Groundwater Resources Association of California, Fresno, CA June 13, 2012

Source determination of anthropogenic NO_3 in groundwater by analysis of $\delta^{15}N$, $\delta^{18}O$, and $\delta^{11}B$: A case study from San Diego County, California

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Nitrate is a major contaminant of water resources worldwide. Previous studies have used the isotopic composition of nitrate ($\delta^{15}N$, $\delta^{18}O$) to determine source(s) of nitrate in groundwater. Mineral fertilizer, animal manure, and wastewater are anthropogenic sources of nitrate with characteristic ranges of $\delta^{15}N$ and $\delta^{18}O$ values. However, the nitrate isotopic composition in animal manure and wastewater largely overlap, making them difficult to distinguish. In addition, denitrification causes isotopic fractionation that can make it difficult to determine the isotopic composition of the original source. Therefore, using nitrate nitrogen and oxygen isotopic compositions alone can lead to ambiguous nitrate source attributions for areas where animal manure and wastewater sources are co-located. Co-contaminants such as pharmaceutical compounds, artificial sweeteners, herbicides and pesticides, and major ions or trace elements in soil amendments or animal feed can help to distinguish among likely sources of nitrate. Another useful tracer of groundwater nitrate is the isotopic composition of dissolved boron ($\delta^{11}B$). Unlike nitrate isotopes, boron isotopes are believed to behave conservatively in surface water and groundwater systems, and animal manure and wastewater have significantly different $\delta^{11}B$ signatures. We measured the water, nitrate, and boron isotopic composition of samples from domestic drinking water wells tapping shallow groundwaters collected in San Diego County under the GAMA Domestic Well Program. The range in $\delta^{15}N$ is +1.7 to +30.5 ‰, while the range in $\delta^{18}O$ for San Diego is +1.2 to +18.0 ‰. Some of the samples fall within the overlapping isotopic range of animal manure and wastewater. The range in $\delta^{11}B$ is -0.82 to +64.38 ‰. Most samples, and particularly samples with high nitrate concentrations, have $\delta^{11}B$ values greater than +20‰, typical of an animal manure nitrate source, or possibly, saline water of non-marine origin. Considering the contribution of both natural and anthropogenic sources of boron to groundwater, we demonstrate that the combined use of $\delta^{15}N$ and $\delta^{11}B$ suggest animal manure is a significant source of nitrate in the majority of groundwaters sampled in San Diego County. The coupled nitrate and boron isotopic analyses in the context of water isotopic and land-use data can be used to fingerprint nitrate sources with less ambiguity than each isotopic system in isolation.

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Source determination of anthropogenic NO_3 in shallow groundwaters by analysis of $\delta^{15}N$, $\delta^{18}O$, and $\delta^{11}B$: Case study from San Diego County, California

Groundwater Resources Association of California, Fresno, CA
June 13, 2012

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Anthropogenic NO_3

NO_3 is a threat to the safety of the water supply
WHO/US EPA limit of 10 mg/L

Elevated groundwater NO_3 due to anthropogenic contamination:
- *NH_4 fertilizer*
- *NO_3 fertilizer*
- *Human wastewater (septic)*
- *Animal manure*

Different nitrate sources have distinct isotopic signatures
Nitrate isotopic composition (*$\delta^{15}N$, $\delta^{18}O$*) *is useful in fingerprinting nitrate source*

Co-contaminants can also be useful in fingerprinting nitrate source(s)
- *Trace organic compounds*
  - (e.g., pharmaceuticals, personal care products, pesticides and herbicides)
- ***Boron isotope composition ($\delta^{11}B$)***

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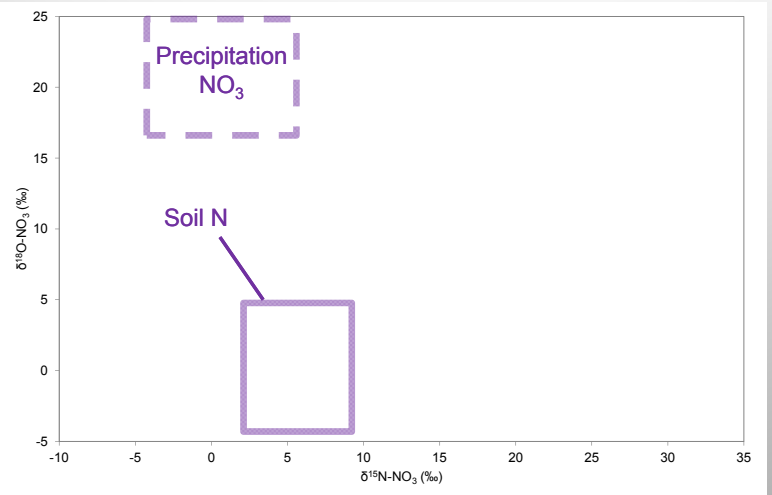
Eppich et al. (2012)

Nitrate isotopic fingerprinting

Nitrate does occur naturally

***Nitrate- $\delta^{18}O$ vs nitrate- $\delta^{15}N$:* Natural sources**

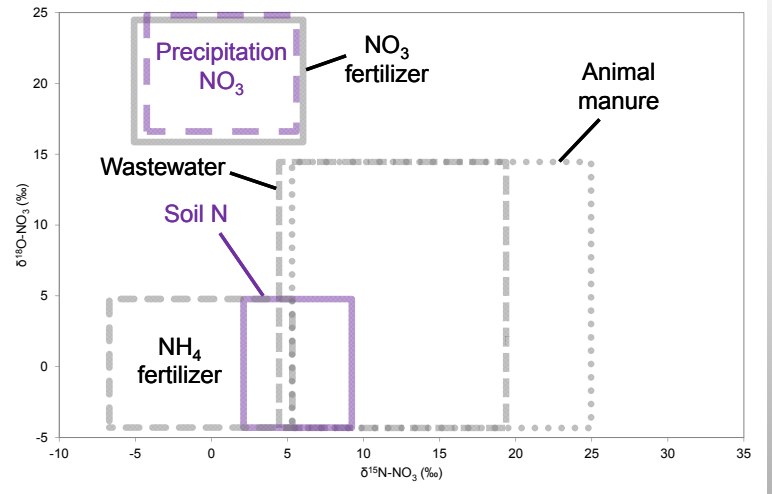


Modified from Kendall et al. (1998)

Nitrate isotopic fingerprinting

Some anthropogenic sources can be distinguished, some cannot

***Nitrate- $\delta^{18}O$ vs nitrate- $\delta^{15}N$:* Anthropogenic sources**



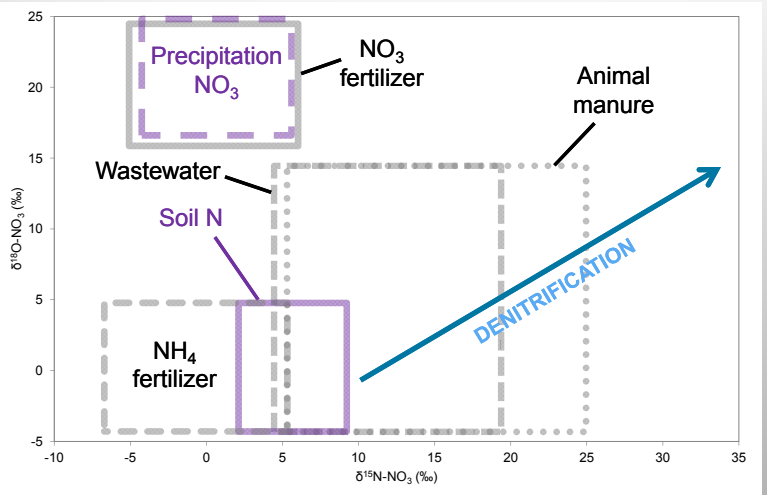
Modified from Kendall et al. (1998)

Eppich et al. (2012)

Nitrate isotopic fingerprinting

Subsurface transport can also affect isotopic composition

***Nitrate- $\delta^{18}O$ vs nitrate- $\delta^{15}N$:* Geochemistry**



Modified from Kendall et al. (1998)

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GAMA Domestic Well Program

GAMA Domestic Well Project is a voluntary water quality program managed by the State Water Resources Control Board

- ~600,000 private domestic wells in California are not routinely monitored
- Private well owners volunteer to have their wells sampled.
- Analyses include minerals, bacteria, major anions, metals, organic compounds, radionuclides
- *Technical lead: State Water Board (John Borkovich)*

LLNL applies isotopic techniques to supplement Domestic Well Project

- Water (δD, $\delta^{18}O$): routine
- Nitrate ($\delta^{15}N$, $\delta^{18}O$): routine
- Boron ($\delta^{11}B$): a GAMA Special Study

San Diego County focus area

- 137 domestic wells sampled
- Predominantly shallow wells in quaternary alluvium and crystalline bedrock
- Results can be found in March 2010 report at:
  http://www.waterboards.ca.gov/gama/docs/sdreport.pdf

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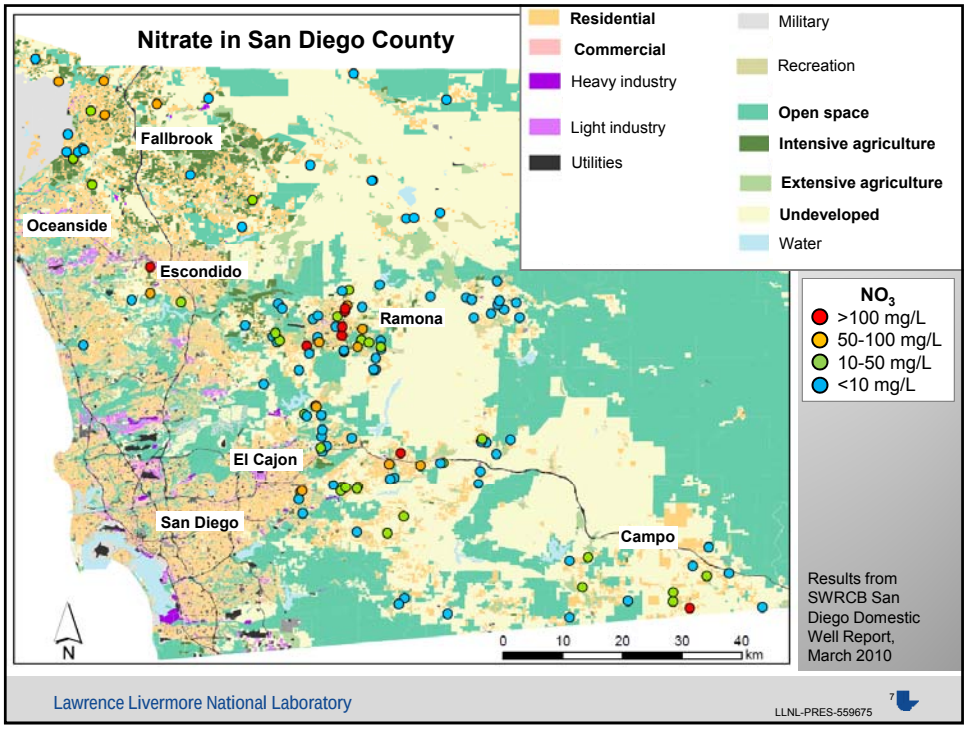
Nitrate in San Diego County
Residential
Commercial
Heavy industry
Light industry
Utilities
Military
Recreation
Open space
Intensive agriculture
Extensive agriculture
Undeveloped
Water
Fallbrook
Oceanside
Escondido
Ramona
El Cajon
San Diego
Campo
N
0 10 20 30 40 km
NO3
>100 mg/L
50-100 mg/L
10-50 mg/L
<10 mg/L
Results from SWRCB San Diego Domestic Well Report, March 2010
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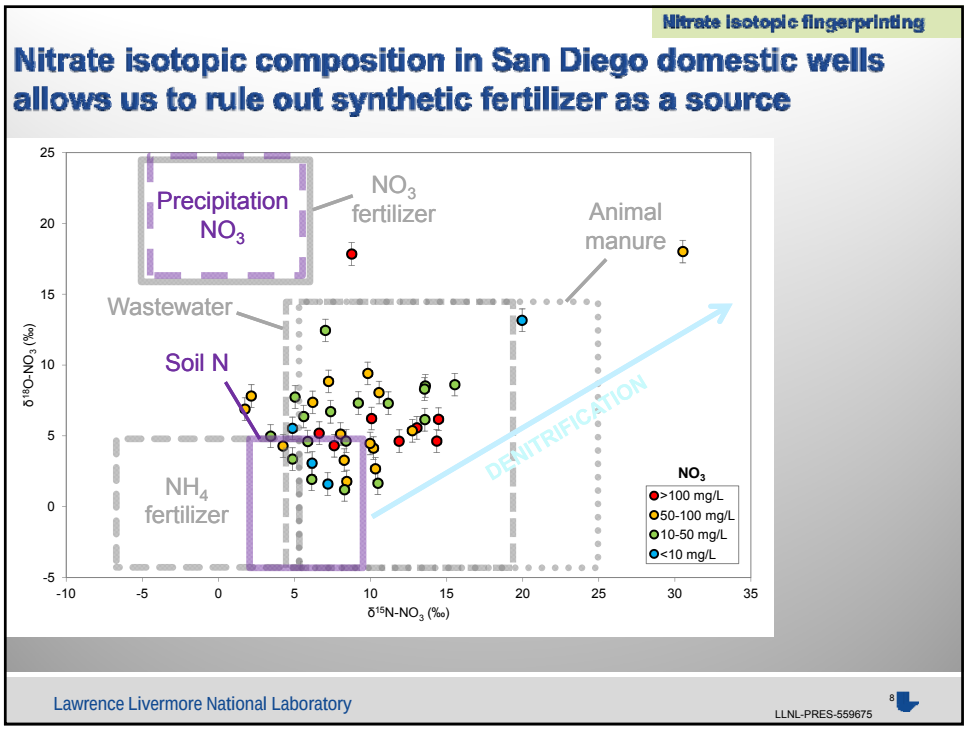
Nitrate isotopic fingerprinting
Nitrate isotopic composition in San Diego domestic wells allows us to rule out synthetic fertilizer as a source
Precipitation NO3
NO3 fertilizer
Animal manure
Wastewater
Soil N
NH4 fertilizer
DENITRIFICATION
δ18O-NO3 (‰)
δ15N-NO3 (‰)
NO3
>100 mg/L
50-100 mg/L
10-50 mg/L
<10 mg/L
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Boron is isotopically variable in nature

Two stable isotopes with a large (9%) mass difference.

^{10}B	NATURAL ABUNDANCE	^{11}B
~19.9 %		~80.1 %

Naturally-occurring element in groundwater
Common sources:
Weathering of rock
Seawater intrusion
Precipitation

Isotopic fractionation caused by:
Evaporation and condensation
Boron bio-uptake by plants and animals
Sorption to clay minerals

Anthropogenic sources
- *NH_4, NO_3 fertilizers – low B concentration*
- ***Human wastewater** – high B concentration (detergents)*
- ***Animal manure** – high B concentration (nutrient consumption)*

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LLNL standard method for boron isotopic analysis

1 **Ion exchange – boron separation**
Amberlite IRA 743 boron-specific ion exchange resin
Standards SRM 951, IAEA-B-2, IAEA-B-3, and NASS-5 for QC
Chemical separations performed in batches of 20
- *Total procedural duplicate of one sample per batch*
- *Three standards per batch*
- *One blank per batch*

2 $\delta^{11}B$ measured on a Thermo Neptune MC-ICP-MS at UC-Davis
Standard-sample-standard bracketing to correct for mass bias using SRM 951
Blank-corrections performed for each sample and standard
Instrumental wash-out was main source of blank
Analyses performed in three campaigns (July 2011 – Feb 2012)

3 Treatment of measurement uncertainty
QC standards typically within 0.75 ‰ of certified values
Uncertainty of $\delta^{11}B$ measurements presented here as ±1.5 ‰

Adapted from Lemarchand et al. (2002); Guerrot et al. (2011)

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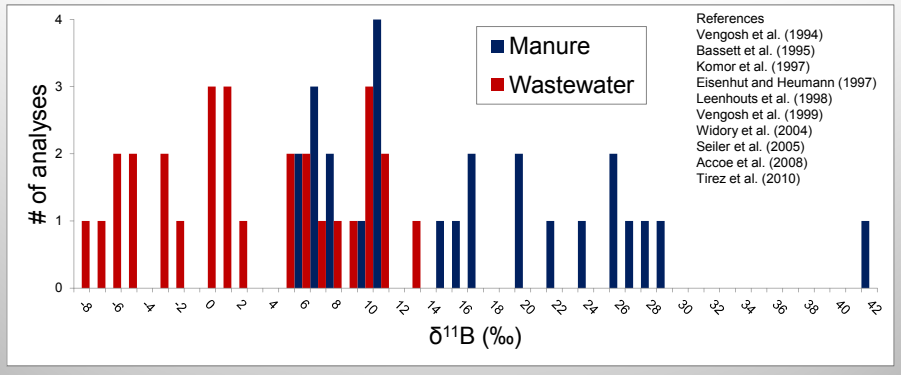
The case for boron isotopic fingerprinting



Anthropogenic sources

Boron source	Typical B concentration	Minimum $\delta^{11}B$	Maximum $\delta^{11}B$
Mineral fertilizer	Typically low	-3 ‰	+25 ‰
Animal manure	Moderate to high	**+6 ‰**	**+42 ‰**
Wastewater	High	**-8 ‰**	**+13 ‰**

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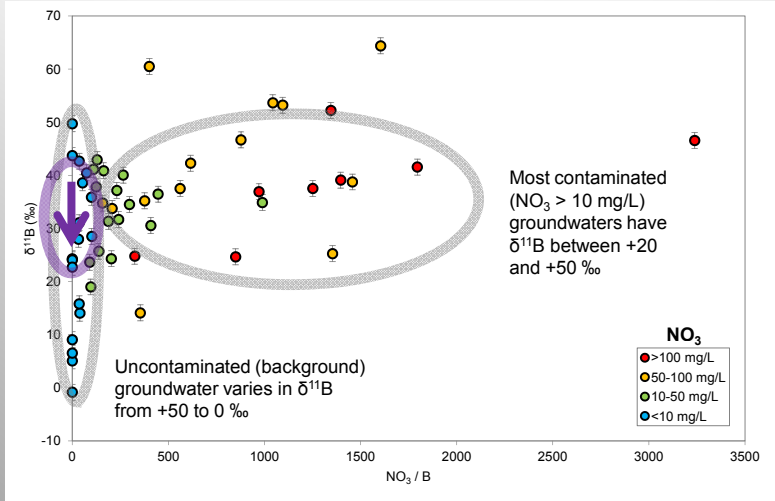
Patterns emerge when B isotopic composition is plotted against the NO_3/B concentration ratio

Boron isotopic fingerprinting

Groundwater $\delta^{11}B$ vs NO_3/B (color-coded by nitrate concentration)



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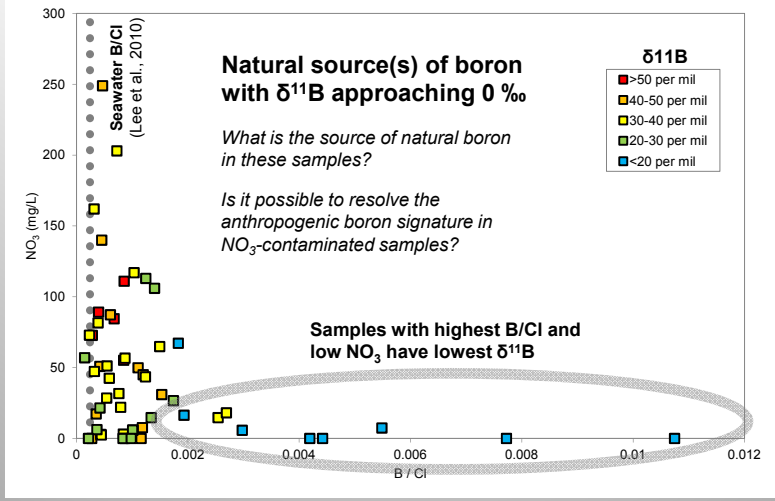
Boron isotopic fingerprinting

The natural boron isotopic signature is low

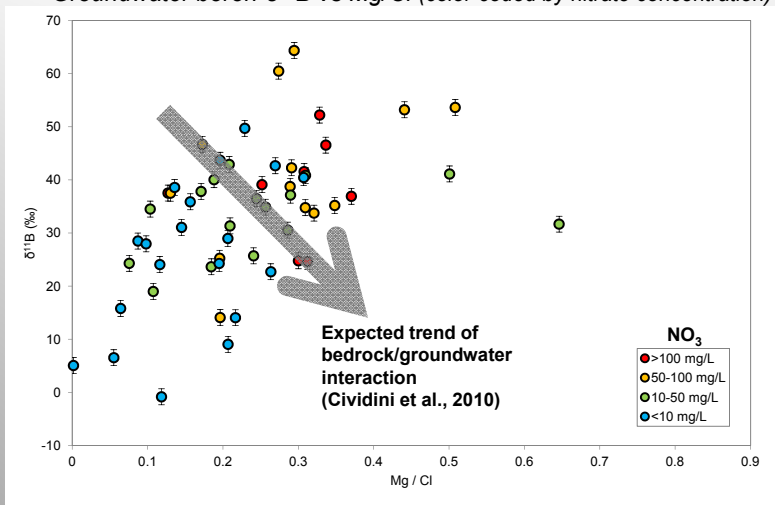
Groundwater nitrate-$\delta^{15}N$ vs B/Cl (color-coded by $\delta^{11}B$)



Boron isotopic fingerprinting

The source of natural boron is NOT crystalline bedrock

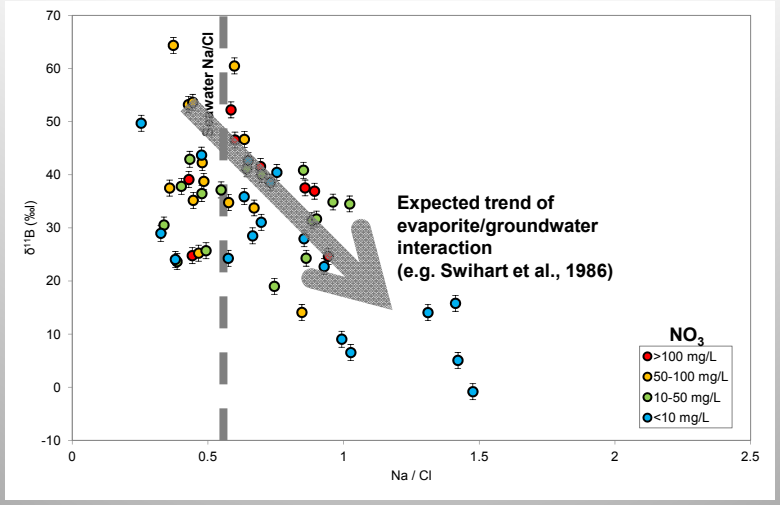
Groundwater boron-$\delta^{11}B$ vs Mg/Cl (color-coded by nitrate concentration)



Boron isotopic fingerprinting

The source of natural boron MAY BE non-marine evaporite sediments

Groundwater boron-$\delta^{11}B$ vs Na/Cl (color-coded by nitrate concentration)



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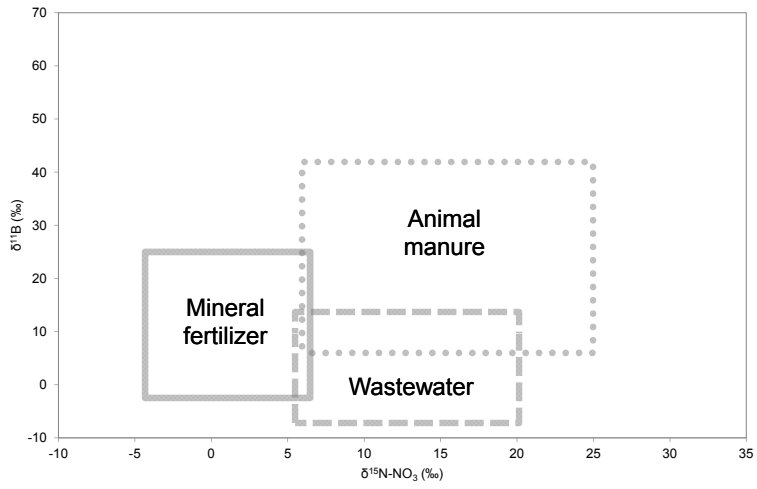
Boron isotopic fingerprinting

A multi-isotope approach may allow discrimination of septic and manure nitrate sources

Groundwater boron-$\delta^{11}B$ vs nitrate-$\delta^{15}N$

$\delta^{11}B$ ranges from:
Vengosh et al. (1994)
Bassett et al. (1995)
Komor et al. (1997)
Eisenhut and Heumann (1997)
Leenhouts et al. (1998)
Vengosh et al. (1999)
Widory et al. (2004)
Seiler et al. (2005)
Accoe et al. (2008)
Tirez et al. (2010)

$\delta^{15}N$ ranges modified from:
Kendall et al. (1998)



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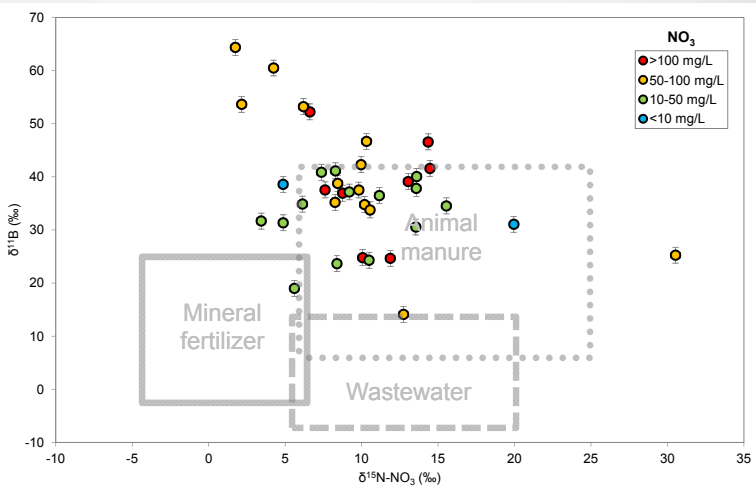
Boron isotopic fingerprinting

The San Diego County data are consistent with an animal manure source of nitrate & boron

Groundwater boron-$\delta^{11}B$ vs nitrate-$\delta^{15}N$ (color-coded by nitrate concentration)

$\delta^{11}B$ ranges from:
Vengosh et al. (1994)
Bassett et al. (1995)
Komor et al. (1997)
Eisenhut and Heumann (1997)
Leenhouts et al. (1998)
Vengosh et al. (1999)
Widory et al. (2004)
Seiler et al. (2005)
Accoe et al. (2008)
Tirez et al. (2010)

$\delta^{15}N$ ranges modified from:
Kendall et al. (1998)



Conclusions

1 Nitrate isotopic composition – ambiguous determination of nitrate source

- *Nitrate-$\delta^{15}N$ and $\delta^{18}O$ in groundwater from sampled San Diego County domestic wells falls within overlapping range of septic wastewater and animal manure (with possible denitrification)*
- *Can rule out NO_3 fertilizer*
- *Unable to determine nitrate source using only nitrate isotopic data*

2 Boron – natural sources

- *Natural boron varies from +50 to 0 ‰*
- *End-member natural boron source of ~0 ‰ (possible interaction with non-marine evaporites*

3 Anthropogenic boron

- *Possible to resolve isotopic signatures of animal manure and wastewater*
- *High-NO_3 samples in San Diego County study area consistent with an animal manure NO_3 source.*

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