Groundwater Quality Monitoring and Assessment in California

State Board Meeting - Item 11
April 19, 2011

John Borkovich, PG
GAMA Program
State Water Resources Control Board

Water Boards

GAMA is:

Groundwater
Ambient
Monitoring and
Assessment

Water Boards

Why GAMA?

- California Relies Heavily on Groundwater
  - 35% of water for irrigation and public use is from groundwater
  - 43% of Californians are served by groundwater
  - Many communities rely 100% on groundwater
  - Contaminated groundwater results in treatment costs, well closures, and new well construction which increases costs for consumers

Water Boards

Why GAMA?

- Water Quality Testing is Not Complete
  - Water quality from 16,000 wells used for public supply is regulated by CDPH and regularly tested (36M people)
  - Water quality from 600K private domestic wells is not regulated and is rarely tested (1.4M people)

Water Boards

Why GAMA?

- Budget Act of 2000
- Water Code Section 10780
  - Groundwater Quality Monitoring Act of 2001
    (AB 599, Liu)
  - Groundwater Quality Monitoring
    (2008. AB 2222, Caballero)

Water Boards

GAMA Program Functions

- Coordinate with water agencies
- Collect new data
- Combine new and existing data

  (water quality, water level, contaminant sources)
- Assess groundwater quality
- Serve information to the public

Water Boards

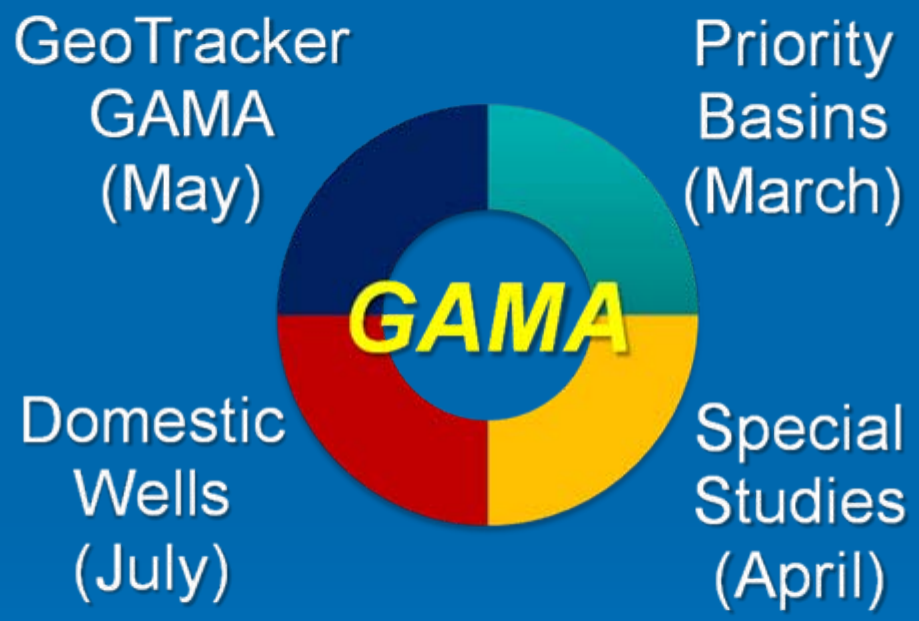
GAMA Program

- Projects staffed by State Board, USGS, LLNL to assess CA groundwater quality
- Well owners volunteer wells to be sampled
- Over 4,000 wells sampled since 2000
- GAMA tests groundwater for:
  - Drinking water standard contaminants
  - Hundreds of contaminants for trace levels

Water Boards

GAMA Program
Current Projects & Schedule for Board Meetings

Informational Items



Sampling conducted in *Voluntary Cooperation* with Participants

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USGS science for a changing world

Status: Priority Basins Project

- First statewide sampling cycle nearly complete
- 2,200 wells sampled
- Dozens of Reports, Fact Sheets published

- *USGS Presentation on Findings - March*

Water Boards

Status: Special Studies - LLNL

- Studies on nitrates from dairies, fertilizer, human wastewater
- Wastewater Indicator studies on effect of septic systems on shallow groundwater and areas influenced by recycled water
- Changes in chemistry of groundwater by recharge of surface water

LLNL Presentation on Findings – Today

Water Boards

Status: Domestic Well Project

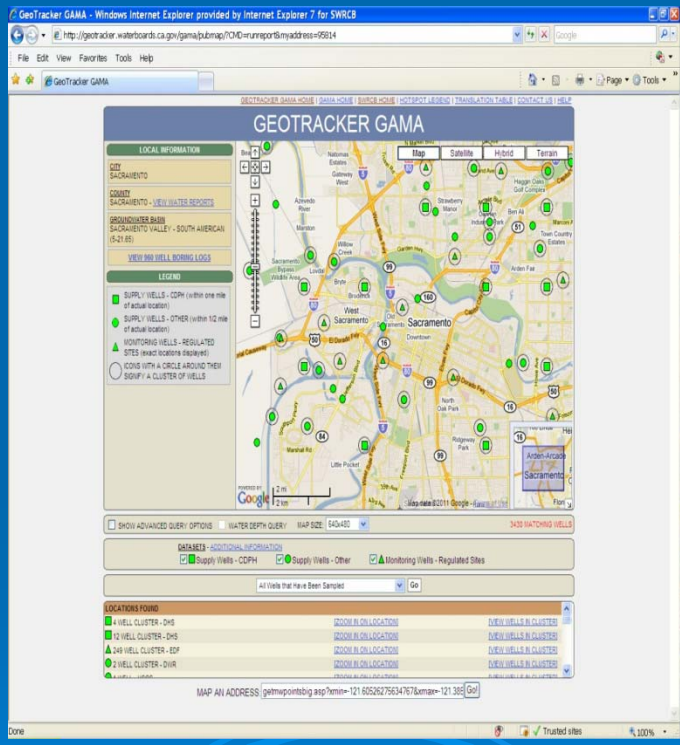
- 1,067 Wells sampled by Board staff from 2003-09
- Key Results – *El Dorado, Yuba, Tehama, Tulare, San Diego Counties*
  - Total Coliform: 28% wells tested Positive
  - Nitrate: Average 10% wells tested above MCL
  - Nitrate: 41% Tulare County wells tested above MCL
  - Radionuclides: 33% San Diego above MCL
- Monterey County sampling to begin in May

Presentation on Findings – July 19

Water Boards

GeoTracker GAMA:
Groundwater Quality Data System

- Fulfills AB599 intent: Central Data Source
- Data from CDPH, USGS, LLNL, DWR, DPR, State and Regional Water Boards
- Water quality, water levels, contaminant sources, groundwater publications
- Groundwater quality data collected with State funds must comply with AB 599 - but electronic submittal not specified



Presentation of System – May 17

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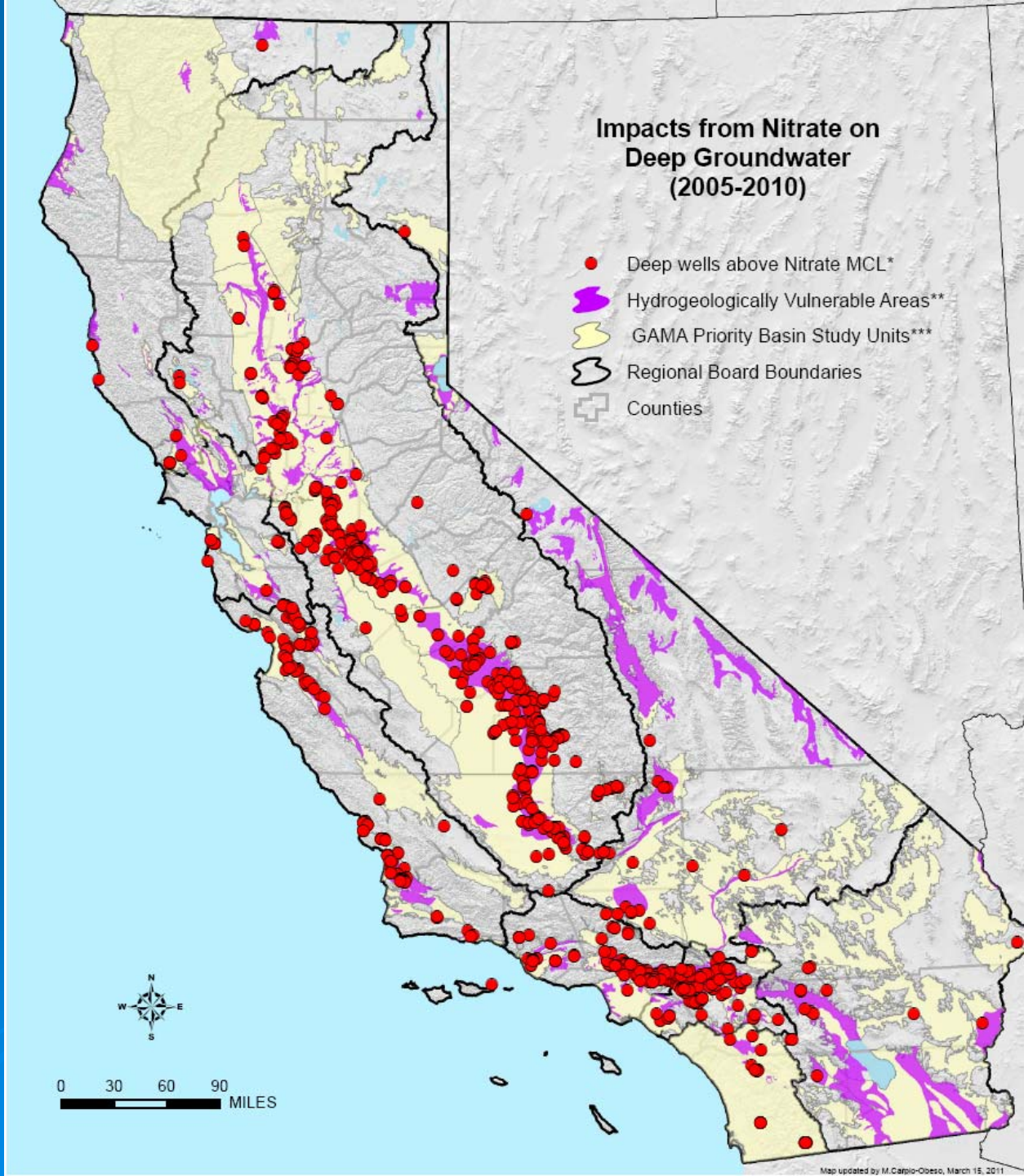
In Summary:

- Most land uses negatively affect groundwater
- Shallow groundwater is poor in many areas
- Deeper water has better quality, but contains several contaminants-usually in trace amounts
- To sustain groundwater resource and reduce negative trend, action is needed
- Monitoring groundwater quality is critical to track impacts over time

Water Boards

Hydrogeologically Vulnerable Areas and GAMA Priority Basins

Nitrate above MCL in Public Supply Wells



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Future Funding

- Bond Funds run out 2013
- Without replacement funding,
  Priority Basin Project funding will end
- AB 2222 Report to Legislature:
  Options to extend GAMA to 2024

Water Boards

GAMA Special Studies Project

Dr. Bradley Esser, LLNL

Water Boards

GAMA Special Studies: Focused Water Quality Investigations of State Wide Relevance

A Presentation to
State Water Resources Control Board
April 19, 2011
by
Bradley K. Esser (LLNL)
Item 11

Water Boards

Lawrence Livermore National Laboratory

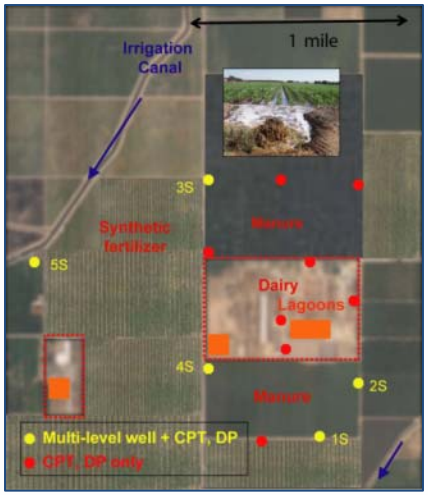
What is a GAMA Special Study?

- **A focused water-quality investigation**
  - Local scale and limited duration
  - Specific water quality issue
- **Of state-wide relevance**
  - Common or emerging water quality issue affecting groundwater used for drinking water
- **Using innovative & scientifically credible methods**
  - Scientifically credible case studies using cutting-edge science
  - Publications in peer-reviewed literature
- **With outreach to the professional community & public**
  - Work with local agencies, well owners & stakeholders
  - Involve & train students

Goal: Science-Informed Policy

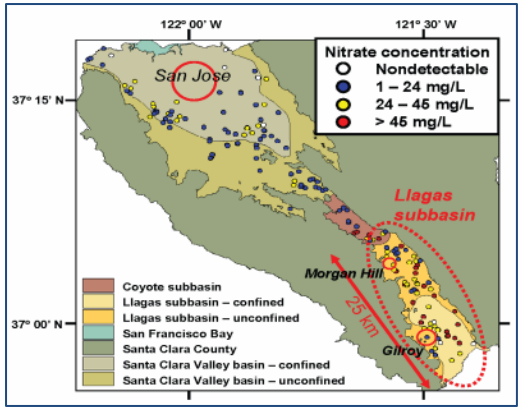
A Focused Water Quality Investigation

Municipal well
Is high nitrate from orchards or farm supply?



Small dairy farm
Transport & fate of dairy-derived nitrate to underlying aquifer

Managed Aquifer Recharge Operation
Is high arsenic caused by recent recharge operation?



Groundwater basin
Sources of nitrate and impact of nutrient management plans

Of State-Wide Relevance

- **Nitrate in groundwater – sources, fate and transport**
  - Nitrate impacts from point & non-point sources
    - Basins with nitrate management plans or PSW exceedences
    - Central Valley dairies
    - Municipal wells
  - Development & demonstration of source attribution for nitrate
    - Isotopic composition and co-contaminants

- **Groundwater recharge and transport**
  - Water quality changes during groundwater recharge
  - Development of new age tracers for groundwater recharge
    - Introduced tracers (to replace SF6) and natural tracers
  - Identification of recharge area and surface/groundwater interaction

- **Wastewater impacts on groundwater**
  - Development of new tracers of wastewater in groundwater
    - Pharmaceuticals (carbamazepine) and artificial sweeteners
  - Impact of septic discharge and recycled municipal wastewater

Using Innovative Approaches

Groundwater Age Dating

- Delineate groundwater recharge, flow & contaminant transport
- Proxy for aquifer susceptibility
- Tool for assessment of management practices

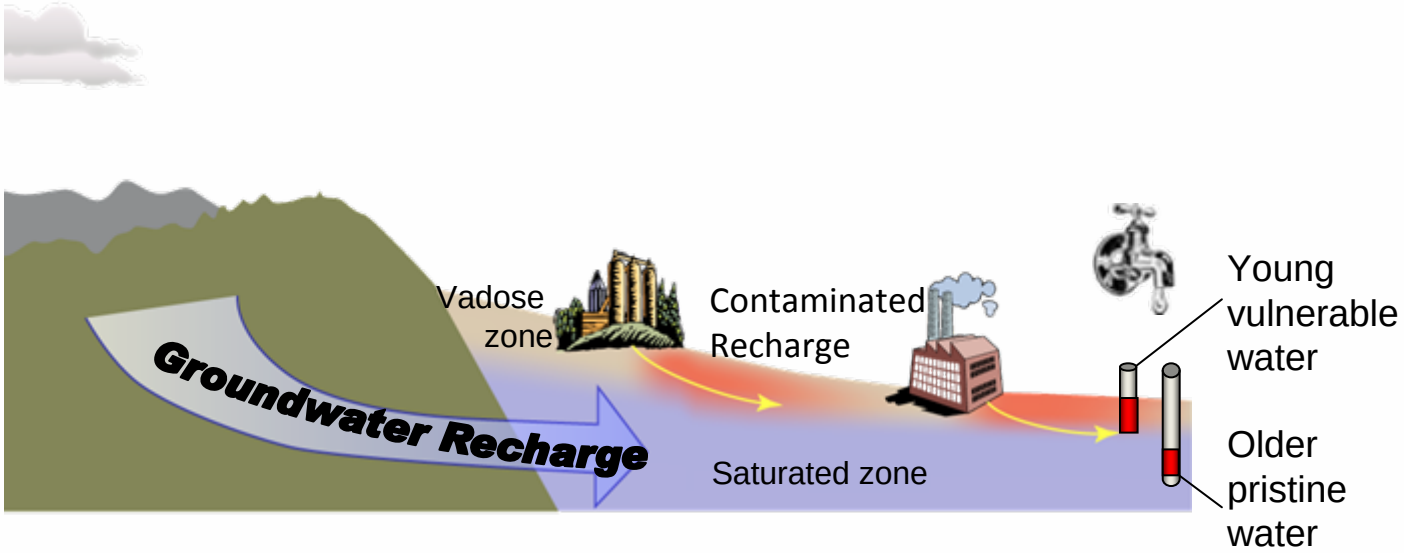
Isotope & Dissolved Gas Geochemistry

- Water source (stable isotopes of water)
- Water “tagging” (introduced gas tracers)
- Contaminant source (isotopic composition)
- Contaminant degradation (e.g. denitrification)

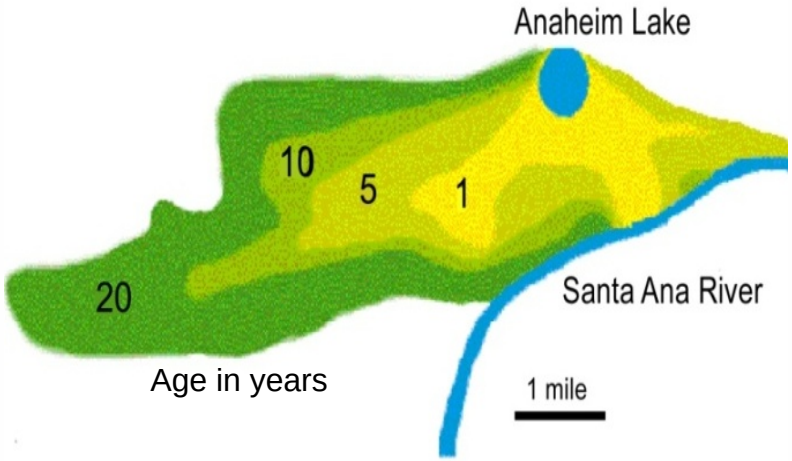
Industrial VOCs & Emerging Contaminants

- Proxy for aquifer susceptibility
- Contaminant source tracers
- Emerging contaminant transport & degradation in subsurface

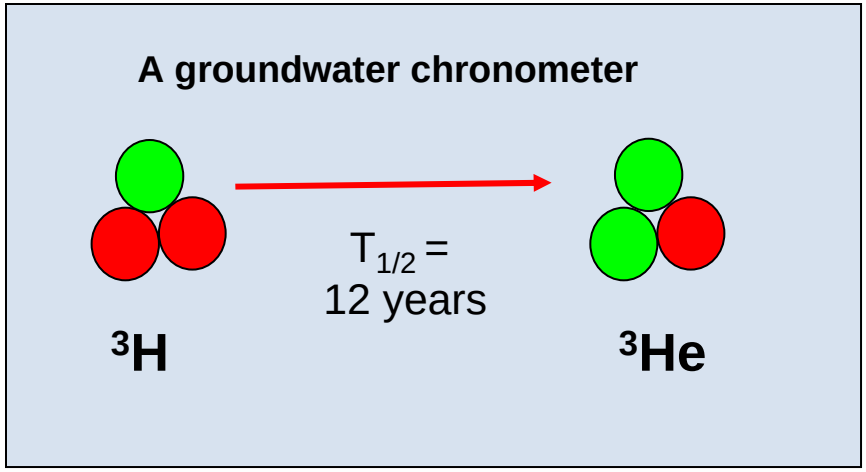
Groundwater age tracers act as proxies for groundwater susceptibility



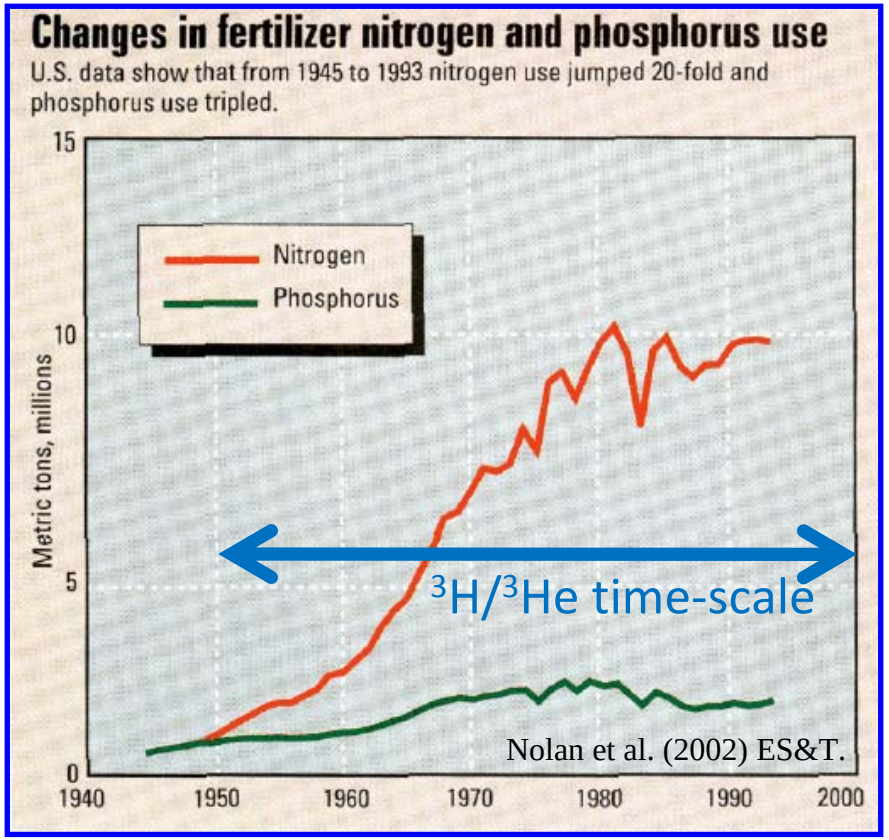
- **Groundwater age by Tritium/Helium ($^3H/^3He$)**
  - To determine mean age
- **Low Level VOCs**
  - To detect recent recharge
- **Stable isotopic composition of water**
  - To distinguish sources of water



The tritium/helium ($^3H/^3H$) method measures groundwater age on an appropriate time-scale for water resource studies



- *The method is useful over the last 50 years with an uncertainty of 1-2 years.*
- *Tritium has both natural and anthropogenic sources in the atmosphere.*



Most public-drinking water wells in California produce water with measurable tritium.

Tritium-Helium ($^3H/^3He$) age dating and noble gas geochemistry is a signature LLNL capability

Noble Gas Mass Spectrometry

The detection level for ^3He is 1 Zeptomole (600 atoms). LLNL routinely measures 10^5 atoms of ^3He.

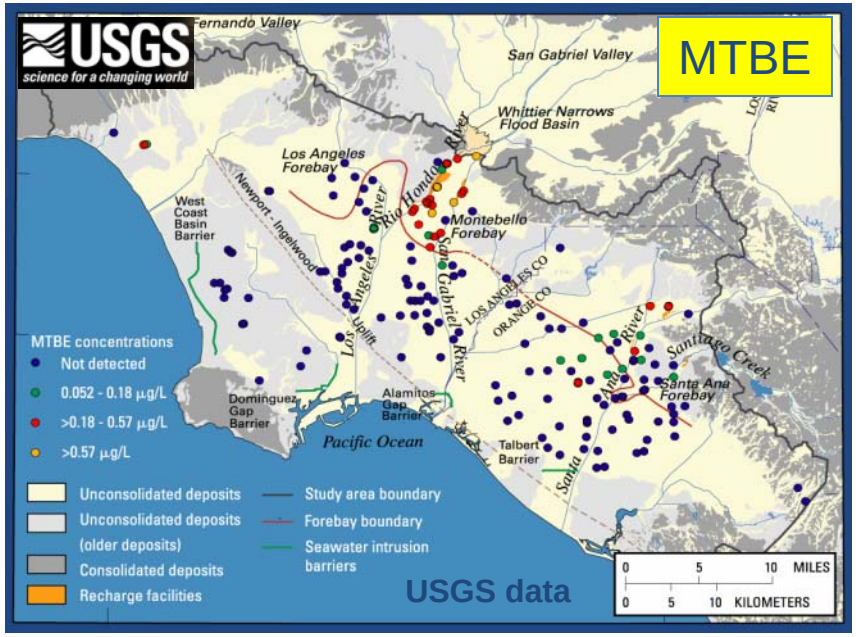
LLNL is one of two high-throughput noble gas mass spectrometry labs in the country

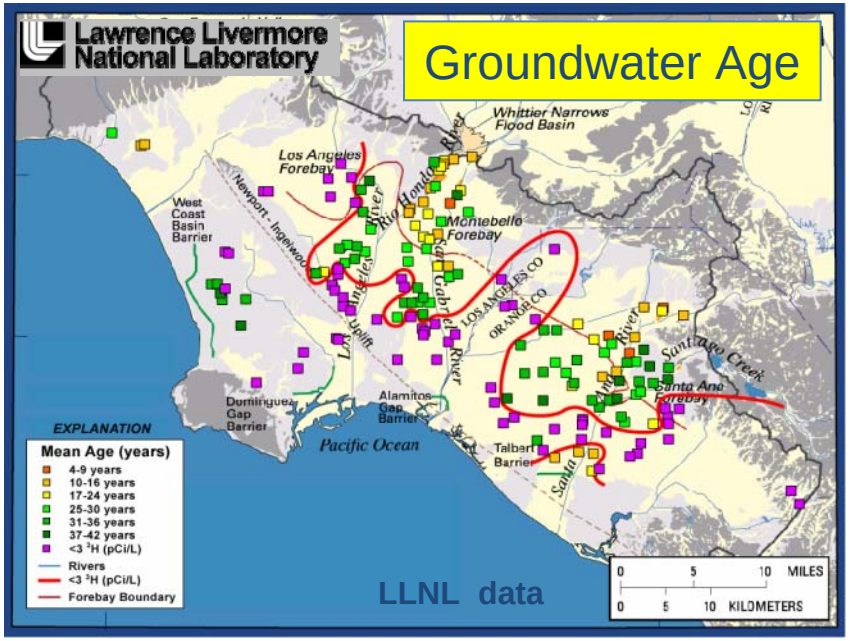
- 500-1,000 samples per year
- ^3He accumulation for ^3H determination

Over the past 15 years, LLNL has made age-dating accessible to water resource managers

GAMA validated using groundwater age as a proxy for susceptibility assessment in the California Aquifer Susceptibility Project

In the Los Angeles Basin, old groundwaters are devoid of contamination, despite the ubiquity of leaking underground fuel tanks and their proximity to production wells





Significant findings of the California Aquifer Susceptibility project

- Coastal aquifers are well-protected from surface contamination
- Central Valley aquifers are not well-protected from surface contamination

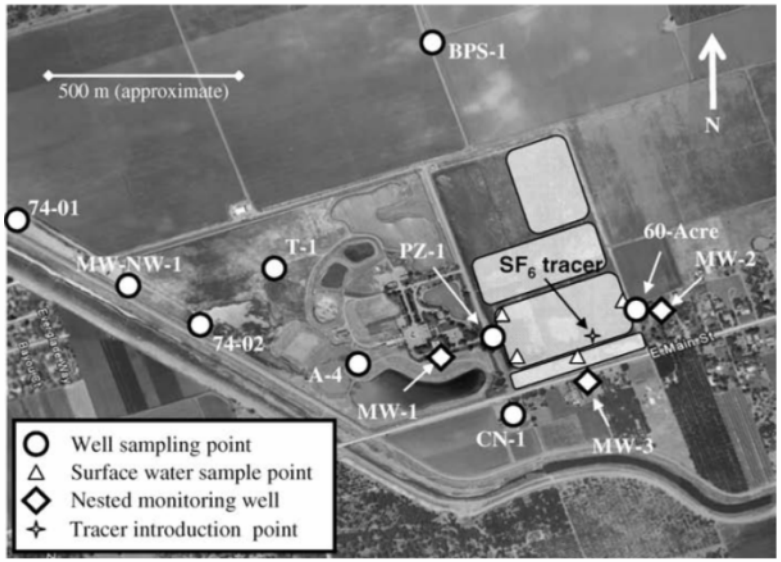
Aquifer Storage and Recovery Projects are vital for California's water supply

Investigated a groundwater banking project in California's Central Valley:

- Introduced SF_6 tracer
- Tritium/helium-3 age dating
- Geochemical modeling

Key Findings:

- **Identification of suitable areas**
- **Travel times** for banked water
- **Water quality changes in** banked high-quality water
- **Transport of emerging contaminants** associated with groundwater recharge

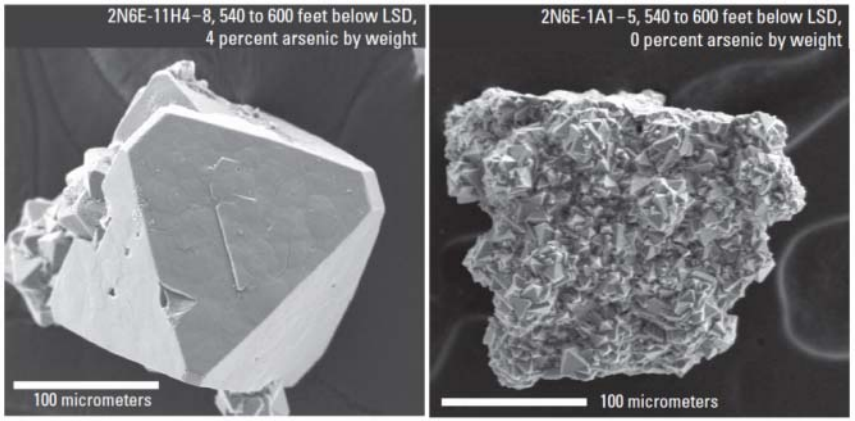


A key finding was that the highest groundwater arsenic concentrations occurred in the most recently recharged water.

Water quality can be affected by groundwater banking under specific recharge conditions

Arsenic release is controlled by local geology and the composition of the recharge water

- Arsenic is rapidly released from naturally occurring iron oxides in the aquifer to recharge waters, which have higher pH than ambient water



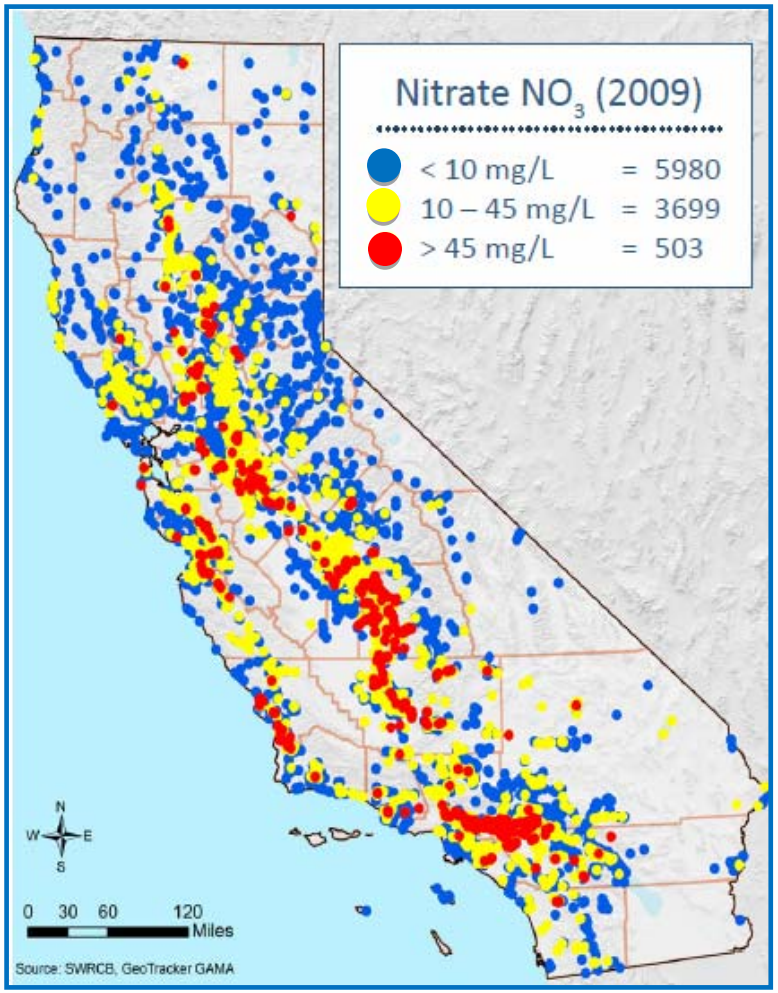
Izbicki et al. 2008. USGS OFR-2008-1272.

Specific recommendations can be made on recharge management

- Low-oxygen conditions during recharge will result in dissolution of ferric oxides, and release of much higher concentrations of arsenic.
- High oxygen demand in recharging water should be avoided.
- The current operation is sustainable with monitoring

McNab WW, Singleton MJ, Moran JE, and Esser BK, 2009. Ion exchange and trace element surface complexation reactions associated with applied recharge of low-TDS water in the San Joaquin Valley, California. *Applied Geochemistry* ***24, 129-137.***

Nitrate contamination is a water-quality issue of state-wide relevance

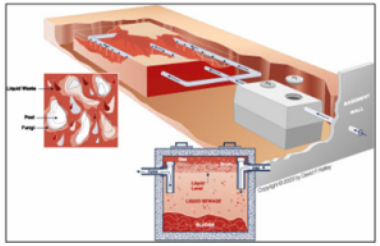


Animal Manure

Fertilized Agriculture

http://www.scinetcc/cgi-bin/picpost/posts/346.shtml

Septic Systems



Organic Soil N

Sources of nitrate are often co-located and non-point source.

Nitrate-contaminated groundwater: Distinguishing sources

Shallow groundwater is contaminated by nitrate

- Deeper groundwater is primary source of drinking water

What is the source & age of the contamination?

- High-density septic systems?
- Legacy or current agricultural practices?

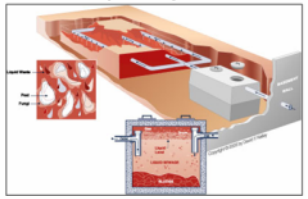
An isotopic approach: Distinguishing synthetic fertilizers, manure, and wastewater

The dual-isotope approach can distinguish synthetic fertilizers from organic N sources, but cannot distinguish manure from septic sources

Animal Manure

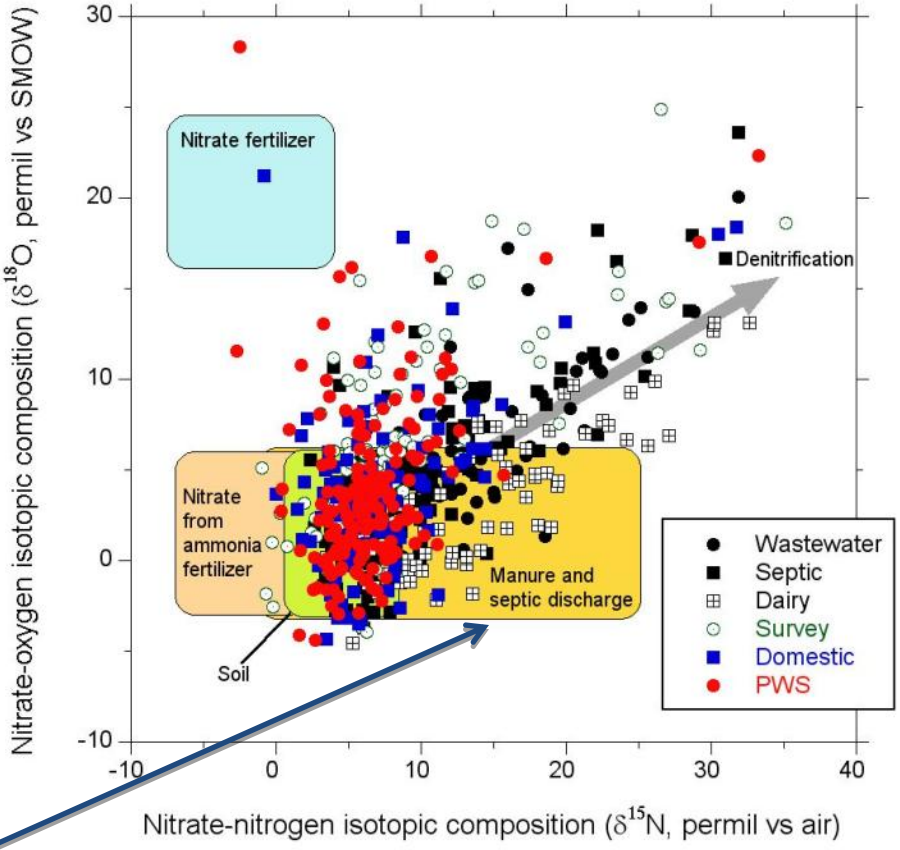
Fertilized Agriculture

Septic Systems



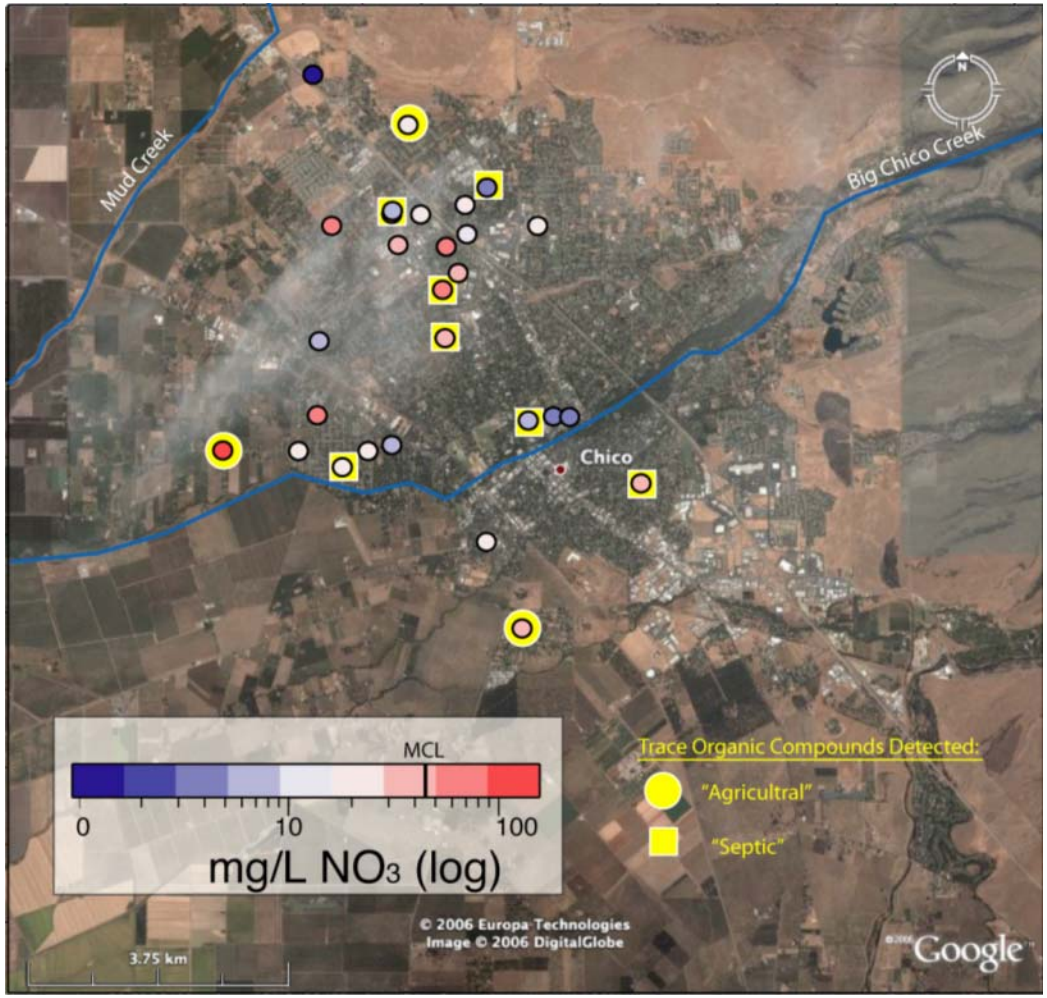
Organic Soil N

Nitrogen & oxygen isotopic composition of nitrate in GAMA Special Study groundwaters



Nitrate from Chico falls mostly in the "manure and septic discharge" field

Trace organics can be used to distinguish between septic & agricultural sources of nitrate



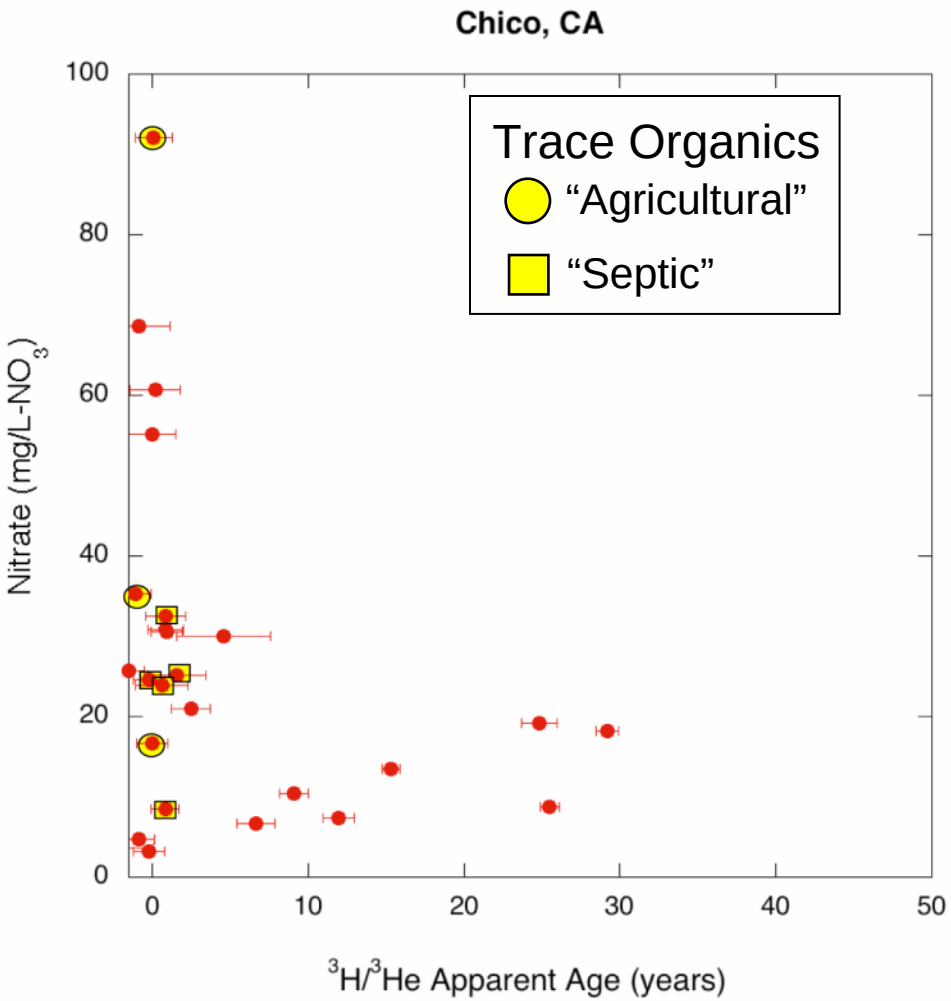
Trace Organics
- "Agricultural"
- "Septic"

"Agricultural "
- Herbicides (1)
- Herbicide degradates (2)

"Septic"
- DEET (1)
- Caffeine (2)
- Surfactants (1)
- Carbamazepine (4)

Current & future studies:
boron isotopes, artificial sweeteners

Tritium/helium-3 age dating can be used to distinguish between recent and past sources of nitrate



- **Nitrate contamination in Chico**
  - High-density septic system discharge is a source of nitrate within the city limits
  - Manure from agricultural operations is a source of nitrate on the periphery of the city
  - Nitrate contamination is ongoing and associated with current practices

We used a similar approach to distinguish nitrate sources in the Livermore-Amador Basin:

The International Association of GeoChemistry selected the paper – "Moore et al. (2006) *Sources of Groundwater Nitrate Revealed Using Residence Time and Isotope Methods*" -- as the year's most significant paper published in *Applied Geochemistry*, the IAGC's monthly scientific journal.

What are the general findings?

- **Groundwater age is a valuable tool**
  - as a predictor of groundwater susceptibility
  - as a constraint on groundwater flow

- **Multi-disciplinary approaches provide valuable new information and approaches for water management**
  - Managed aquifer recharge can impact water quality
  - Contaminant attribution often requires multiple tracers

Current Studies

- **We are developing new short time-scale tracers for artificial recharge**
  - *Sulfur-35*, a natural cosmogenic nuclide with an short half life (81 days)
  - *Helium* as an introduced tracer using field-portable instrumentation

- **We are developing a new tracers for wastewater recharge to distinguish septic/municipal from agricultural sources of nitrate**
  - *Artificial sweeteners,* e.g. saccharin and acesulfame
  - *Boron isotopic composition* in domestic wells

- **We are using tritium to identify un-affected "ambient" groundwater**

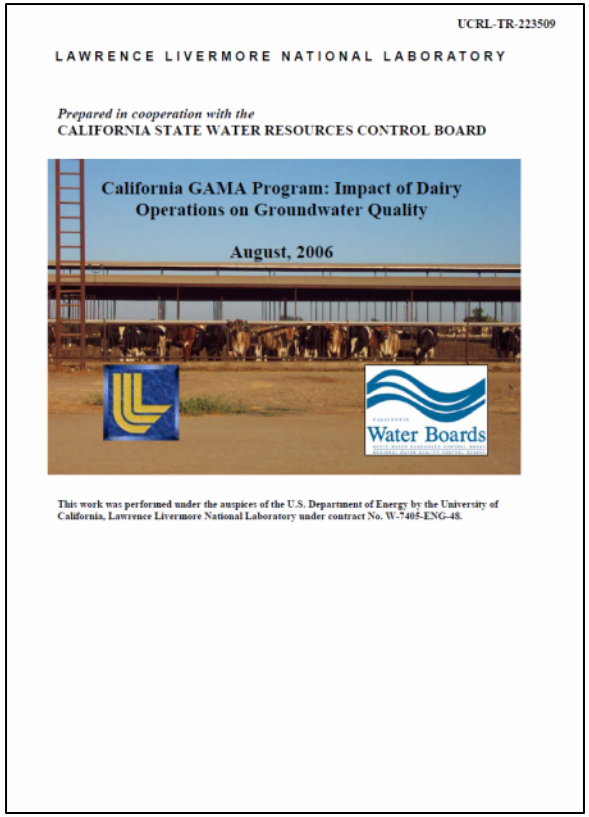
- **We are studying ground/surface water interactions in Salinas Valley**

Future Studies

- **Climate Change Impacts**
  - We are investigating the potential impact of climate change on recharge and groundwater quality in high-elevation basins
- **Groundwater Age Map:**
  - We will develop a map and database of groundwater age for all groundwaters collected by the GAMA project
- **Geotracker Database:**
  - We are uploading archival data from the GAMA Special Studies and California Aquifer Susceptibility Projects to Geotracker

Technical Publications

Technical Reports



UCRL-TR-223509

LAWRENCE LIVERMORE NATIONAL LABORATORY

Prepared in cooperation with the
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

California GAMA Program: Impact of Dairy Operations on Groundwater Quality

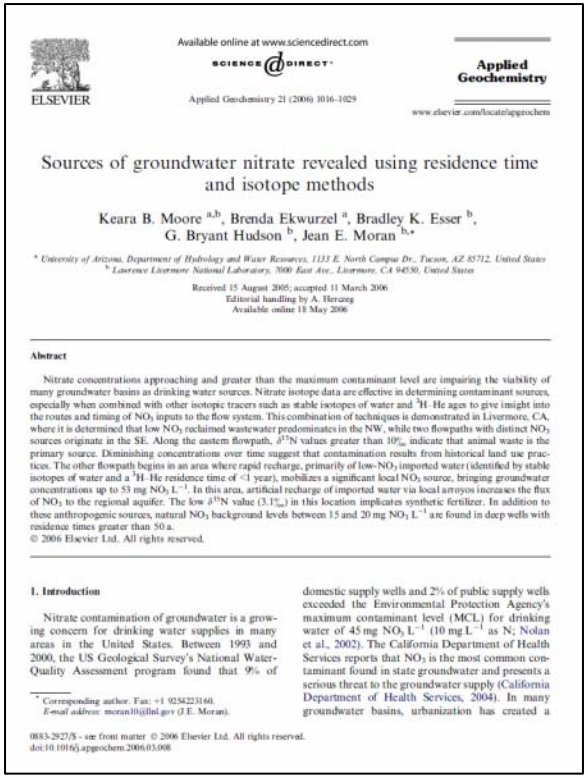
August, 2006

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

14 published

www.swrcb.ca.gov/water_issues/programs/gama/gamadocs.shtml

Peer-reviewed Publications



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Applied Geochemistry 21 (2006) 1016–1029

Applied Geochemistry
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Sources of groundwater nitrate revealed using residence time and isotope methods

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Received 15 August 2005; accepted 11 March 2006
Editorial handling by A. Herczeg
Available online 18 May 2006

Abstract

Nitrate concentrations approaching and greater than the maximum contaminant level are impairing the viability of many groundwater basins as drinking water sources. Nitrate isotope data are effective in determining contaminant sources, especially when combined with other isotopic tracers such as stable isotopes of water and ^3H–He ages to give insight into the routes and timing of NO_3 inputs to the flow system. This combination of techniques is demonstrated in Livermore, CA, where it is determined that low NO_3 reclaimed wastewater predominates in the NW, while two flowpaths with distinct NO_3 sources originate in the SE. Along the eastern flowpath, $\delta^{15}N$ values greater than 10‰ indicate that animal waste is the primary source. Diminishing concentrations over time suggest that contamination results from historical land use practices. The other flowpath begins in an area where rapid recharge, primarily of low-NO_3 imported water (identified by stable isotopes of water and a ^3H–He residence time of <1 year), mobilizes a significant local NO_3 source, bringing groundwater concentrations up to 53 mg NO_3 L^{-1}. In this area, artificial recharge of imported water via local arroyos increases the flux of NO_3 to the regional aquifer. The low $\delta^{15}N$ value (3.1‰) in this location implicates synthetic fertilizer. In addition to these anthropogenic sources, natural NO_3 background levels between 15 and 20 mg NO_3 L^{-1} are found in deep wells with residence times greater than 50 a.
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1. Introduction

Nitrate contamination of groundwater is a growing concern for drinking water supplies in many areas in the United States. Between 1993 and 2000, the US Geological Survey's National Water-Quality Assessment program found that 9% of domestic supply wells and 2% of public supply wells exceeded the Environmental Protection Agency's maximum contaminant level (MCL) for drinking water of 45 mg NO_3 L^{-1} (10 mg L^{-1} as N; Nolan et al., 2002). The California Department of Health Services reports that NO_3 is the most common contaminant found in state groundwater and presents a serious threat to the groundwater supply (California Department of Health Services, 2004). In many groundwater basins, urbanization has created a

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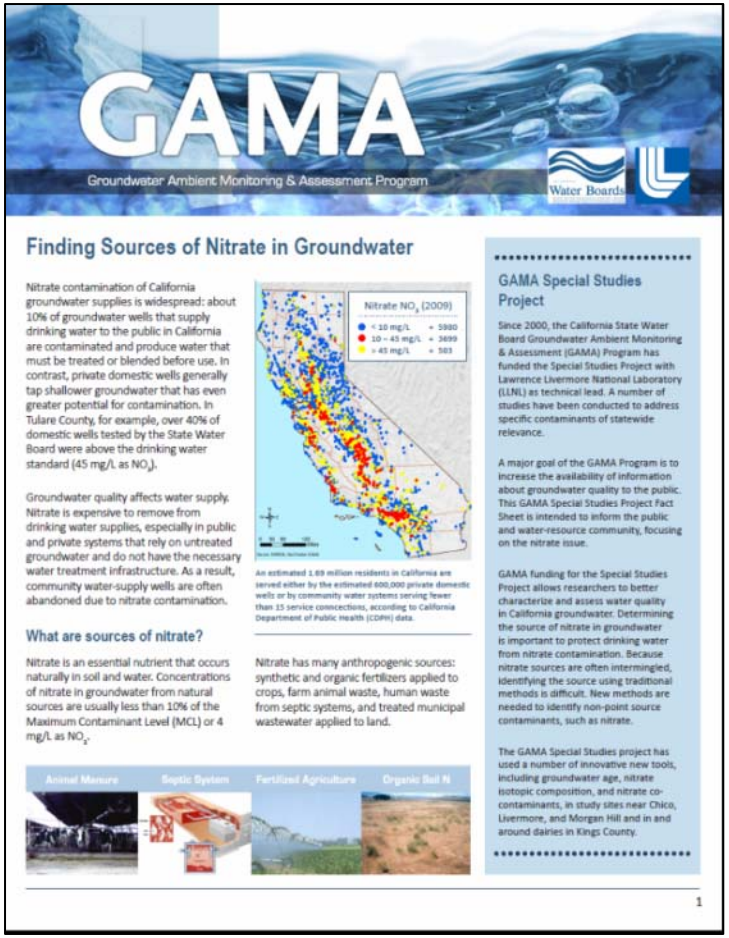
doi:10.1016/j.apgeochem.2006.03.008

9 published

Environmental Science & Technology
Applied Geochemistry
Ground Water

General Audience Publications

Fact Sheets



GAMA

Groundwater Ambient Monitoring & Assessment Program

Water Boards

Finding Sources of Nitrate in Groundwater

Nitrate contamination of California groundwater supplies is widespread: about 10% of groundwater wells that supply drinking water to the public in California are contaminated and produce water that must be treated or blended before use. In contrast, private domestic wells generally tap shallower groundwater that has even greater potential for contamination. In Tulare County, for example, over 40% of domestic wells tested by the State Water Board were above the drinking water standard (45 mg/L as NO_3).

Groundwater quality affects water supply. Nitrate is expensive to remove from drinking water supplies, especially in public and private systems that rely on untreated groundwater and do not have the necessary water treatment infrastructure. As a result, community water-supply wells are often abandoned due to nitrate contamination.

What are sources of nitrate?

Nitrate is an essential nutrient that occurs naturally in soil and water. Concentrations of nitrate in groundwater from natural sources are usually less than 10% of the Maximum Contaminant Level (MCL) or 4 mg/L as NO_3.

Nitrate NO_3 (2009)

< 10 mg/L = 5900
10 – 45 mg/L = 3699
> 45 mg/L = 583

An estimated 1.69 million residents in California are served either by the estimated 600,000 private domestic wells or by community water systems serving fewer than 15 service connections, according to California Department of Public Health (CDPH) data.

Nitrate has many anthropogenic sources: synthetic and organic fertilizers applied to crops, farm animal waste, human waste from septic systems, and treated municipal wastewater applied to land.

Animal Manure | Septic System | Fertilized Agriculture | Organic Soil N

GAMA Special Studies Project

Since 2000, the California State Water Board Groundwater Ambient Monitoring & Assessment (GAMA) Program has funded the Special Studies Project with Lawrence Livermore National Laboratory (LLNL) as technical lead. A number of studies have been conducted to address specific contaminants of statewide relevance.

A major goal of the GAMA Program is to increase the availability of information about groundwater quality to the public. This GAMA Special Studies Project Fact Sheet is intended to inform the public and water-resource community, focusing on the nitrate issue.

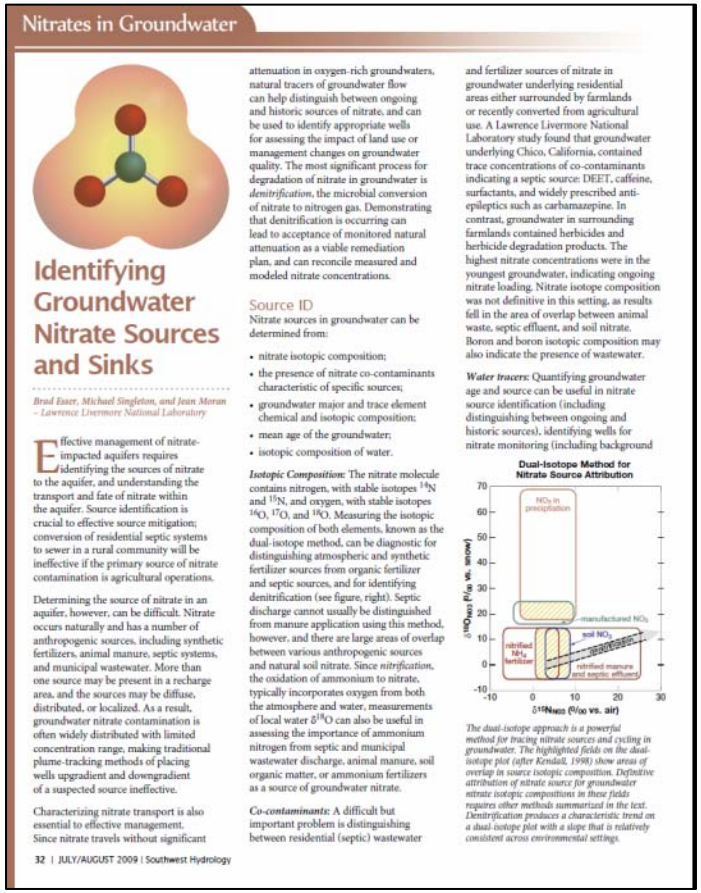
GAMA funding for the Special Studies Project allows researchers to better characterize and assess water quality in California groundwater. Determining the source of nitrate in groundwater is important to protect drinking water from nitrate contamination. Because nitrate sources are often intermingled, identifying the source using traditional methods is difficult. New methods are needed to identify non-point source contaminants, such as nitrate.

The GAMA Special Studies project has used a number of innovative new tools, including groundwater age, nitrate isotopic composition, and nitrate co-contaminants, in study sites near Chico, Livermore, and Morgan Hill and in and around dairies in Kings County.

1

1 published

Non-technical publications



Nitrates in Groundwater

Identifying Groundwater Nitrate Sources and Sinks

Brad Esser, Michael Singleton, and Jean Moran – Lawrence Livermore National Laboratory

Effective management of nitrate-impacted aquifers requires identifying the sources of nitrate to the aquifer, and understanding the transport and fate of nitrate within the aquifer. Source identification is crucial to effective source mitigation; conversion of residential septic systems to sewer in a rural community will be ineffective if the primary source of nitrate contamination is agricultural operations.

Determining the source of nitrate in an aquifer, however, can be difficult. Nitrate occurs naturally and has a number of anthropogenic sources, including synthetic fertilizers, animal manure, septic systems, and municipal wastewater. More than one source may be present in a recharge area, and the sources may be diffuse, distributed, or localized. As a result, groundwater nitrate contamination is often widely distributed with limited concentration range, making traditional plume-tracking methods of placing wells upgradient and downgradient of a suspected source ineffective.

Characterizing nitrate transport is also essential to effective management. Since nitrate travels without significant attenuation in oxygen-rich groundwaters, natural tracers of groundwater flow can help distinguish between ongoing and historic sources of nitrate, and can be used to identify appropriate wells for assessing the impact of land use or management changes on groundwater quality. The most significant process for degradation of nitrate in groundwater is *denitrification*, the microbial conversion of nitrate to nitrogen gas. Demonstrating that denitrification is occurring can lead to acceptance of monitored natural attenuation as a viable remediation plan, and can reconcile measured and modeled nitrate concentrations.

Source ID

Nitrate sources in groundwater can be determined from:

- nitrate isotopic composition;
- the presence of nitrate co-contaminants characteristic of specific sources;
- groundwater major and trace element chemical and isotopic composition;
- mean age of the groundwater;
- isotopic composition of water.

Isotopic Composition: The nitrate molecule contains nitrogen, with stable isotopes ^{14}N and ^{15}N, and oxygen, with stable isotopes ^{16}O, ^{17}O, and ^{18}O. Measuring the isotopic composition of both elements, known as the dual-isotope method, can be diagnostic for distinguishing atmospheric and synthetic fertilizer sources from organic fertilizer and septic sources, and for identifying denitrification (see figure, right). Septic discharge cannot usually be distinguished from manure application using this method, however, and there are large areas of overlap between various anthropogenic sources and natural soil nitrate. Since *nitrification*, the oxidation of ammonium to nitrate, typically incorporates oxygen from both the atmosphere and water, measurements of local water $\delta^{18}O$ can also be useful in assessing the importance of ammonium nitrogen from septic and municipal wastewater discharge, animal manure, soil organic matter, or ammonium fertilizers as a source of groundwater nitrate.

Co-contaminants: A difficult but important problem is distinguishing between residential (septic) wastewater and fertilizer sources of nitrate in groundwater underlying residential areas either surrounded by farmlands or recently converted from agricultural use. A Lawrence Livermore National Laboratory study found that groundwater underlying Chico, California, contained trace concentrations of co-contaminants indicating a septic source: DEET, caffeine, surfactants, and widely prescribed anti-epileptics such as carbamazepine. In contrast, groundwater in surrounding farmlands contained herbicides and herbicide degradation products. The highest nitrate concentrations were in the youngest groundwater, indicating ongoing nitrate loading. Nitrate isotope composition was not definitive in this setting, as results fell in the area of overlap between animal waste, septic effluent, and soil nitrate. Boron and boron isotopic composition may also indicate the presence of wastewater.

Water tracers: Quantifying groundwater age and source can be useful in nitrate source identification (including distinguishing between ongoing and historic sources), identifying wells for nitrate monitoring (including background

Dual-Isotope Method for Nitrate Source Attribution

NO_3 in precipitation
manufactured NO_3
soil NO_3
nitrified NH_4 fertilizer
nitrified manure and septic effluent
$\delta^{18}O_{NO3}$ (‰ vs. snow)
$\delta^{15}N_{NO3}$ (‰ vs. air)

The dual-isotope approach is a powerful method for tracing nitrate sources and cycling in groundwater. The highlighted fields on the dual-isotope plot (after Kendall, 1998) show areas of overlap in source isotopic composition. Definitive attribution of nitrate source for groundwater nitrate isotopic compositions in these fields requires other methods summarized in the text. Denitrification produces a characteristic trend on a dual-isotope plot with a slope that is relatively consistent across environmental settings.

32 | JULY/AUGUST 2009 | Southwest Hydrology

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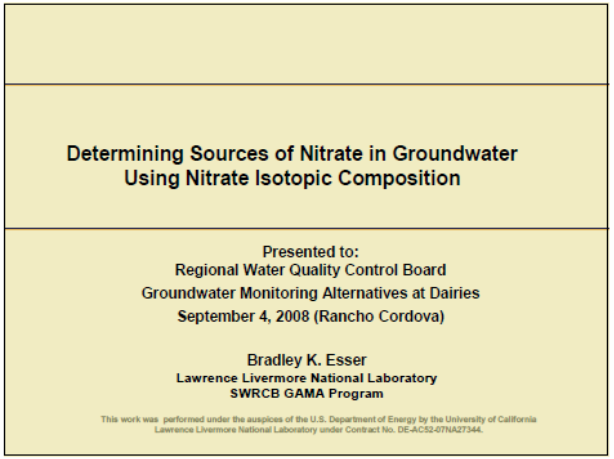

Scientific conferences

Stakeholder & professional workshops & meetings

Acknowledgements

LLNL GAMA Project Team

Steve Carle, Brad Cey, Wayne Culham. Brad Esser, Darren Hillegonds, G. Bryant Hudson, Roald Leif, Walt McNab, Jean Moran, Michael Singleton, Mike Sharp, Sarah Roberts, Ate Visser

Agency Collaborations

SWRCB (State & Regional)
DWR
UC Cooperative Extension
Numerous Water Districts
Numerous Well Owners

LLNL Student Programs

LLNL Summer Intern Program
LLNL Postdoc Program

University collaborations

California State University, East Bay
University of California, Davis
University of Arizona
University of Texas, Austin

For more information

State Water Board GAMA Program Website:

http://www.waterboards.ca.gov/gama

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