivore) contributions of fecal matter in

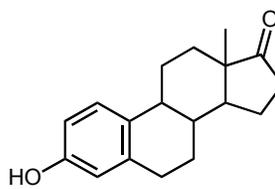
polluted water led to a technique developed by Leeming et al. (1994, 1996), which involves determining the relative amounts of specific C₂₇ and C₂₉ sterols present in a particular sample. This approach has been used in a variety of locations and has been useful in tracing sources in which multiple fecal contamination inputs may be present (Gregor et al., 2002; Leeming et al., 1998; Isobe et al., 2002).

Miscellaneous Compounds

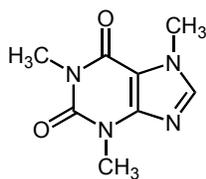
In addition to the selected target compounds, the concentrated extracts from the water samples were monitored for non-target organic contaminants during the GC/MS full-scan runs. Compound identifications were made using authentic standards and tentative compound identifications were based on suitable 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).



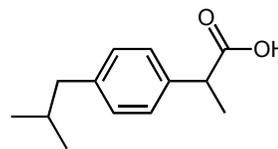
Estradiol



Estrone

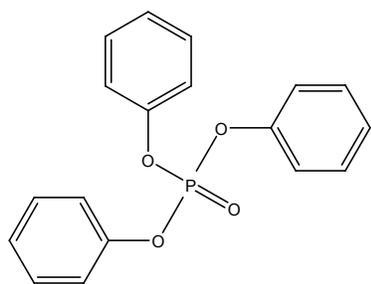


Caffeine

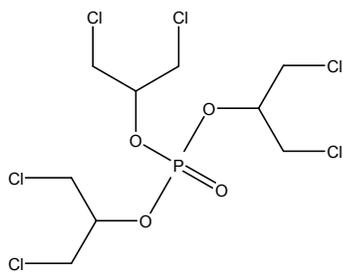


Ibuprofen

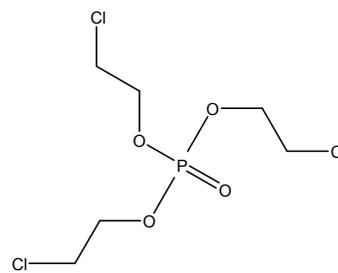
Figure 1. Structures of selected wastewater indicators analyzed by LC/MS/MS for this project. The value of “n” for APEOs is 3 to 20. Not all metabolites in the biodegradation of NPEOs to NP are shown, but the relationships among APEOs, APECs, and NP can be ascertained from the figure.



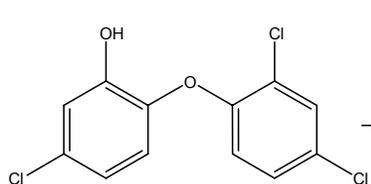
Triphenyl phosphate



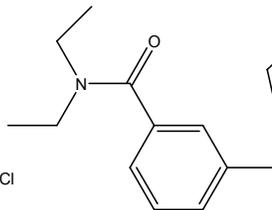
Tris (1,3-dichloroisopropyl) phosphate



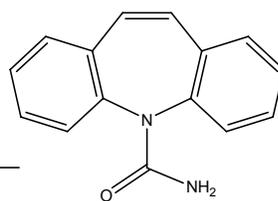
Tris (2-chloroethyl) phosphate



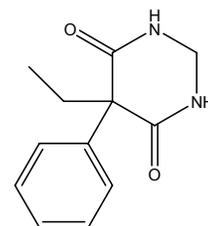
Triclosan



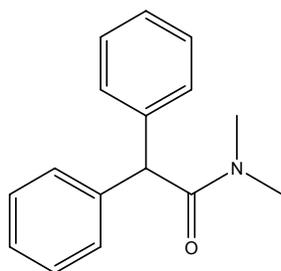
DEET



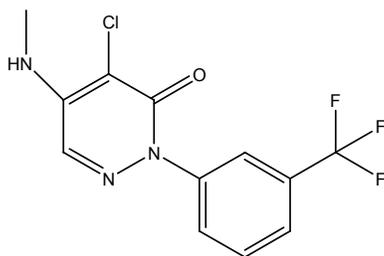
Carbamazepine



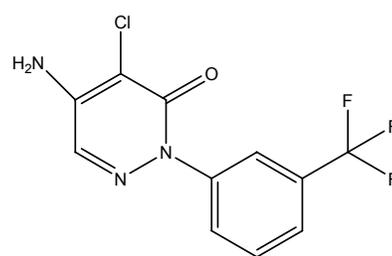
Primidone



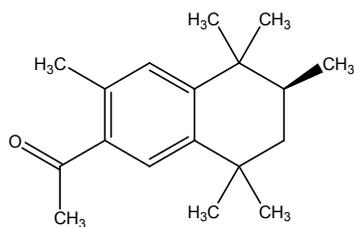
Diphenamid



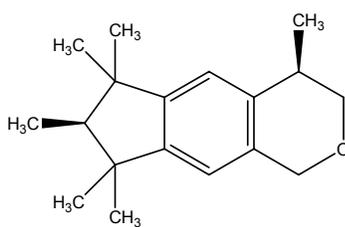
Norflurazon



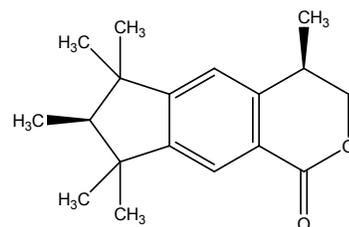
Desmethyl norflurazon



3S-AHTN (Tonalide)



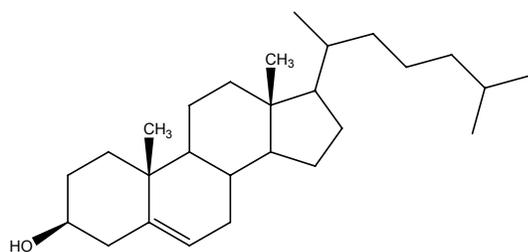
4R,7S-HHCB (Galaxolide)



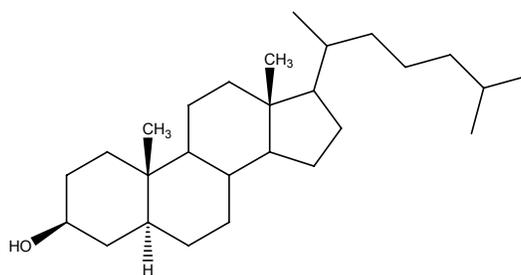
4R,7S-HHCB-lactone (Galaxolidone)

Figure 2. Structures of selected wastewater indicators analyzed by GC/MS.

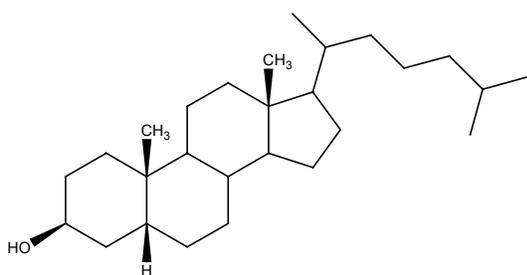
C₂₇ Sterols



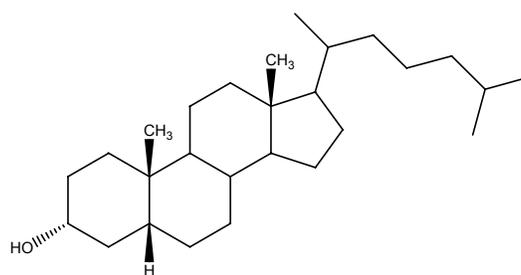
5-Cholesten-3b-ol (Cholesterol)



5a-Cholestan-3b-ol (Cholestanol)



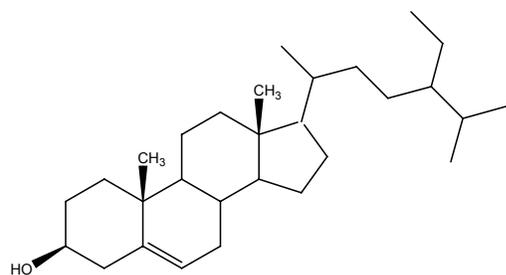
5b-Cholestan-3b-ol (Coprostanol)



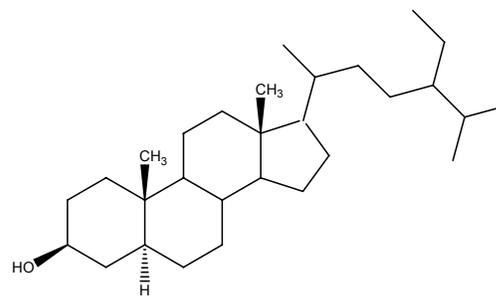
5b-Cholestan-3a-ol (Epicoprostanol)

Figure 2 (cont). Structures of selected wastewater indicators analyzed by GC/MS.

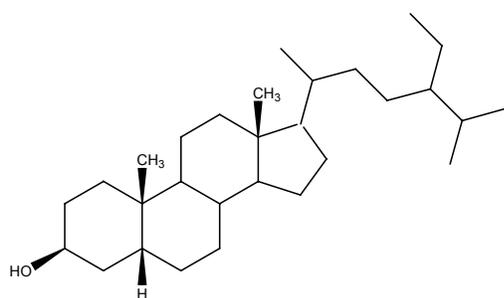
C₂₉ Sterols



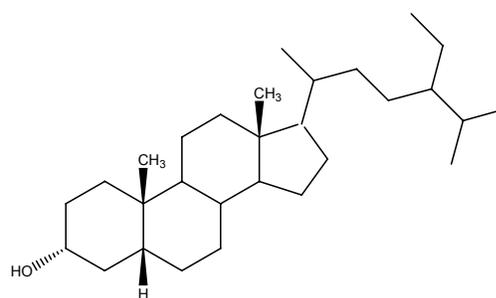
24-Ethylcholesterol



24-Ethylcholestanol



24-Ethylcoprostanol



24-Ethyl-epicoprostanol

Figure 2 (cont). Structures of selected wastewater indicators analyzed by GC/MS.

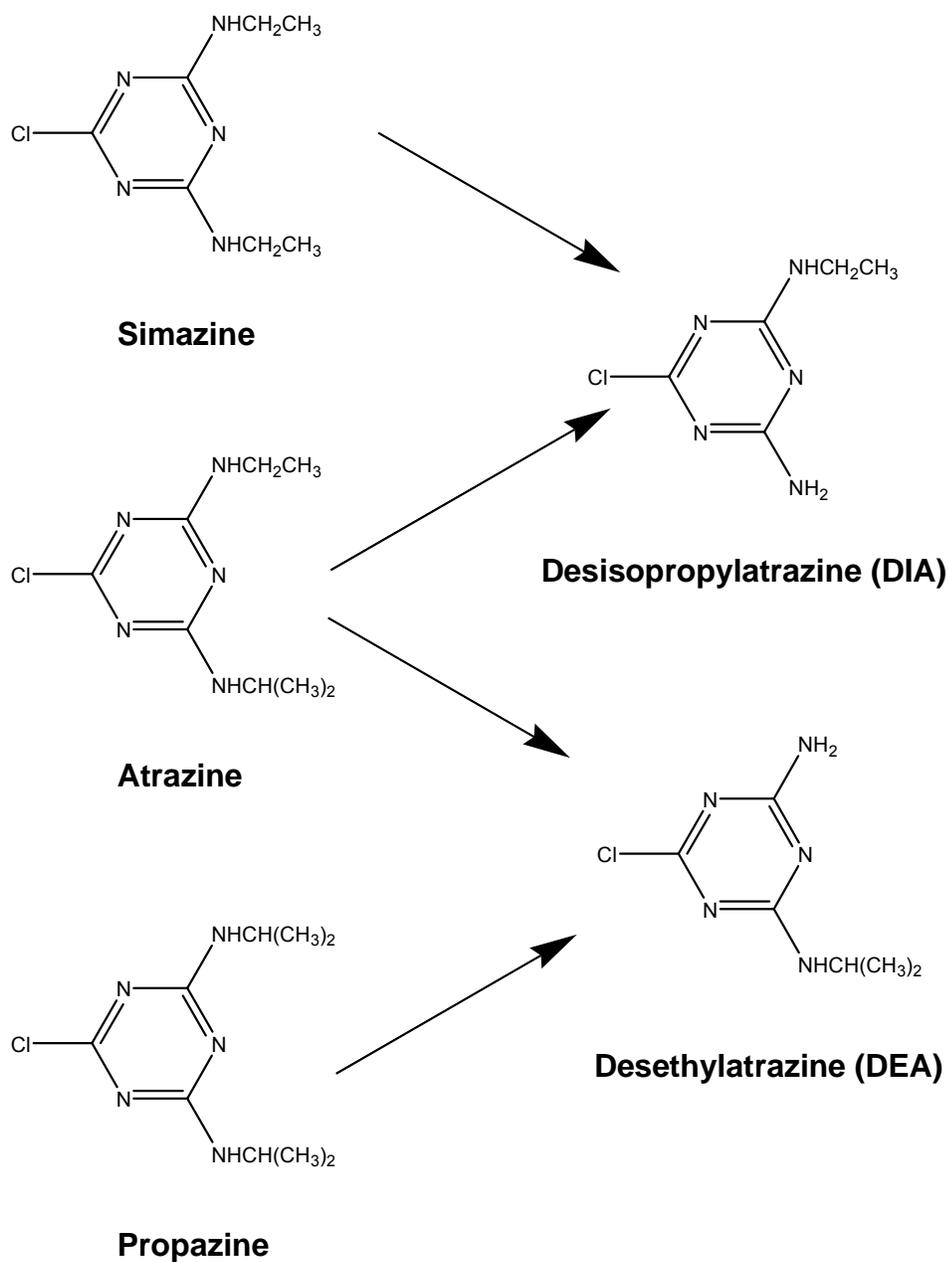


Figure 2 (cont). Structures of selected wastewater indicators analyzed by GC/MS.

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*-¹³C₆]-*n*-nonylphenol (Cambridge Isotope Laboratories, Andover, MA). For the other APEO metabolites studied (NP1EC and NP2EC), the internal standard was ¹³C₂-*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 ¹³C₃ (Sigma Aldrich, MO). For ibuprofen, the internal standard was ibuprofen-propionic-¹³C₃ (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., 17 β -estradiol and estrone), an aliquot of the methanol extract was concentrated (e.g., 10-fold from 2 mL to 200 μ L) 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 C₁₈ column (150 x 2.1 mm, 4- μ m particle size; Waters Corporation) was used for chromatographic separation of analytes. The sample injection volume was 25 μ L. The mobile phase typically consisted of methanol:water mixtures, with the flow rates ranging from 100-200 μ L/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°C for the source block and 300°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 μ L/min for a 200 μ g/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-¹³C₂, 99%; ¹⁵N, 98%) and unlabeled acetaminophen standard were acquired. Standard compound solutions (200 μ g/L) were infused through a syringe pump at a flow rate of 20 μ L/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 (<i>m/z</i>)	Mass fragment or transition for internal std. (<i>m/z</i>) ^c	Detection limit ^d (ng/L)
Caffeine	SPE, ENVI-18 disks	Positive Electrospray	LC/MS/MS	<i>m/z</i> 195 → <i>m/z</i> 138	<i>m/z</i> of 198 → <i>m/z</i> 140	5-10
4-Nonylphenol	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	<i>m/z</i> 219 → <i>m/z</i> 133	<i>m/z</i> 225 → <i>m/z</i> 112	10-15
NP1EC ^e	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	<i>m/z</i> 277 → <i>m/z</i> 219	<i>m/z</i> 279 → <i>m/z</i> 219	10
NP2EC ^f	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	<i>m/z</i> 321 → <i>m/z</i> 219	<i>m/z</i> 279 → <i>m/z</i> 219 ^e	10
17β-estradiol	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	<i>m/z</i> 271 → <i>m/z</i> 143, 145, 183	<i>m/z</i> 274 → <i>m/z</i> 145, 185	1-10
Estrone	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	<i>m/z</i> 269 → <i>m/z</i> 143, 145	<i>m/z</i> 274 → <i>m/z</i> 145, 185 ^g	1-10
Ibuprofen	SPE, ENVI-18 disks	Negative Electrospray	LC/MS/MS	<i>m/z</i> 205 → <i>m/z</i> 161	<i>m/z</i> 208 → <i>m/z</i> 163	5-10
DEET	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 119	<i>m/z</i> 217 ^h	10
Tris (2-chloroethyl)phosphate	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 63	<i>m/z</i> 217 ^h	100
Tris (1,3-dichloroisopropyl) phosphate	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 75	<i>m/z</i> 217 ^h	100
Triphenyl phosphate	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 326	<i>m/z</i> 217 ^h	100
Triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether)	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 290	<i>m/z</i> 217 ^h	100
Coprostanol ¹	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 215	<i>m/z</i> 217 ^h	100
Cholesterol ¹	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 275	<i>m/z</i> 217 ^h	100
Stigmastanol ¹	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 215	<i>m/z</i> 217 ^h	100

Ethylenediamine tetraacetic acid (EDTA) ^j	Rotary evaporation	Electron Impact	GC/MS	<i>m/z</i> 174	<i>m/z</i> 180 ^j	100
Linear alkylbenzenesulfonates (LAS) ^j	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 185	<i>m/z</i> 91 ^k	1000
Carbamazepine	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 193	<i>m/z</i> 217 ^h	20
Primadone	SPE, OASIS HLB cartridges	Electron Impact	GC/MS	<i>m/z</i> 146	<i>m/z</i> 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., ¹³C, ²H, ¹⁵N) 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 17 β -estradiol was also used for estrone.

^h Internal standard is 5 α -cholestane.

ⁱ C₂₇ and C₂₉ 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 μ L (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 μ L 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 μ L 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 μ m 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 (5 α -cholestane), with %RSDs $\leq 20\%$.

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 (D₁₂-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 BF₃/MeOH solution (10%) and reacted at 85°C for 45 min. to methylate the EDTA and D₁₂-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 D₁₂-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 (D₁₂-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 17 β -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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (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 $n=90$).

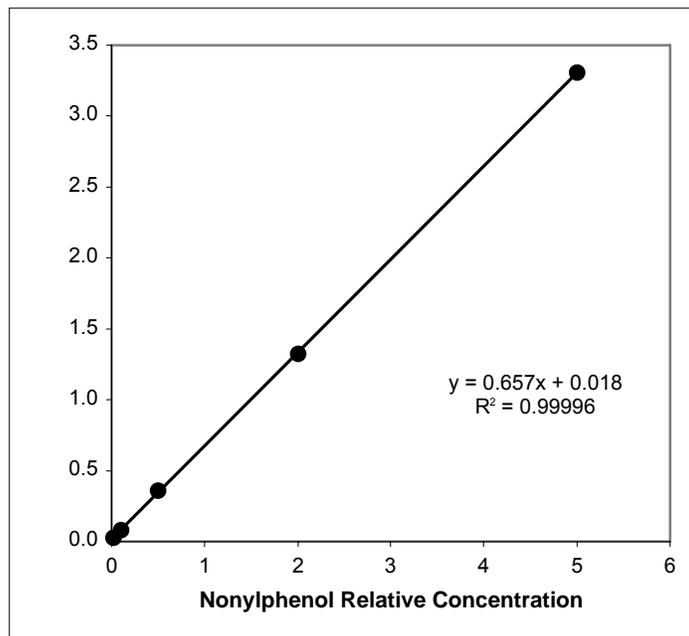


Figure 3. Internal standard calibration for NP. Standard concentrations (accounting for a 1-L sample processed through SPE) range from 10 to 2500 ng/L.

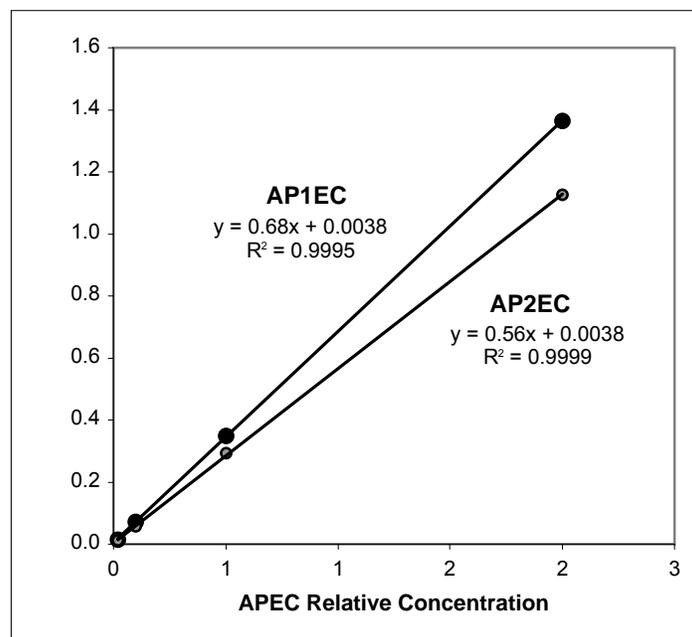


Figure 4. Internal standard calibration for AP1EC and AP2EC. Standard concentrations (accounting for a 1-L sample processed through SPE) range from 10 to 1000 ng/L.

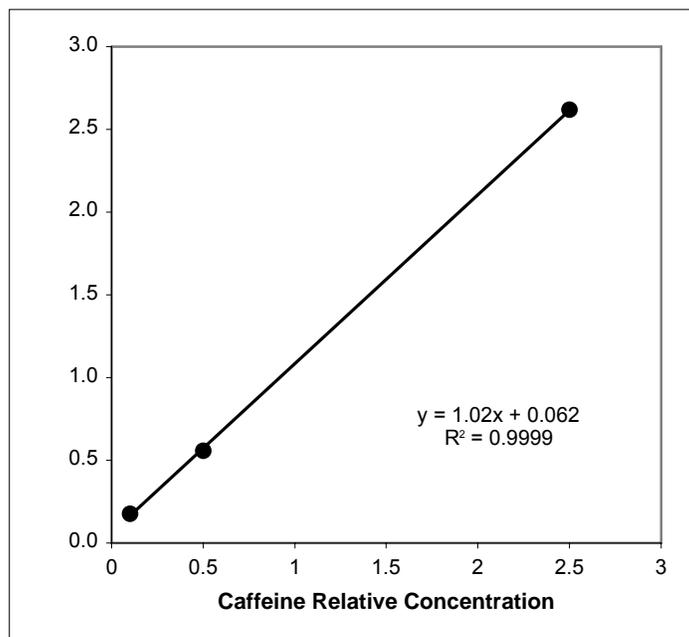


Figure 5. Internal standard calibration for caffeine. Standard concentrations (accounting for a 1-L sample processed through SPE) range from 10 to 250 ng/L.

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	022N001E28J002 M		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.

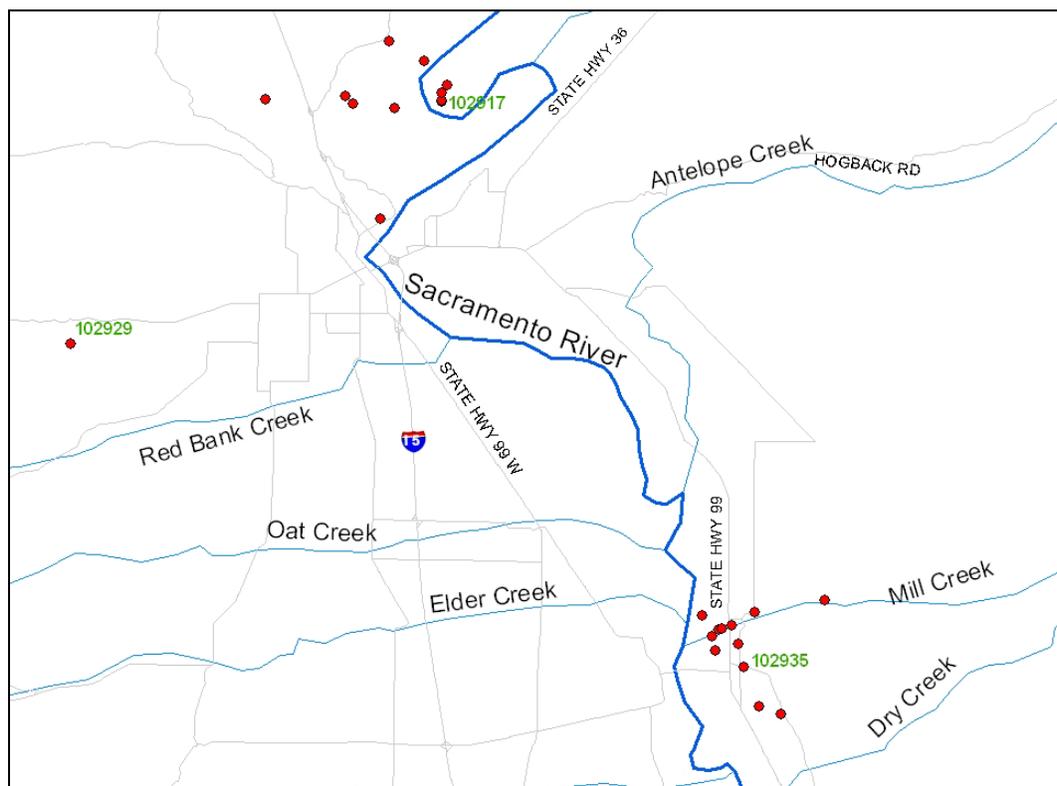


Figure 6. Map showing locations of private domestic wells sampled for wastewater indicator compounds. Numerical labels refer to three samples discussed in the text.

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 $\mu\text{g/L}$. 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.

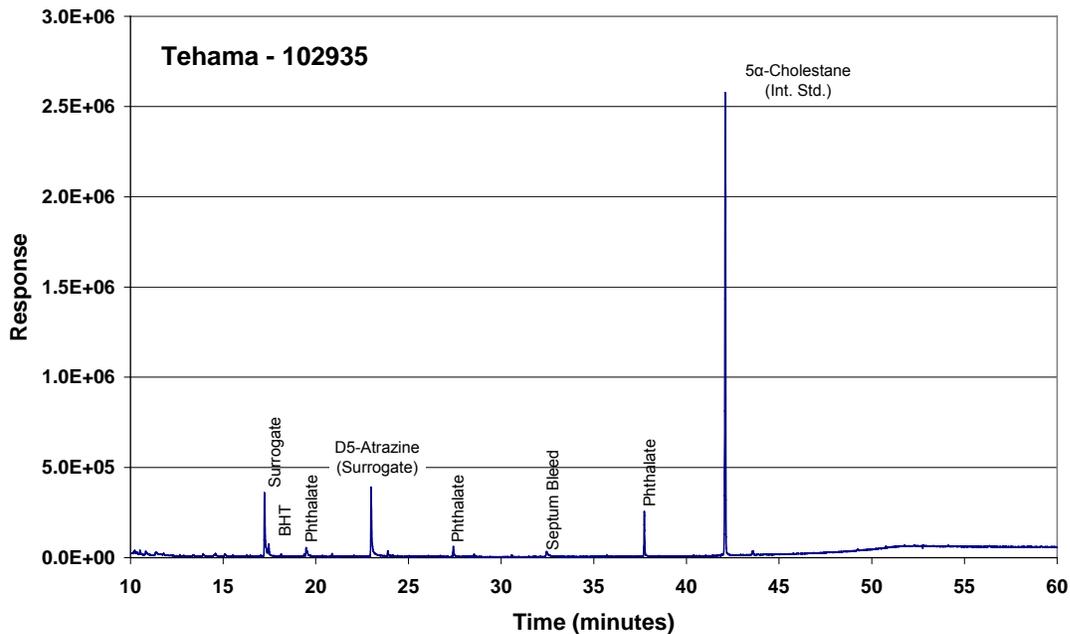


Figure 7. TIC of sample 102935. This GC/MS chromatogram is representative of the typical water extract from the Tehama study area.

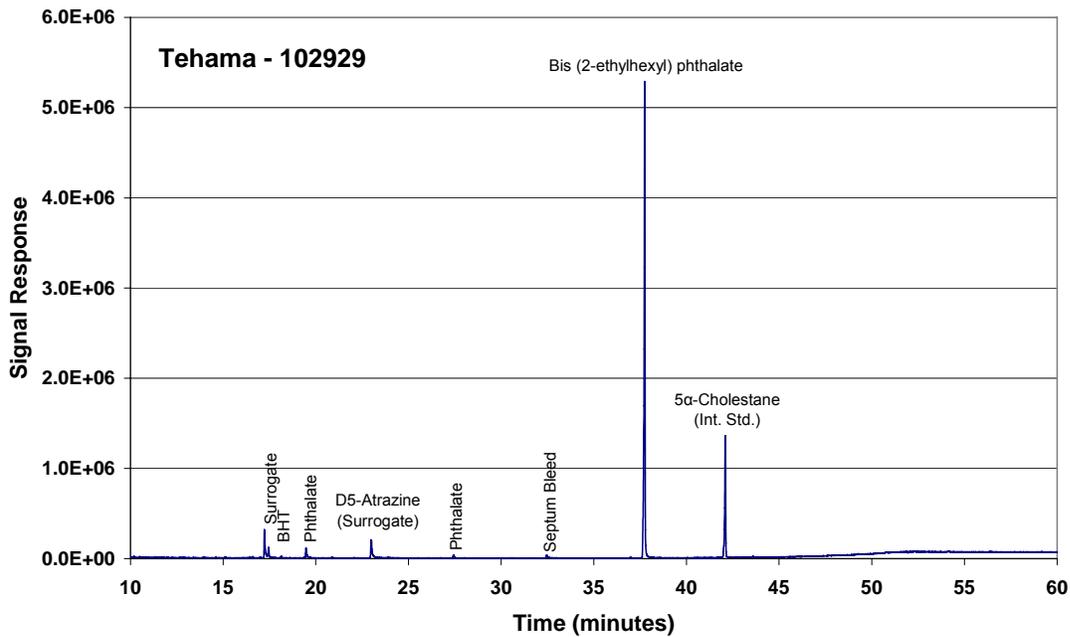


Figure 8. TIC of sample 102929, showing an unusually large amount of bis (2-ethylhexyl) phthalate.

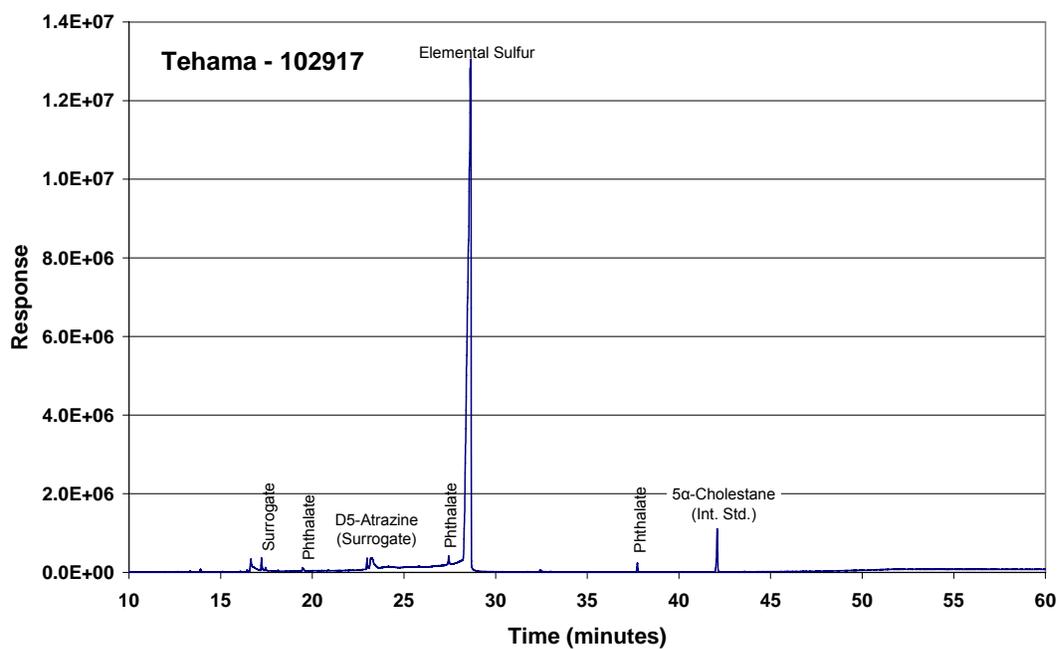


Figure 9. TIC of sample 102917. This sample had a high concentration of elemental sulfur.

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 C₂₇ and C₂₉ 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 dairy 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 dairy 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 ³/₄” 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, C₂₇: coprostanol is a human fecal biomarker, and cholesterol, cholestanol, C₂₉: 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.

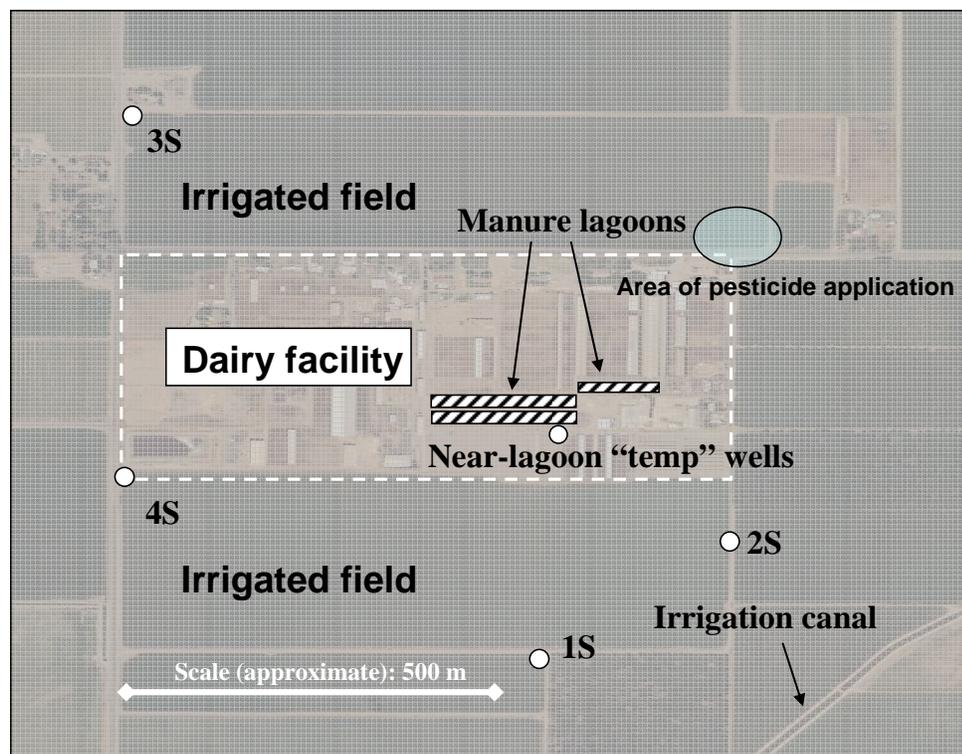


Figure 10. Location map for Kings County dairy site. Nonylphenol was detected at high concentrations in near-lagoon “temp” wells. Pesticides and degradates were found in 2S and 3S nested wells.

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.

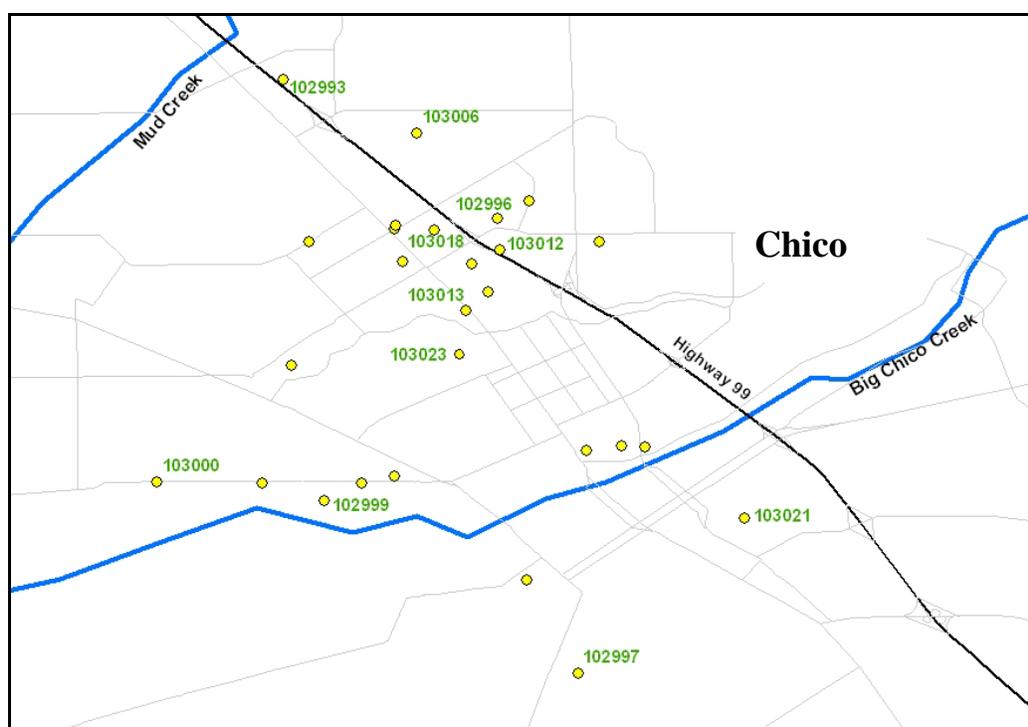


Figure 11. Map showing locations of private domestic wells sampled for wastewater indicator compounds. Numerical labels refer to samples discussed in the text.

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.

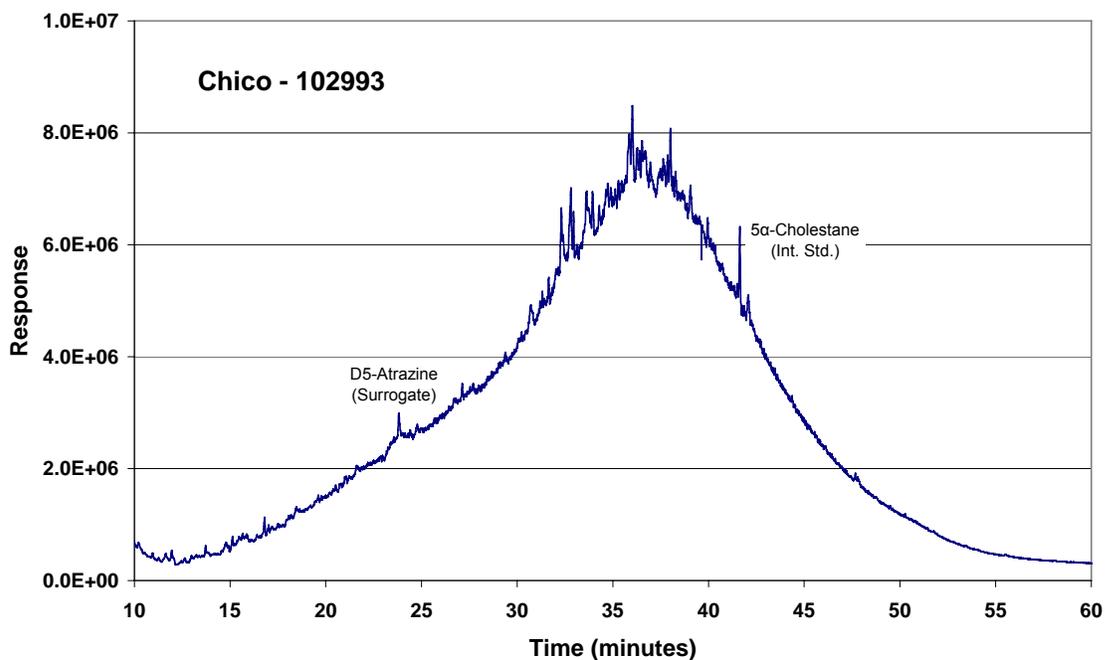


Figure 12. TIC of Chico sample 102993 showing the large amount of unresolved organic material present in this water sample. For scale, the internal standard in this sample represents 1 $\mu\text{g/L}$.

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.

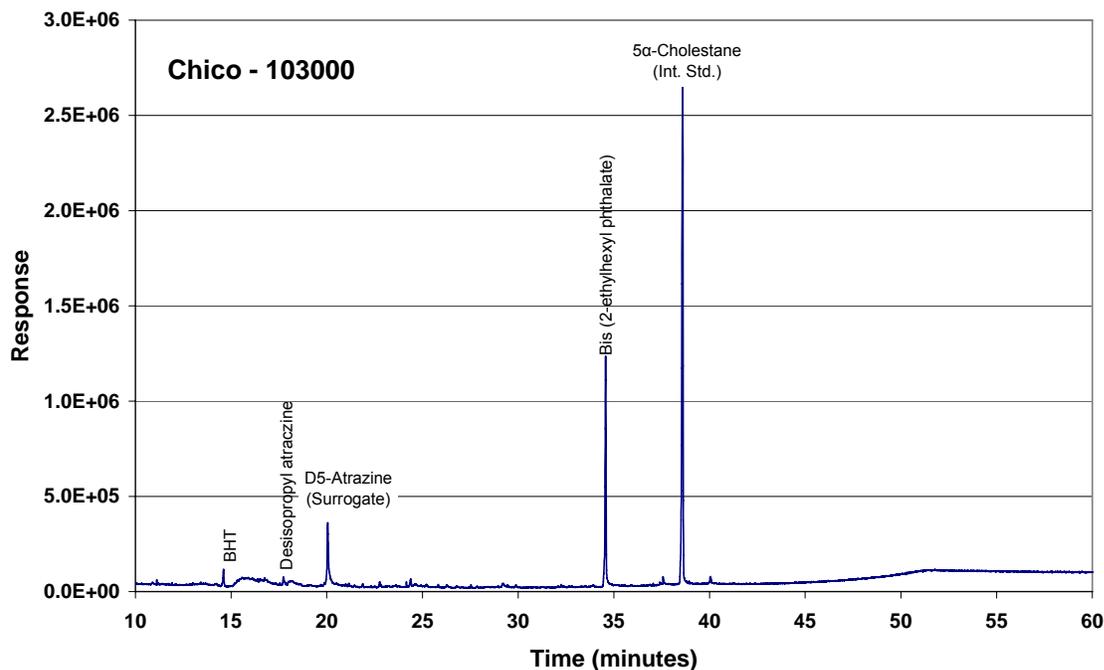


Figure 13. TIC of sample 103000, showing internal standard, surrogate compound, and desisopropyl atrazine (25 ng/L).

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).

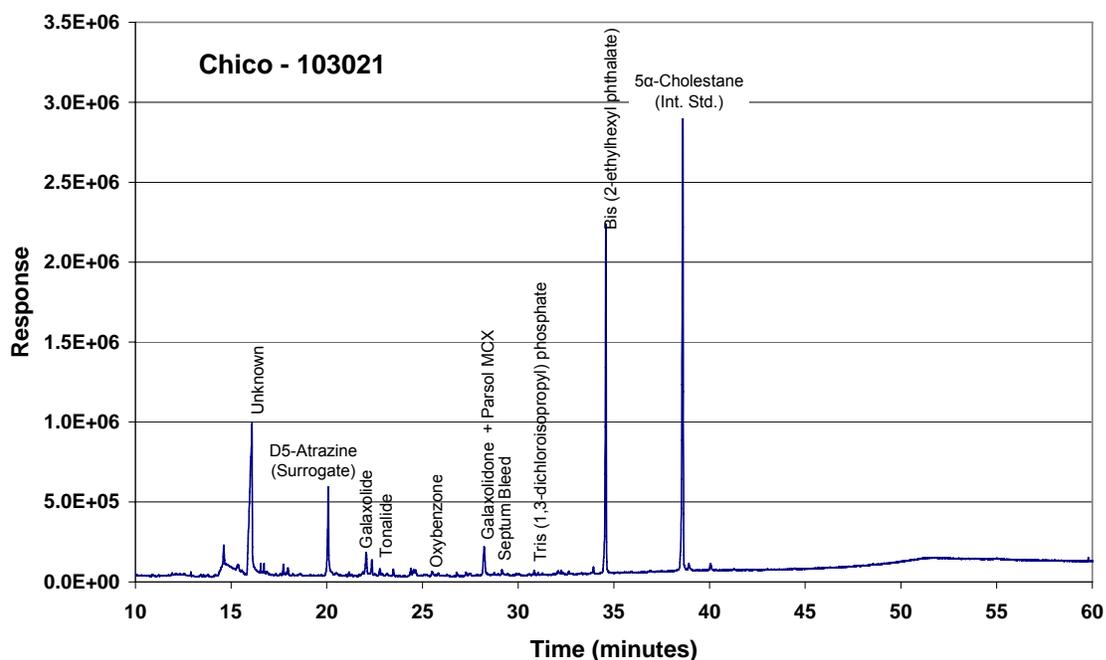


Figure 14. TIC of sample 103021, showing polycyclic musks, sunscreen compounds and tris (1,3-dichloroisopropyl) phosphate.

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.

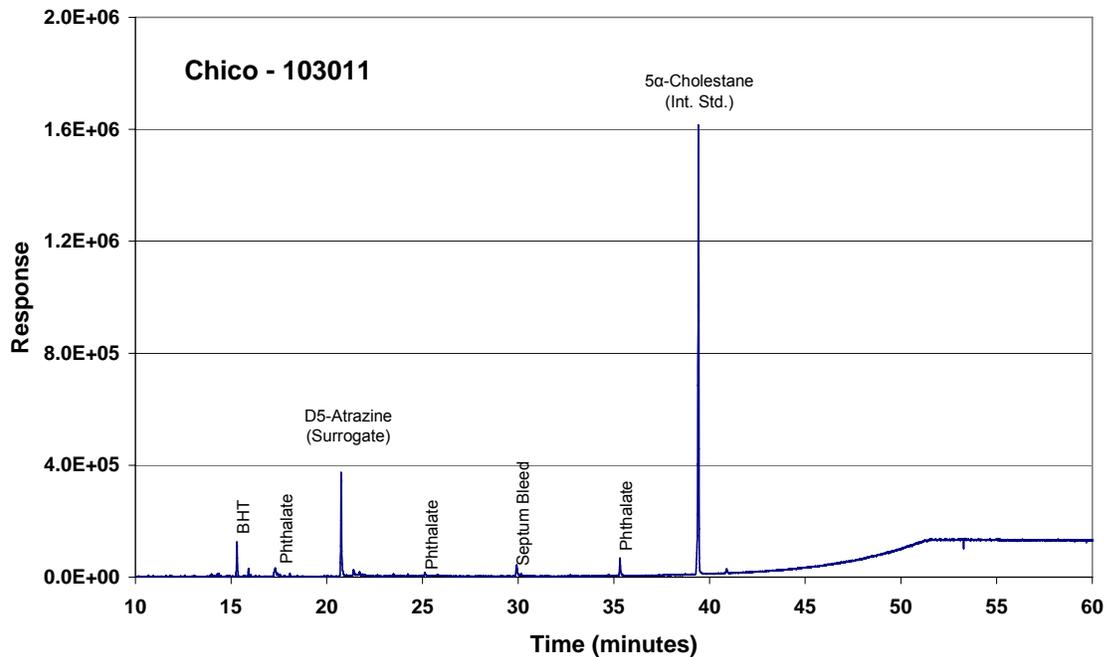


Figure 15. TIC of sample 103011. The GC/MS chromatogram is representative of the clean water extracts from the Chico study area.

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.

$\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ is also likely due to evaporation, either at the treatment plant or after water is applied to fields. Strongly enriched $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ 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 $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$, is characteristic of denitrification. A denitrification step was added to the SCRWA treatment process in 1995.

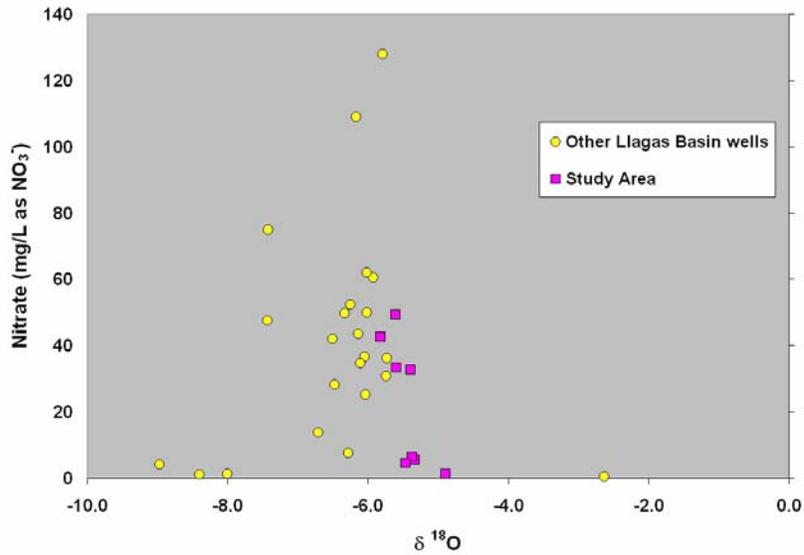


Figure 17. The ratio of nitrate versus stable isotope signatures of oxygen in wells from the region affected by wastewater irrigation (pink symbols) and in other shallow wells in the Llagas Basin (yellow symbols). Wastewater-influenced groundwater is shifted to more enriched isotopic values compared to ambient groundwater.

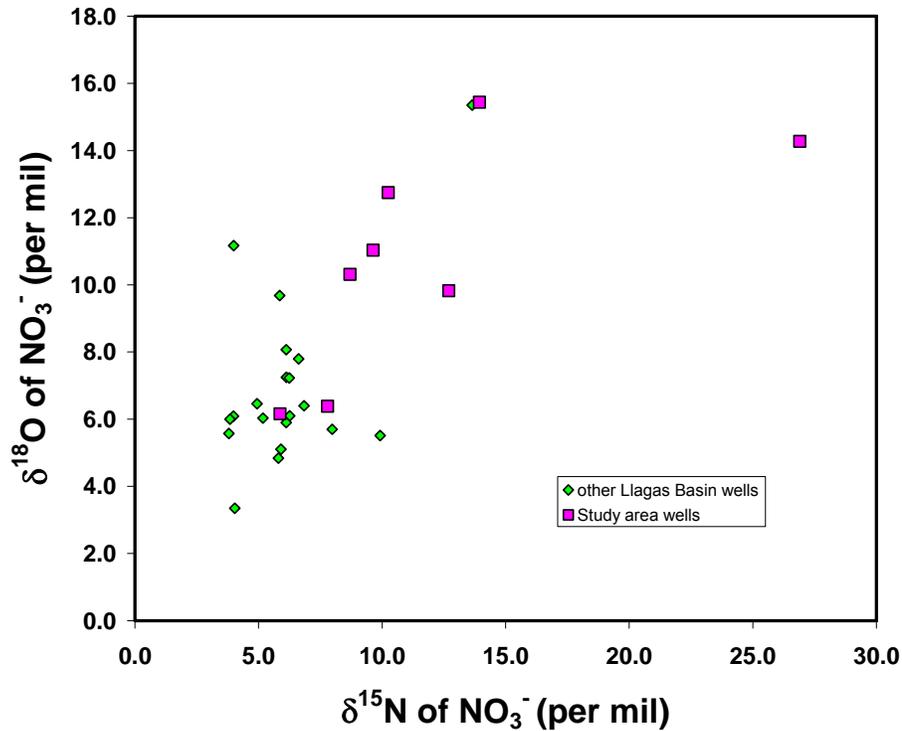


Figure 18. Nitrogen and oxygen isotope ratios in nitrate show a pattern characteristic of denitrification in samples influenced by recharge of wastewater.

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.

Gilroy 103443

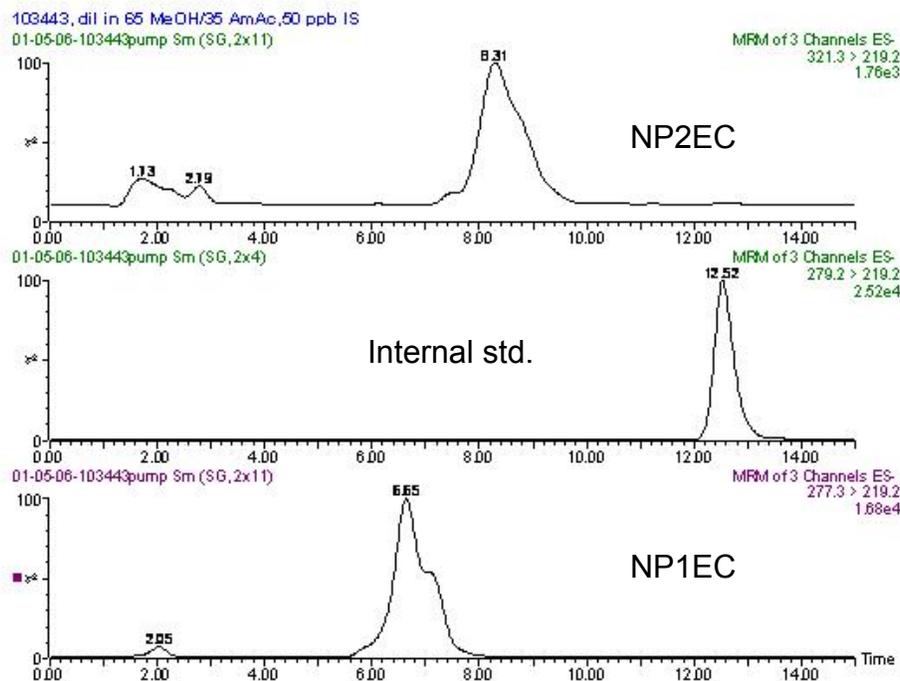


Figure 19. LC/MS/MS chromatogram of NP1EC (m/z 277 \rightarrow 219) and NP2EC (m/z 321 \rightarrow 219) in a Gilroy groundwater sample. The effective concentration of the internal standard (m/z 279 \rightarrow 219) is 1 $\mu\text{g/L}$. The likely reason that the NP1EC and NP2EC peaks are broader than 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 (Stamatelatos 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.

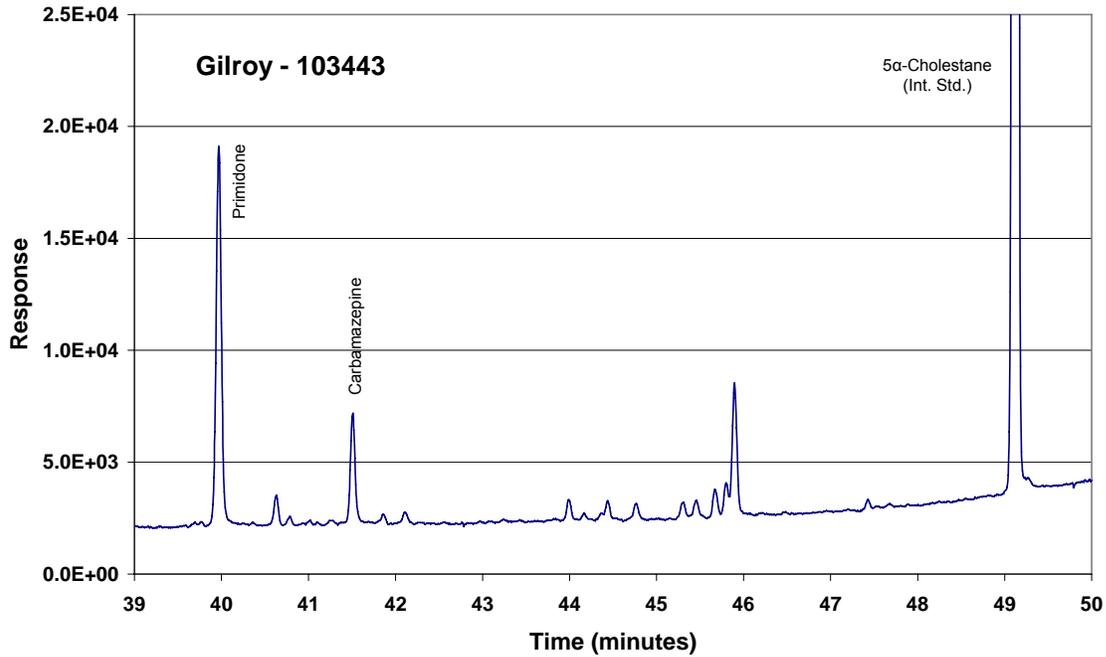


Figure 20. TIC of sample 103443, showing the anticonvulsants primidone and carbamazepine.

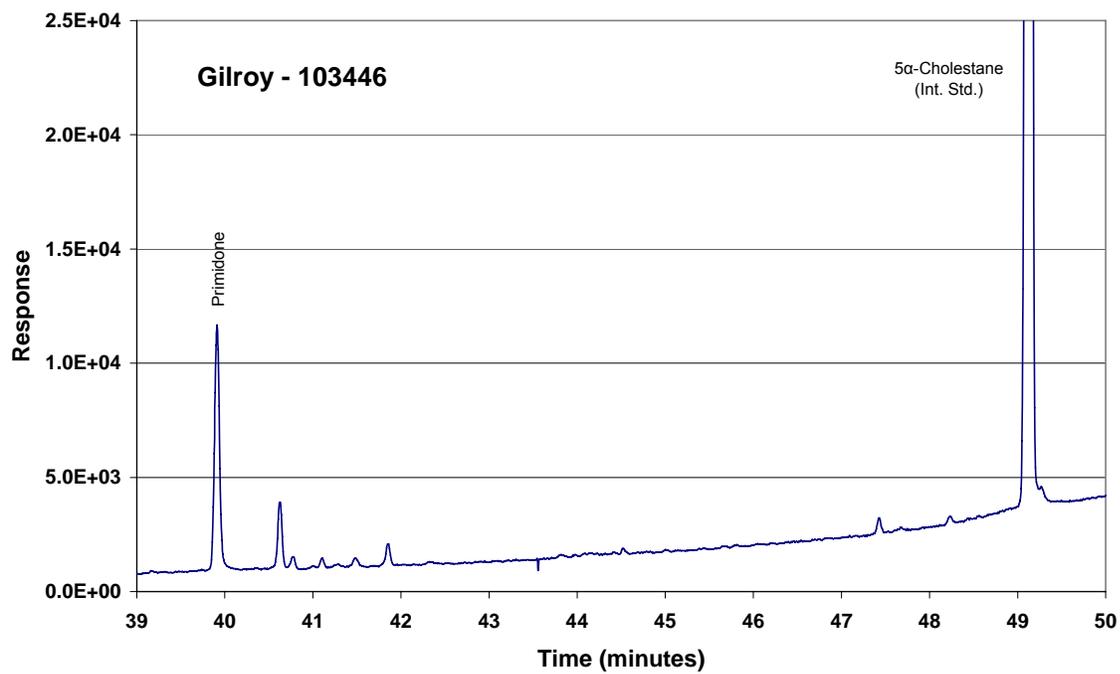


Figure 21. TIC of sample 103446, showing common plasticizer contaminants and primidone.

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 (^3H). 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 ^3H 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 ^3H through the LWRP. Combining these data with ^3H - ^3He groundwater age results, it was possible to 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.

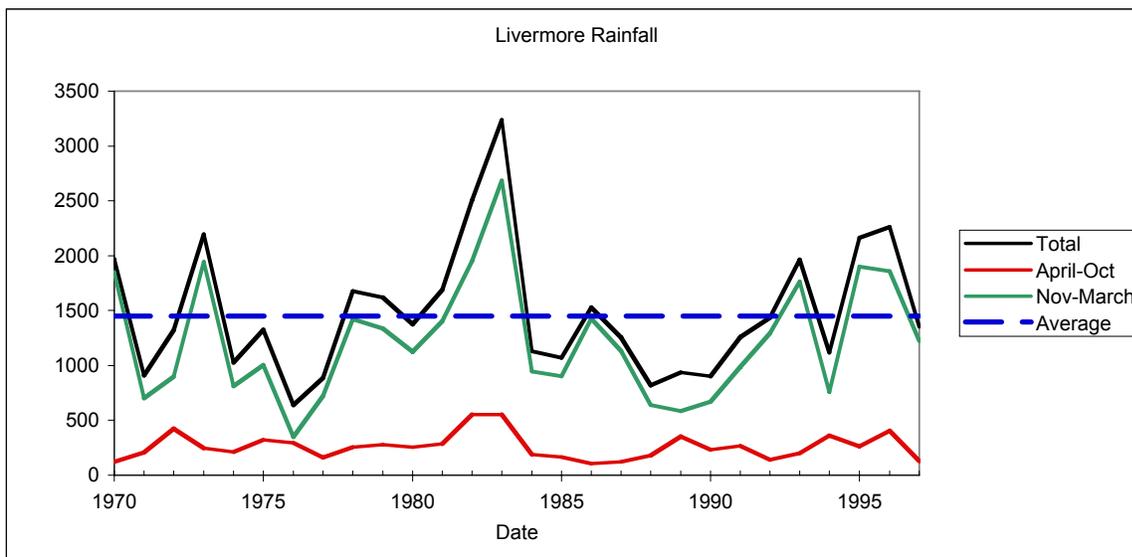


Figure 23. Rainfall trends for the study area since 1970.

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.

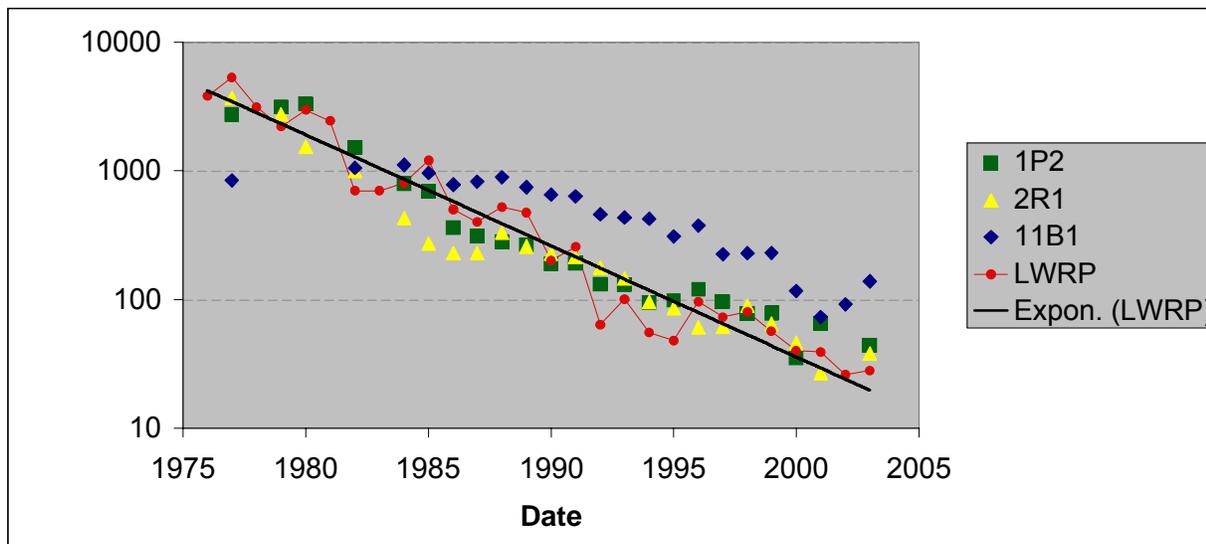


Figure 24. Time trends for tritium concentrations in LWRP effluent and selected monitoring wells.

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 ($\delta^{18}\text{O}$, 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 $\delta^2\text{H}$ and $\delta^{18}\text{O}$ 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.

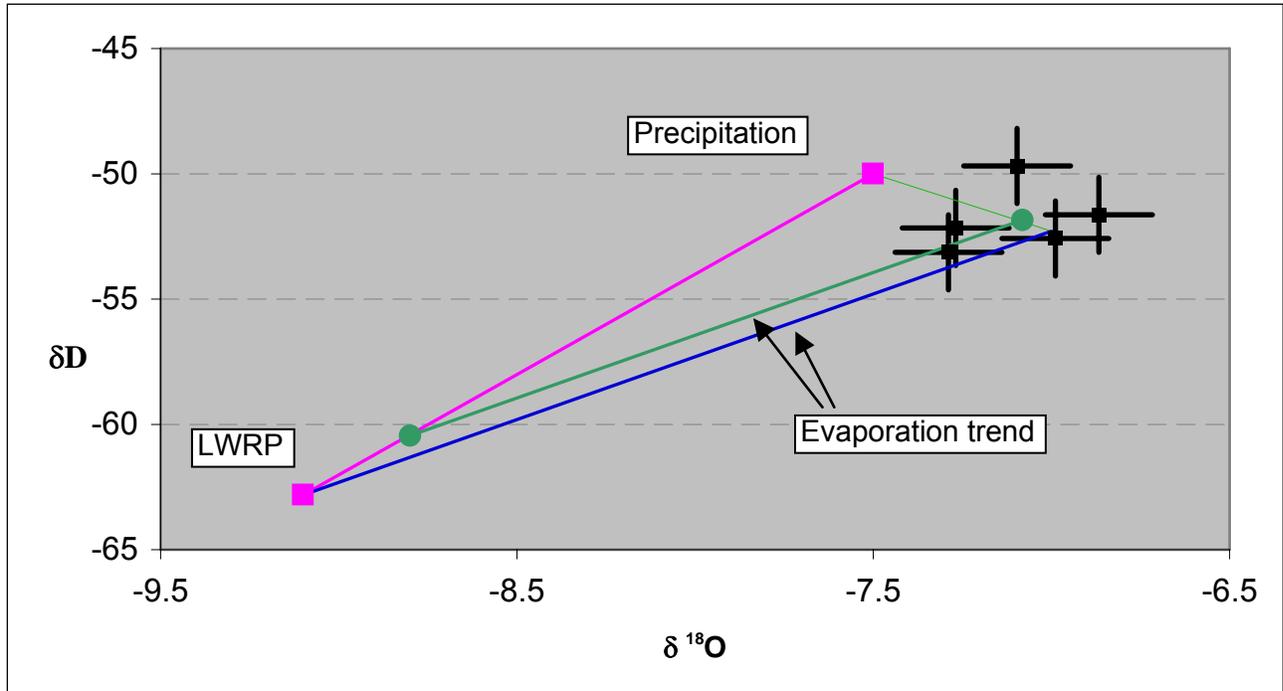


Figure 25. Isotopic signatures for LWRP effluent and LPGC groundwater samples.

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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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).

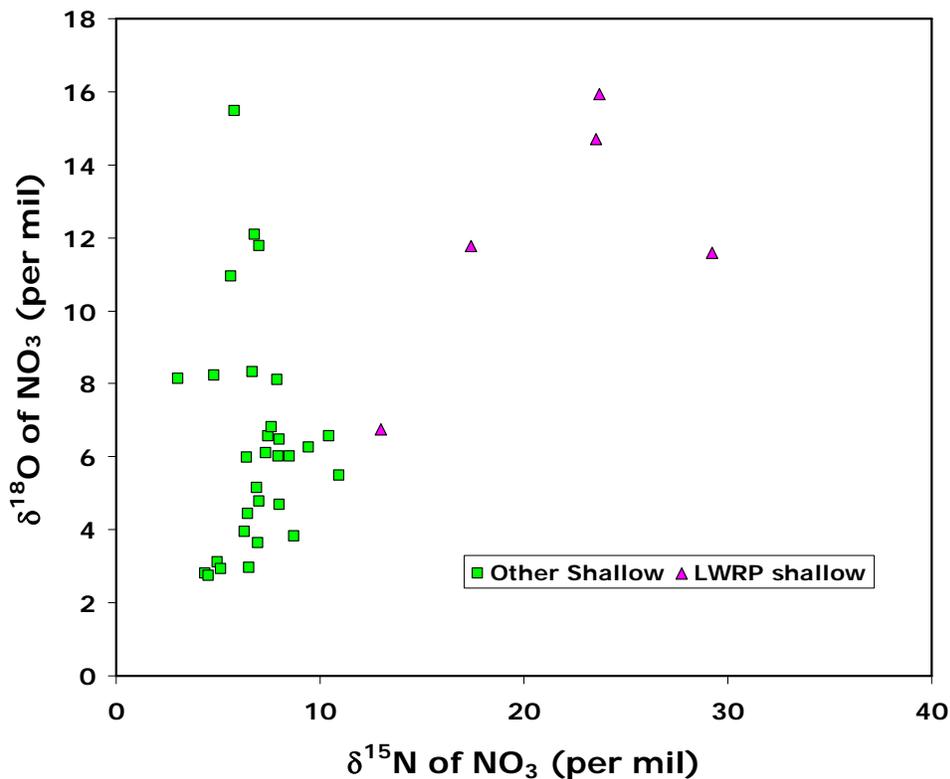


Figure 26. Shallow wells whose recharge source is treated wastewater from LWRP have isotopic signatures of nitrate that are distinct from other wells and indicate isotopic fractionation mediated by denitrification.

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.]

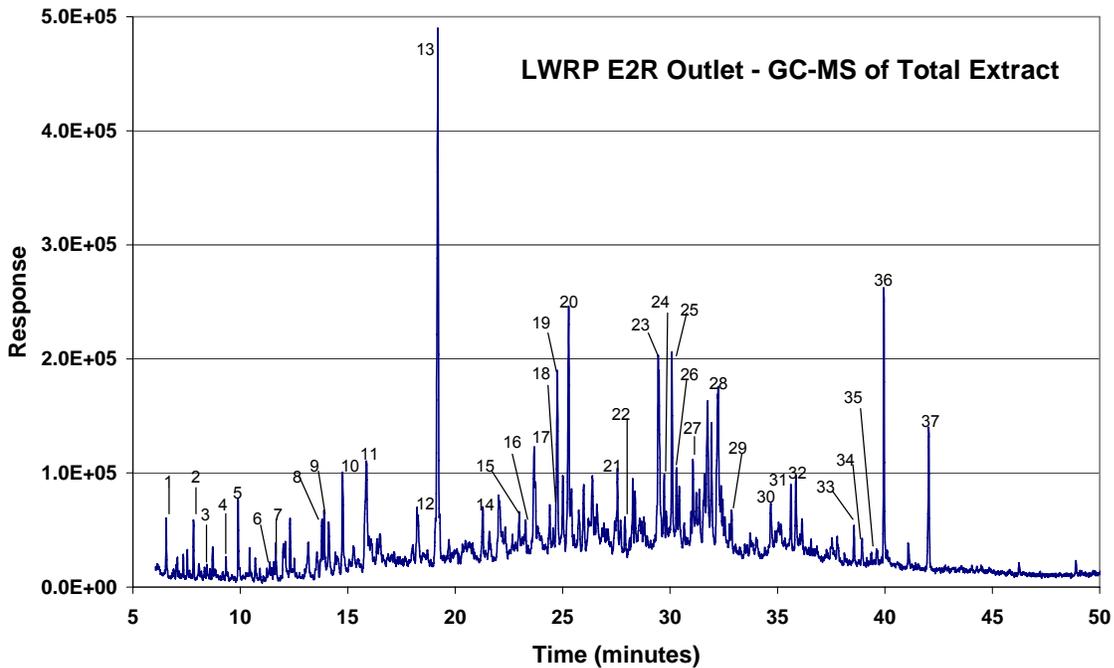


Figure 27. GC/MS TIC of total extract from E2R Outlet, Livermore Water Reclamation Plant with major peaks identified.

- | | |
|--|--|
| 1. Benzaldehyde | 21. Tris (2-chloroethyl) phosphate |
| 2. Dichlorobenzene | 22. N-Butylbenzenesulfonamide |
| 3. 3,3,5-Trimethylcyclohexane | 23. HHCB |
| 4. Acetophenone | 24. AHTN |
| 5. Tetramethylpyrazine | 25. 89, <u>109</u> ,151 |
| 6. Camphene hydrate | 26. Diphenylhydramine |
| 7. 2-(1,1-Dimethylethyl)-cyclohexanol | 27. Gemfibrozil |
| 8. Benzothiazole | 28. 107,135,165, <u>193</u> |
| 9. 4-(1,1-Dimethylethyl)-cyclohexanone | 29. Elemental sulfur |
| 10. (<u>68</u> ,80,83,107,109,135) | 30. <u>58</u> ,91,119,134 |
| 11. Dimethylphenol | 31. 145, <u>173</u> |
| 12. <u>57</u> ,82,85,125 | 32. 58, <u>257</u> ,272 |
| 13. <u>57</u> ,69, <u>109</u> ,151,169 | 33. Tris (1,3-dichloroisopropyl) phosphate |
| 14. <u>77</u> ,79, <u>107</u> | 34. Carbamazepine |
| 15. N-Cyclohexyl-2-pyrrolidone | 35. Triphenyl phosphate |
| 16. N,N-Diethyl-3-methylbenzamide (DEET) | 36. Tris (2-butoxyethyl) phosphate |
| 17. 2-(Methylthio)-benzothiazole | 37. Bis (2-ethylhexyl) phthalate |
| 18. Benzophenone | |
| 19. <u>109</u> ,151,213 | |
| 20. 91,119,157, <u>191</u> | |

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.

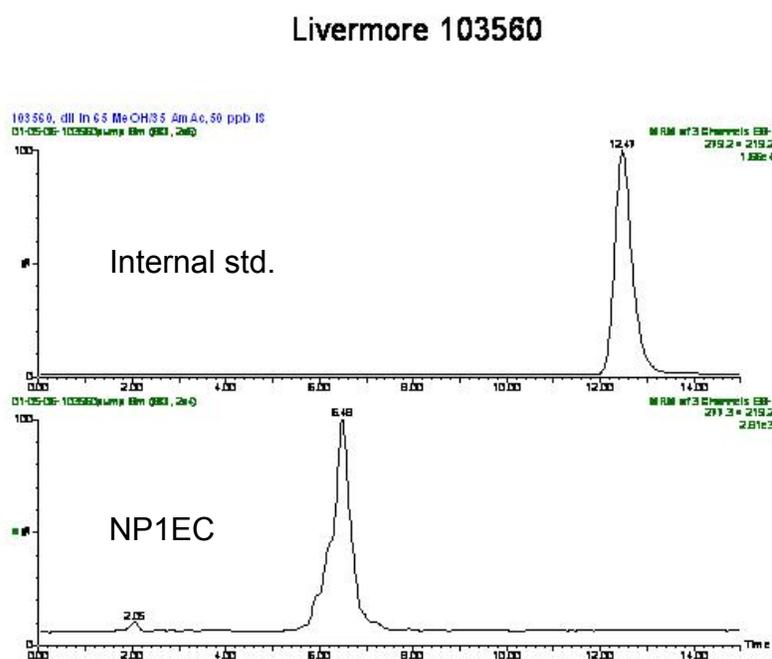


Figure 28. LC/MS/MS chromatogram of AP1EC (m/z 277→219) in a Livermore golf course groundwater sample. The effective concentration of the internal standard (m/z 279→219) is 1 $\mu\text{g/L}$.

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.

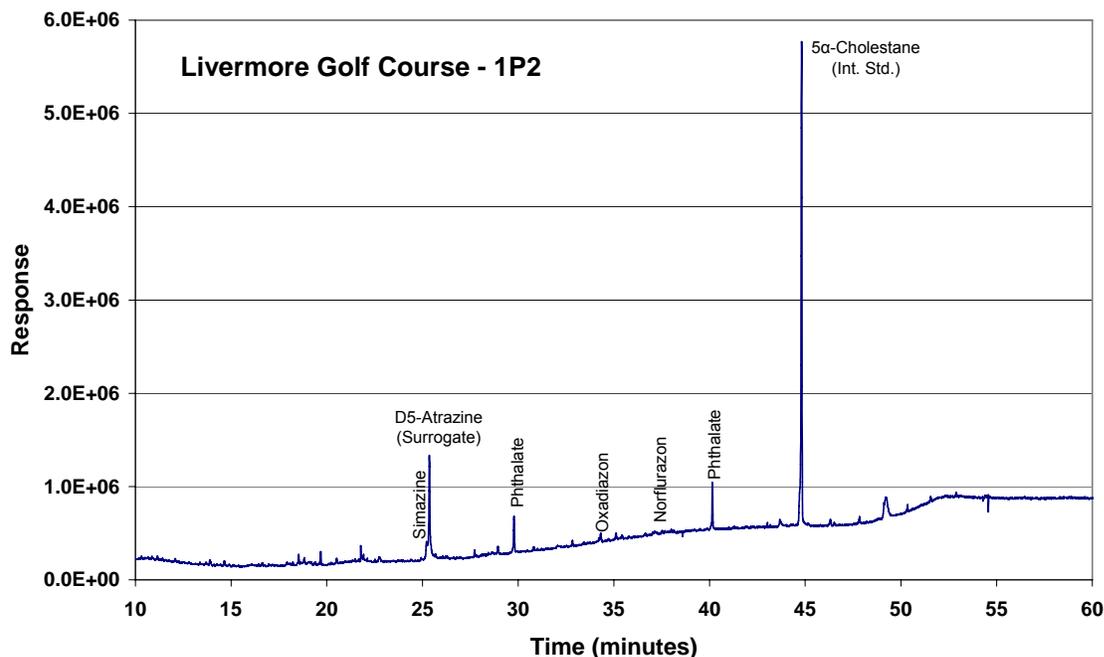


Figure 29. The GC/MS TIC of well 1P2 (sample 103559).

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; Klopfer 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.

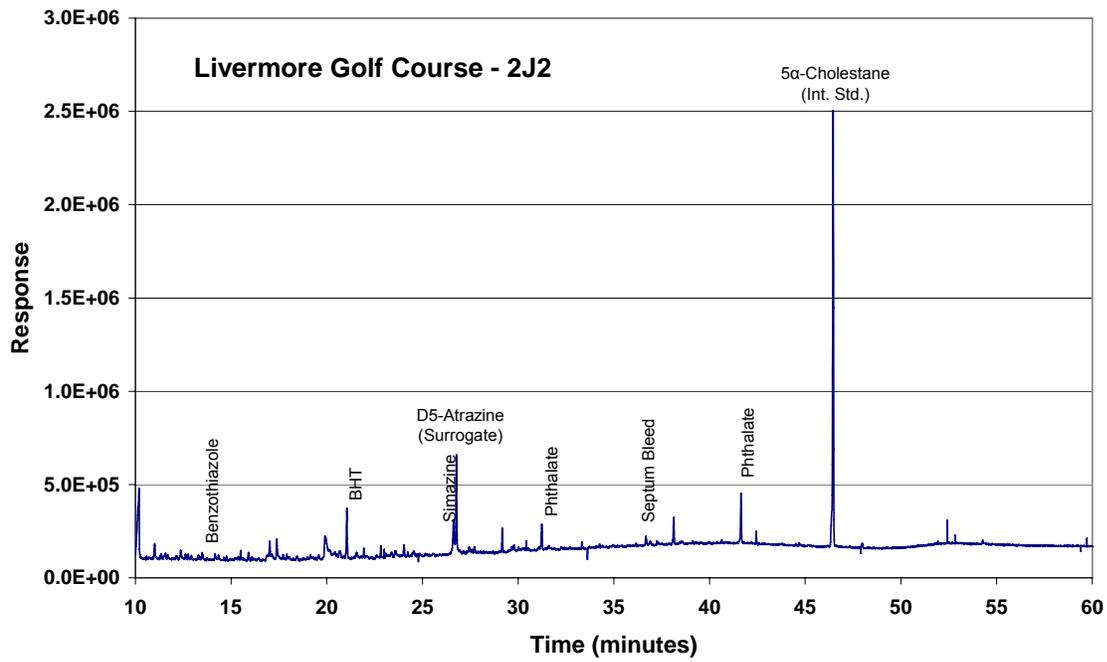


Figure 30. The GC/MS TIC of sample 103560 (Well 2J2).

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, $\delta^{18}\text{O}$ 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 ₂ O (%)	Target compounds detected (ng/L)
LPGC	2J2	31	19	36-49	NPECs, herbicides, benzothiazole
LPGC offsite	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 $\mu\text{g/L}$ 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.

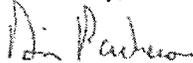
I am a 47 year-old dairyman and have known Jim for most of my life. I first became acquainted with Jim when I was a member of the Future Farmers of America. The Kerman FFA Chapter did not have a dairy cattle judging team and my instructor contacted another chapter and found out that Jim was coaching 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 "T"

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: Jim and Amelia Sweeney

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

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

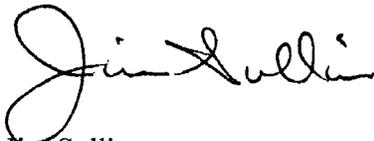
To Whom It May Concern:

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 Sopy 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

est 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

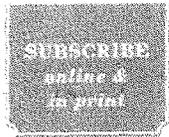
Model for sustainability

If a country had among the Earth's highest output per acre for its food and feed crops and among the low-

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

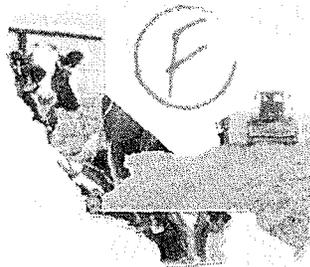
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HOARD'S DAIRYMAN

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/7104
<http://www.news.colostate.edu/Release/7104>

To comment, email your remarks to intel@hoards.com, [mailto:intel@hoards.com?Subject=intel comment](mailto:mailto:intel@hoards.com?Subject=intel%20comment)

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May 27, 2014