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# *California GAMA Special Study:* Excess nitrogen and methane in noble gas samples

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Michael J. Singleton, and Bradley K. Esser

*Lawrence Livermore National Laboratory*
**California State University, East Bay*

**August 2017**

**Report for the California**
**State Water Resources Control Board**

GAMA Special Studies Task 16.5:
*Analyzing nitrogen and methane in noble gas samples*

**Auspices Statement**

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# GAMA: AMBIENT GROUNDWATER MONITORING & ASSESSMENT PROGRAM SPECIAL STUDY

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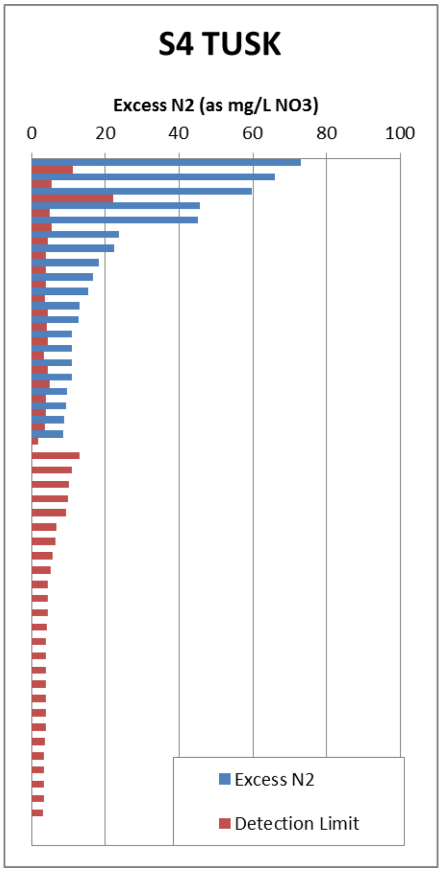
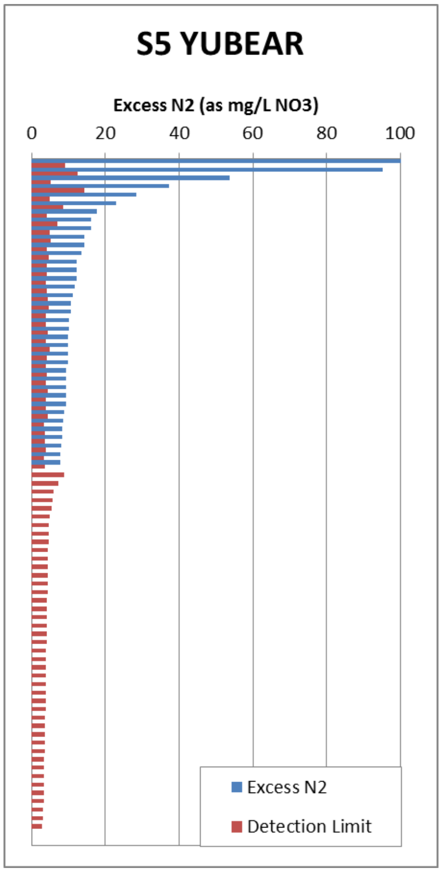

S4 TUSK


S5 YUBEAR

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## Key Points

- The analytical capability of the Noble Gas Mass Spectrometer was extended to include measurement of the concentrations of dissolved abundant gases, nitrogen ($N_2$), carbon dioxide ($CO_2$), methane ($CH_4$) and ethane ($C_2H_6$).
- Concentrations are measured during routine noble gas measurements with no additional sample preparation effort, within the same analysis time and at no additional cost.
- Based on more than 200 measurements of $N_2$/Ar ratios, calculated excess nitrogen values show that saturated zone denitrification appears to be a widespread process in California groundwater.
- Denitrification is more common under dairy operations, especially when high concentrations of agricultural nitrate are present in groundwater, possibly enabled by higher availability of electron donors in the form of dissolved organic carbon from animal manure.
- The nitrate isotopic composition is a record of both unsaturated zone and saturated zone denitrification, and does not correlate with excess $N_2$ (which is only preserved in the saturated zone) in a subset of samples from the UC Davis Domestic well study.
- Methane was detected in groundwater samples at concentrations of up to 88 mg/L.
- Ethane was not detected, indicating that the source of measured methane was likely of biological origin and not related to oil and gas production.

*Ate Visser, Jean E. Moran, Nathan W. Veale, Michael J. Singleton, and Bradley K. Esser* (2017) **California GAMA Special Study: Excess nitrogen and methane in noble gas samples**. Lawrence Livermore National Laboratory LLNL-TR-728423, 23 pp.

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# 1 INTRODUCTION

The most prominent constituent causing concern for drinking water resources in California is nitrate. Denitrification in the unsaturated zone and in groundwater naturally reduces nitrate concentrations, controls the fate of groundwater nitrate and determines the time scale over which changes in management practice will result in improvements in water quality. Quantifying denitrification is also important in estimating nutrient loading to groundwater through time. Measurements of dissolved nitrogen gas can detect and quantify saturated zone denitrification; and LLNL with GAMA funding has developed benchtop instrumentation to measure dissolved nitrogen in groundwater. This technique, membrane-inlet mass spectrometry (MIMS) requires the collection of an additional sample, and is not routinely included in current GAMA water quality monitoring surveys. Incorporating dissolved nitrogen analysis into current water quality monitoring protocols without requiring an additional sample or separate analysis is the most cost-effective way to expand the database of dissolved nitrogen concentrations and document the prevalence of saturated-zone denitrification in California groundwater.

The GAMA Priority Basin, Shallow Aquifer Assessment, and Special Study water quality monitoring programs routinely use dissolved noble gas and tritium analyses to constrain groundwater travel times and recharge. Noble gases are collected as a 10-mL water sample in a crimped copper tube and are analyzed by noble gas mass spectrometry (NGMS). Nitrogen, methane and carbon dioxide, can now also be measured in copper tubes and analyzed by the same LLNL NGMS system, which has been upgraded to allow such analyses. In the case of the GAMA Shallow Aquifer Assessment project, this will automatically provide dissolved nitrogen analyses at little or no incremental cost. A significant advantage of this technique is that archival copper tube noble gas samples can be analyzed using the technique. The dissolved nitrogen analyses – combined with nitrate analyses and the NGMS age information – will provide unique insight into nitrate sources, inputs, transport, and reaction rates.

Another constituent of concern in California groundwater is methane in areas of oil & gas development. Like nitrate, methane occurs naturally in groundwater and the variable natural background concentrations of methane and carbon dioxide in groundwater complicate distinguishing naturally occurring methane from methane introduced through oil and gas development. Better constraints on the naturally occurring dissolved methane concentrations in areas of concern will help distinguish between new impacts and pre-existing conditions. Archived copper tube noble gas samples can also be analyzed for methane and under special circumstances (high concentrations of hydrocarbons and low concentrations of dissolved atmospheric gases) for higher order hydrocarbons such as ethane and propane. The presence of higher order hydrocarbons (e.g. ethane) allows identification of thermogenic versus biogenic methane.

The environmental Noble Gas Mass Spectrometry (NGMS) facility at Lawrence Livermore National Laboratory has analyzed over 3000 groundwater samples from California for dissolved noble gas concentration and the helium isotope ratio. This data set has provided a wealth of information for the California State and Regional Water Boards and other water resource managers. Samples are collected in copper tubes, pinched off to prevent atmospheric contamination. Noble gases are analyzed after “abundant” reactive gases ($N_2$, $O_2$, $CO_2$, $CH_4$) are removed by chemical reactions with “getter” materials in vacuum. This report describes the modification of the NGMS system that allows for the analysis of all abundant gases in the sample. Analysis of abundant gases is interesting for a number of reasons:

- Nitrogen ($N_2$) is produced by denitrification of nitrate ($NO_3$). $N_2$ concentrations in excess of atmospheric are an indication of saturated zone denitrification and can be used to quantify initial nitrate concentrations.
- Carbon dioxide ($CO_2$) is released by subsurface biological processes, chemical weathering reactions with carbonate minerals, or introduced into shallow groundwater by crustal or mantle fluids.
- Methane ($CH_4$) in groundwater can be the result of biological production, or caused by gas migration from oil and gas exploration and production.
- Ethane ($C_2H_6$) can pinpoint of the source of methane in a groundwater sample to oil and gas production, because biological production of methane does not produce ethane.

Oxygen cannot be measured reliably on water samples stored in copper tubes because the dissolved oxygen reacts with the copper.

The remainder of this report details results of the analyses of selected samples for abundant and noble gas concentrations. A description of a calibration test system and modifications to the NGMS and the results of the calibration of the NGMS modification for $N_2$, $CO_2$, $CH_4$ and $C_2H_6$ are detailed in the Appendix to this report.

# 2 METHODS

## 2.1 Design and Calibration

To measure the abundant gases, a small aliquot of the gases (extracted from the water sample) is isolated from the gas inlet manifold. A test system was built to enable extensive calibration without significant down time of the NGMS. After calibration, the test system was incorporated into the NGMS. A detailed description of a calibration test system and modifications to the NGMS and the results of the calibration of the NGMS modification for $N_2$, $CO_2$, $CH_4$ and $C_2H_6$ are in the Appendix to this report.

## 2.2 Analysis of noble gas samples

The analysis of nitrogen, methane, ethane and carbon dioxide was integrated in the routine analysis of noble gases in copper tube samples. Priority Basin samples submitted by the USGS for noble gas analysis were subjected to the extended analysis after installation of the modification in August 2015. Since that date, nitrogen and methane concentrations have been measured on 126 Priority Basin samples, 46 from Study Unit S4 TUSK and 80 from Study Unit S5 YUBEAR. In addition, to test the new capability, 33 replicate archived copper tube samples were analyzed from the Priority Basin Upper Santa Ana Watershed Study Unit (collected in 2006-2007). Samples from USGS Oil and Gas Exploratory Studies from LA County (2014, 13 samples) and Kern County (2014, 4 samples) were analyzed to evaluate methane and ethane from geological sources. Excess $N_2$ was examined in 22 samples collected at LLNL's Site 300 since August 2015, and in archived samples collected for the UC Davis Dairy (15) and UC Davis Domestic Well (20) studies.

# 3 RESULTS

## 3.1 Archived Priority Basin Samples from the Upper Santa Ana Watershed Study Unit

To test the new analytical capability, 33 archived copper tube samples from the Upper Santa Ana Watershed (USAW) Priority Basin Study Unit were re-analyzed for abundant and noble gases at LLNL (Figure 1). This study unit was chosen because the USGS independently analyzed abundant gas concentrations in these samples (Kent and Belitz, 2009). Results of nitrogen and argon are generally consistent between the two labs. Outliers that show higher gas concentrations measured in the copper tubes by LLNL than measured in glass bottles by USGS may result from either gas loss from the glass bottle during sampling or storage (leading to anomalously low gas concentrations) or bubble entrapment in the copper tube (leading to anomalously high gas concentrations). $CO_2$ concentration results are consistently higher in copper tube samples. The $N_2$/Ar ratio showed considerable variation between the results of both labs.

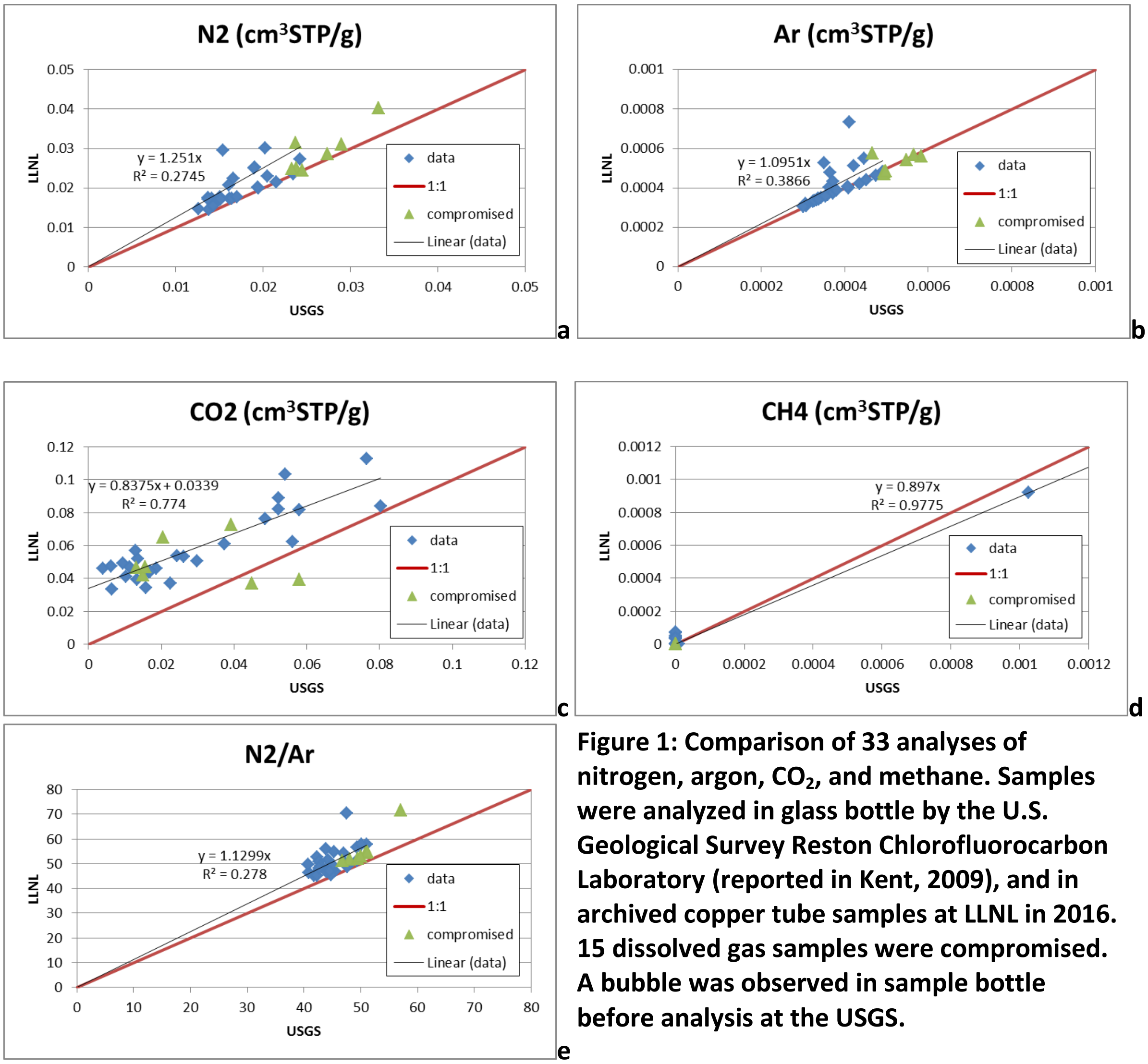

**Figure 1: Comparison of 33 analyses of nitrogen, argon, $CO_2$, and methane. Samples were analyzed in glass bottle by the U.S. Geological Survey Reston Chlorofluorocarbon Laboratory (reported in Kent, 2009), and in archived copper tube samples at LLNL in 2016. 15 dissolved gas samples were compromised. A bubble was observed in sample bottle before analysis at the USGS.**

In the samples analyzed for abundant gases at LLNL, excess $N_2$ was detected in 16 samples (48%), up to 45 mg/L $NO_3$-equivalent. Three samples had excess $N_2$ concentrations over 25 mg/L $NO_3$-equivalent. Methane was detected in 8 samples (24%), but only up to 0.66 mg/L.

## 3.2 Site 300

LLNL's Environmental Restoration Division collects dissolved gas and noble gas samples from Site 300 to monitor residence times and natural attenuation of historical nitrate contamination (Beller et al., 2004). Since the installation of the abundant gas analysis capability on the noble gas mass spectrometer in 2015, 22 noble gas samples collected at Site 300 were analyzed. In 18 samples (82%), excess dissolved $N_2$ attributed to denitrification was detected at concentrations greater than the equivalent of 4.5 mg/L denitrified nitrate (Figure 2). The average excess $N_2$ concentration (in samples with excess $N_2$) was 44 mg/L $NO_3$-equivalent, and the highest concentration was 108 mg/L $NO_3$-equivalent.

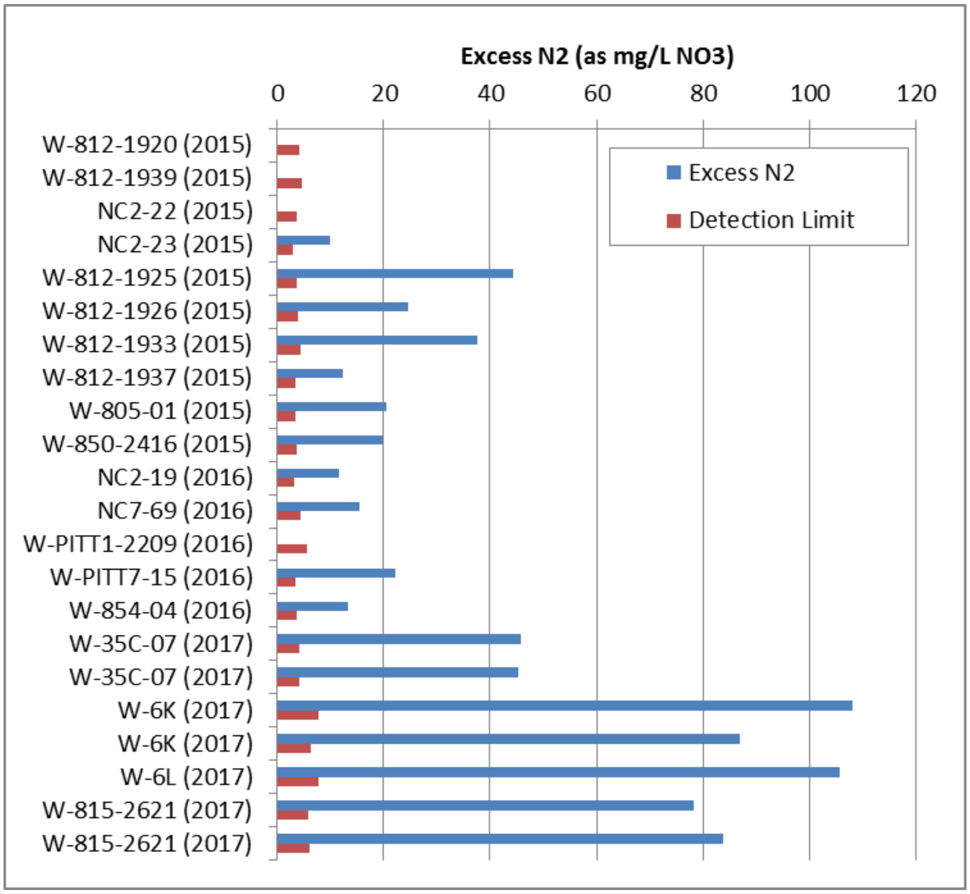

**Figure 2: Excess $N_2$ measured in noble gas samples collected at LLNL's Site 300, to monitor natural attenuation of historical nitrate contamination. Excess $N_2$ was detected in 18 of 22 samples, in concentrations up to the equivalent of 108 mg/L denitrified nitrate.**

## 3.3 USGS Priority Basin Shallow Aquifer Assessment Samples

Noble gas analyses performed for the Priority Basin Shallow Aquifer Assessment (https://ca.water.usgs.gov/gama/) since 2015 included 46 samples for S4 TUSK and 80 samples for S5 YUBEAR. Excess $N_2$ was detected in 20 TUSK samples (43%) at concentrations above the equivalent of 4 mg/L denitrified nitrate (Figure 3).

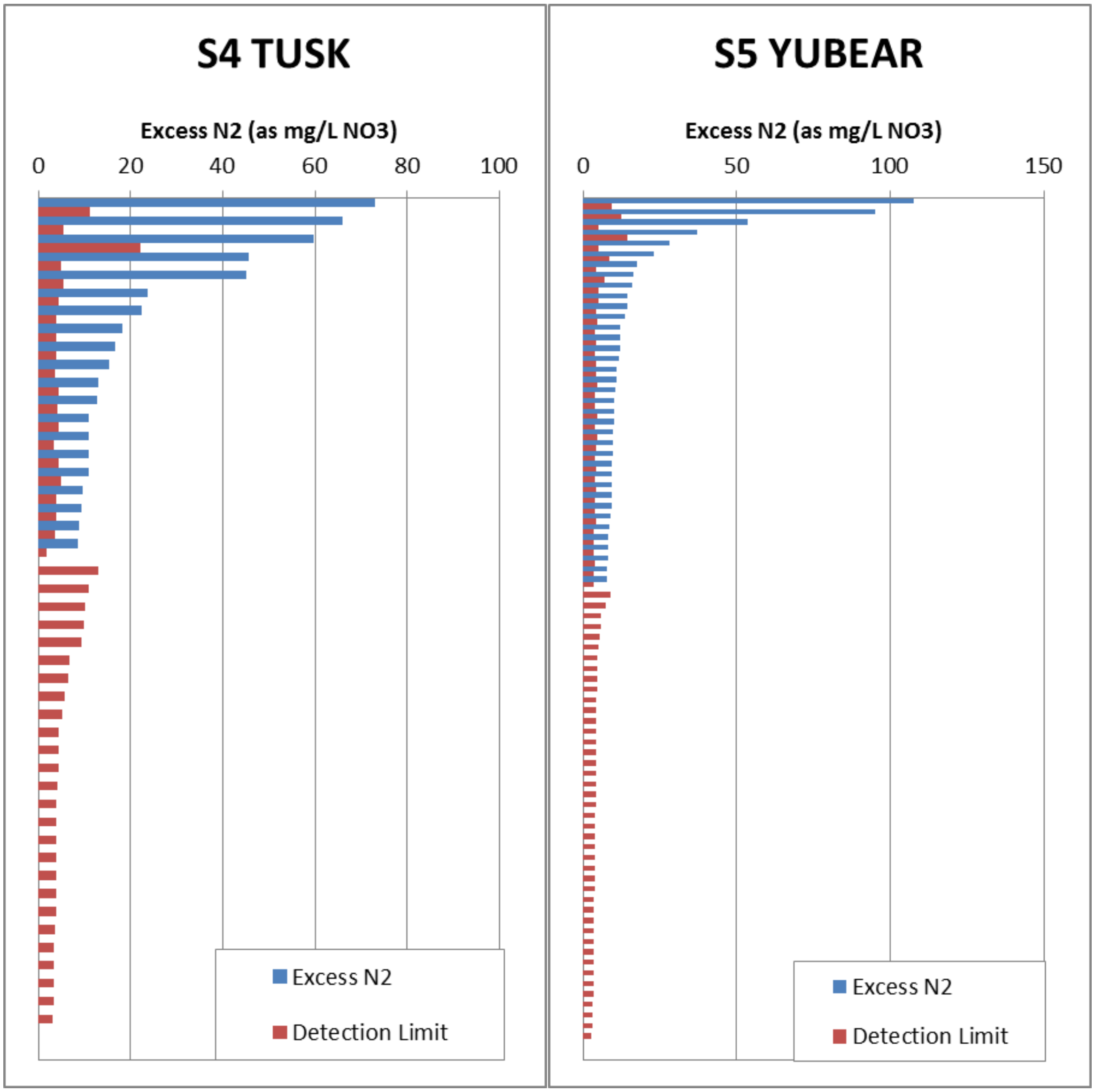

**Figure 3: Excess $N_2$ measured in noble gas samples collected for the USGS Shallow Aquifer Assessment S4 TUSK (left, 46 samples) and S5 YUBEAR (right, 61 samples) study units. Excess $N_2$ was detected in 20 TUSK samples (43%) and 37 YUBEAR samples (46%), in concentrations up to the equivalent of 108 mg/L denitrified nitrate.**

The average excess $N_2$ concentration (in samples with a positive detection) was 25 mg/L $NO_3$-equivalent, with values as high as 73 mg/L $NO_3$-equivalent. Methane was detected in 23 samples (48%) above 0.04 mg/L, but mostly below 1 mg/L (17 of 23 samples). In four samples, the methane concentration exceeded the EPA action level of 10 mg/L, with the highest detected concentration of

88 mg/L. In YUBEAR samples, methane was not detected above 1 mg/L. The statistics of excess nitrogen in YUBEAR samples were similar to statistics for TUSK samples: excess $N_2$ was detected in 37 YUBEAR samples (46%) above 4 mg/L $NO_3$-equivalent. The highest measured excess $N_2$ concentration in YUBEAR samples was 108 mg/L $NO_3$-equivalent.

Nitrate concentrations are not available for these samples. An initial nitrate concentration of more than 25 mg/L is a strong indication of a non-natural nitrate source, like fertilizer. In both study units combined, ten samples (8%) contained excess $N_2$ in concentrations exceeding the equivalent of 25 mg/L denitrified nitrate. In 37% of the samples, denitrification of low concentrations (< 25 mg/L) of naturally occurring nitrate or partial denitrification of high concentrations of anthropogenic nitrate (> 25 mg/L) is observed, leading to excess $N_2$ concentrations of less than 25 mg/L $NO_3$-equivalent. It is probable that even lower concentrations of excess $N_2$ are present at concentrations below the detection limit in the remaining 48 samples. Only in 8% of the samples do we find evidence for denitrification of high (> 25 mg/L) concentrations of nitrate.

## 3.4 UC Davis Dairy Study

In 2008-2009, UC Davis conducted a study on Central Valley dairies, sampling 149 monitoring wells installed on dairy properties (Harter et al., 2013). Samples were analyzed at LLNL for dissolved noble gases. In 2016-2017, 15 replicate samples were analyzed for dissolved abundant gases. In this subset, excess $N_2$ was detected above the detection limit of 5 mg/L $NO_3$-equivalent in 13 samples (87%, Figure 4). Excess $N_2$ was detected above 25 mg/L $NO_3$-equivalent in 6 samples (40%) indicating denitrification of agricultural nitrate. Compared with the detection of excess $N_2$ in USGS Shallow Aquifer Assessment samples, saturated zone denitrification is more common under dairy operations, especially denitrification of high concentrations of agricultural nitrate, possibly enabled by higher availability of electron donors in the form of dissolved organic carbon from animal manure

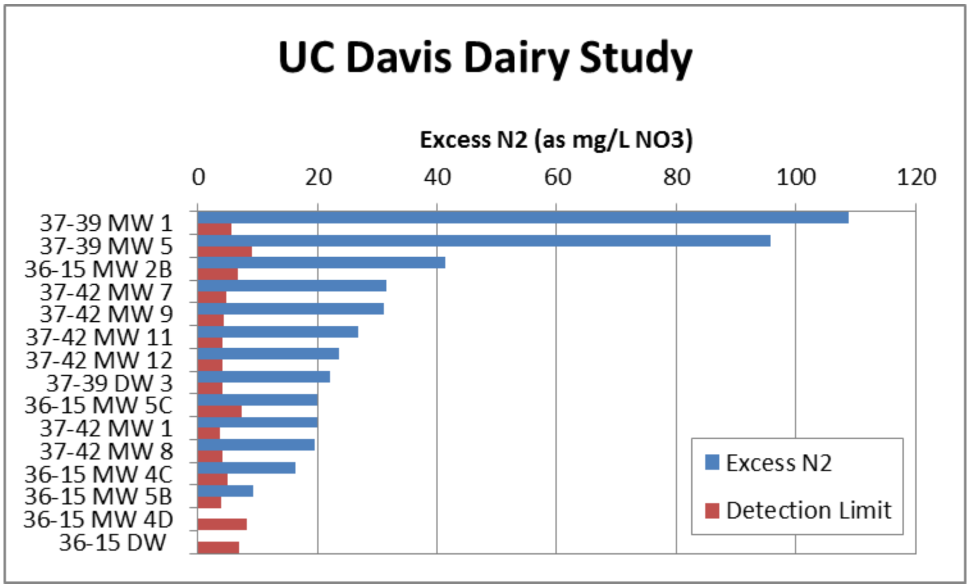

**Figure 4: Excess $N_2$ measured in noble gas samples collected for the UC Davis Dairy Study. Excess $N_2$ was detected in 13 of 15 samples (87%) and above 25 mg/L $NO_3$-equivalent in 6 samples (40%).**

## 3.5 UC Davis Domestic Well Study

In 2011, UC Davis conducted a study on domestic wells in the Central Valley, sampling 208 domestic wells in Stanislaus, Merced, Kings and Tulare Counties (Lockhart et al., 2013). Samples were analyzed at LLNL for dissolved noble gases. In 2017, 20 replicate samples were analyzed for dissolved abundant gases. In this subset, excess $N_2$ was detected above the detection limit of 5 mg/L $NO_3$-equivalent in 6 samples (30%, Figure 5). All samples with excess $N_2$ had an initial $NO_3$ concentration of 50 mg/L or higher.

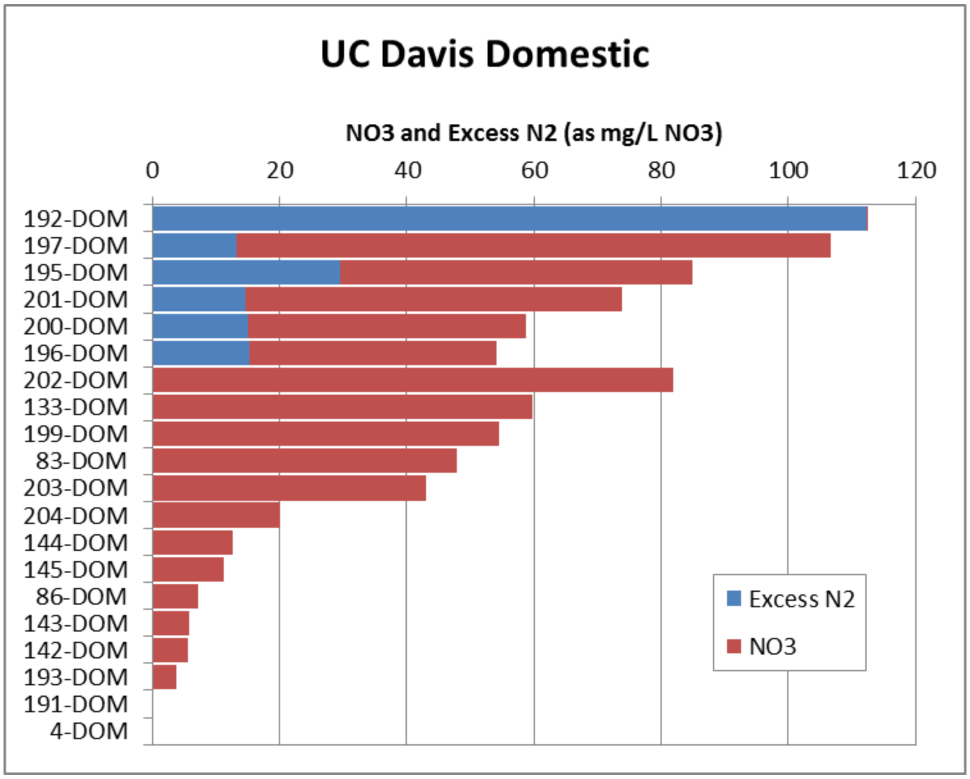

**Figure 5: Excess $N_2$ measured in noble gas samples collected for the UC Davis Domestic Study. Excess $N_2$ was detected in 6 of 20 samples (30%). All samples with excess $N_2$ had an initial $NO_3$ concentration of 50 mg/L or higher.**

Nitrate isotopic composition of samples with excess $N_2$ did not show a distinct denitrification trend, whereas this trend was observed in two samples with no excess $N_2$ detected (Figure 6). Denitrification can take place in the unsaturated zone, resulting in a distinct isotopic composition. $N_2$ produced in the unsaturated zone escapes to the atmosphere and is not trapped in groundwater. A combined study of nitrate isotopes and excess $N_2$ is necessary to characterize denitrification processes in the unsaturated and saturated zone.

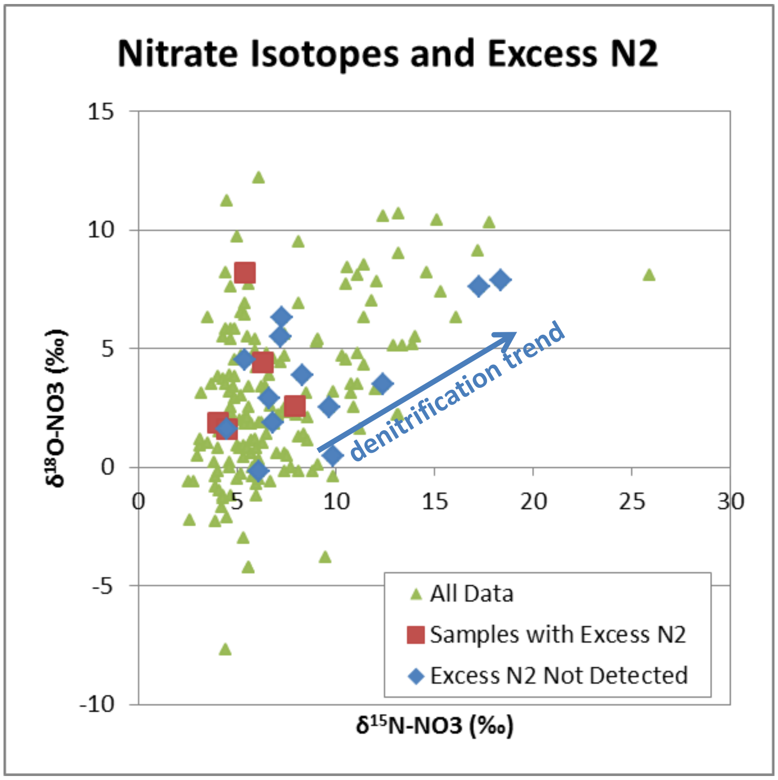

**Figure 6: Nitrate isotopic composition of samples with excess $N_2$ did not show a distinct denitrification trend, whereas this trend was observed in two samples with no excess $N_2$ detected.**

## 3.6 USGS Oil and Gas Exploratory Study

In 2014-2015, the USGS California Water Science Center conducted an exploratory study of groundwater in selected oil and gas areas of Los Angeles, Kern and Kings Counties (Dillon et al., 2016). For that study, 51 samples were analyzed at LLNL for dissolved noble gases including 13 archived samples from LA and 4 archived samples from Kern that were re-analyzed in 2016/2017 for noble gases, nitrogen, methane, ethane and carbon dioxide. Methane was detected above 0.03 mg/L in all but 2 samples, and above 1 mg/L in 7 samples (54%) from LA. Five samples contained methane concentrations above the EPA action level (10 mg/L) with the highest value observed at 81 mg/L. Ethane, evidence of methane associated with oil and gas production, was not detected in noble gas samples (median detection limit: 0.52 mg/L). Detections of ethane by the USGS (using a gas chromatography method) ranged from 0.0002 to 0.43 mg/L. Methane was detected in one sample from Kern, at 0.08 mg/L.

# 4 SUMMARY

A summary of samples analyzed for dissolved abundant gases, with number of samples with excess $N_2$, average and maximum detected excess $N_2$, and number of samples with methane and highest methane concentration, is presented in Table 1. Compared with the detection of excess $N_2$ in USGS USAW samples (48%), denitrification is more common under present-day dairy operations (87%), especially denitrification of high concentrations of agricultural nitrate, possibly enabled by higher availability of electron donors in the form of dissolved organic carbon from animal manure. However, USAW covers a region formerly occupied by dairies and may also exhibit higher than average denitrification. Excess $N_2$ was detected in fewer domestic wells (30%). Saturated zone denitrification appears to be a widespread process in California groundwater. The nitrate isotopic composition is a record of both unsaturated zone and saturated zone denitrification, and does not correlate with excess $N_2$ in the selected analyzed samples from the UC Davis Domestic well study.

Table 1: Summary of samples analyzed: number of samples with excess $N_2$, average and maximum detected excess $N_2$, and number of samples with methane and highest methane concentration.

| Study | Number of samples | Excess $N_2$ detected | Average excess $N_2$ concentration | Highest excess $N_2$ concentration | Methane detected > 1 mg/L | Highest methane concentration |
|---|---|---|---|---|---|---|
| | | samples | mg/L $NO_3$-equivalent | mg/L $NO_3$-equivalent | samples | mg/L |
| **USAW** | 33 | 16 (48%) | 18 | 45 | 0 | 0.66 |
| **O&G LA** | 13 | - | - | - | 7 (54%) | 81 |
| **O&G Kern** | 4 | - | - | - | 0 | 0.08 |
| **Site 300** | 22 | 18 (82%) | 44 | 108 | 0 | 0.18 |
| **S4 TUSK** | 46 | 20 (43%) | 25 | 73 | 4 (8%) | 88 |
| **S5 YUBEAR** | 80 | 37 (46%) | 18 | 108 | 0 | 0.04 |
| **UCD Dairy** | 15 | 13 (87%) | 36 | 109 | 0 | 0.61 |
| **UCD Domestic** | 20 | 6 (30%) | 33 | 112 | 0 | 0.06 |

# 5 REFERENCES

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*GAMA Project reports are available on the State Water Board GAMA website:*
*[http://www.swrcb.ca.gov/water_issues/programs/gama/report_depot.shtml](http://www.swrcb.ca.gov/water_issues/programs/gama/report_depot.shtml)*

# 6 APPENDIX: DESIGN AND CALIBRATION OF NITROGEN, METHANE AND CARBON DIOXIDE ANALYSIS CAPABILITY

## 6.1 Design

The addition to the NGMS must be able to measure various gases at a wide range of concentrations at intermediate (5%) accuracy. To measure the abundant gases, a small aliquot of the gases (extracted from the water sample) is isolated from the gas inlet manifold.
A test system was built to enable extensive calibration without significant down time of the NGMS. Once calibrated, key components of the test system were transferred onto the NGMS system. These key components are:

- A 2-valve assembly to isolate an aliquot of the sample gases from the inlet manifold
- An expansion volume towards an all-metal gas dosing valve (Pfeiffer Vacuum, UDV040)
- A quadrupole mass spectrometer (Stanford Research Systems (SRS) Residual Gas Analyzer (RGA 200)) with dedicated high vacuum turbomolecular pump (Pfeiffer Vacuum HiPace 80)
- A partially closed gate valve to limit the high vacuum turbo pump efficiency and increase mass spectrometer sensitivity.

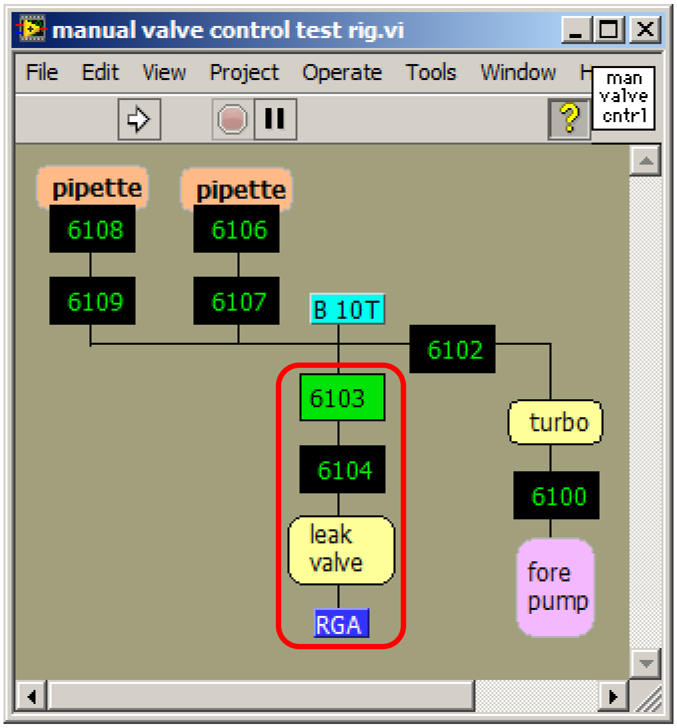

**Figure A1: LabView manual valve control of test system. The 2-valve assembly, leak valve and RGA (red rectangle) were transferred to the NGMS vacuum system.**

These components were assembled, tested and calibrated and the assembly was transferred onto the NGMS system without modifications. In addition, a “manifold” volume of approximately 300 cm$^3$ (mimicking the NGMS gas inlet manifold) was attached to the 2-valve assembly. Two gas pipettes of 0.1 cm$^3$ were attached to the test manifold volume to introduce small aliquots of pure gases or air to create gas mixtures with known composition. A high precision capacitance manometer (MKS Baratron 10Torr) measured the pressure inside the manifold to calculate the gas composition. All valves of the test system were pneumatically actuated, electronically controlled by an HP4788A switchboard. Readout of the RGA and Baratron, as well as switchboard control, was streamlined by modification of the LabView procedures designed for NGMS operation. The LabView procedures of the test system were later integrated into the NGMS LabView procedures. The LabView front view of manual valve control procedure shows a schematic of the test system (Figure A1). The calibration gas and air are introduced through one of the pipettes (valves 6106 and 6107 or 6108 and 6109). The volume between valves 6103 and 6104 is isolated from the test manifold. Valve 6104 is then opened to expand the gas against the gas dosing (leak) valve. After calibration, the test system was incorporated into the NGMS (Figure A2).

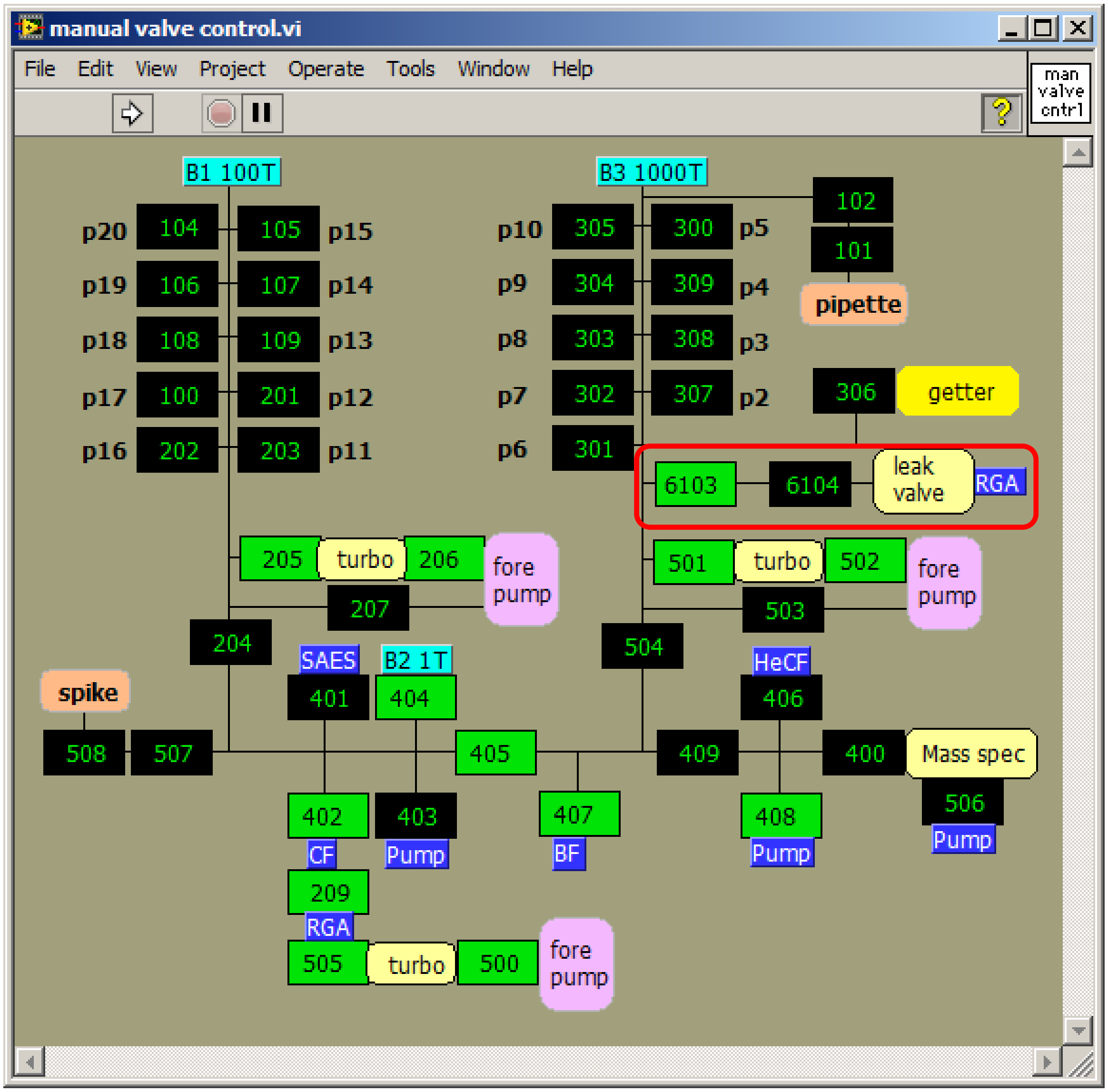

**Figure A2: LabView manual valve control of the NGMS system. The 2-valve assembly, leak valve and RGA (red rectangle) were transferred from the test system.**

## 6.2 Data Reduction

Due to significant non-linearity of RGA response under varying inlet pressures, gases were measured as signal ratios with respect to the argon (Ar) signal. Argon is the most abundant noble gas (0.934% in the atmosphere) and which is measured in the NGMS system by high precision capacitance manometer, after careful separation from other gases. Thanks to its high abundance, Ar can easily be measured simultaneously with nitrogen in the aliquot for abundant gas analysis. The Ar reproducibility of the NGMS (<0.5%) introduces a minor source of uncertainty, at the benefit of a greatly improved accuracy of the measurements of other gases. While small non-linearities were still observed in the pure gas to argon ratios over large ranges of inlet pressures, all calibration results were fitted to a linear response. This reduces the need for multiple point calibration and calculating the relative concentrations of abundant gases requires only a single sensitivity parameter. The sensitivity parameter for each gas represents the relative sensitivity of the system to the specific gas, relative to the sensitivity to Ar

## 6.3 Calibration Procedure

One or more aliquots of a pure gas ($CO_2$, $N_2$) or natural gas (a mixture of $CH_4$ and $C_2H_6$) were introduced into the test manifold using the automated gas pipette. One or more aliquots of air were added from a closed vessel. A closed vessel was needed to prevent variation in air composition in the lab due to releases of Ar, $N_2$ or $CO_2$ to affect the air standard composition. Gas and air aliquots were introduced in ratios between 1:5 and 5:1. For natural gas and $CO_2$, the gas reservoir was a small fixed volume, the pressure in which decreased with every aliquot taken, such that a large range of gas ratios between 0.1 and 100 could be created. The pressure inside the manifold was measured, using a high precision (<0.1% reproducibility) capacitance manometer, before and after introduction of each gas. The typical pressure increase for a single aliquot of gas at atmospheric pressure expanded into the manifold was 0.4792±0.0013 Torr (reproducibility = 0.3%). The gases were allowed to fully mix in the manifold for 10 minutes and the pressure was measured again to ensure no air or calibration gas has leaked into the manifold. An aliquot of the gas mixture is isolated by closing valve 6103. The aliquot is expanded against the leak valve by opening valve 6104. After 30 seconds (to stabilize the pressure in the expansion volume), the RGA is instructed to measure the Faraday cup signal for mass over charge (m/z) ratios 15 ($CH_4$), 27 ($C_2H_6$), 28 ($N_2$), 30 ($C_2H_6$), 40 (Ar) and 44 ($CO_2$) every second for a total of 30 times. Values are recorded, as well as the ratio of every signal with respect to the m/z 40 signal (Ar). Because the leak valve consumes gas sample from the fixed expansion volume, the pressure decreases and the signals decrease slowly over the measured time period. A 2nd order polynomial is fitted through the signal time series and extrapolated to t=0 for both the values and the ratios.

Noble gas samples are typically analyzed in batches of 9, with 4 standards bracketing every 3 samples, and a blank and the beginning and end of every run. Similar sequences of calibration mixtures were analyzed, for compatibility with existing analysis spreadsheets.

## 6.4 Isobaric Interference

A quadrupole mass spectrometer separates gases by accelerating the ions through fast switching electrical fields. The RGA is not able to distinguish ions with the same mass-over-charge (m/z) ratios. This causes isobaric interference because fragments of different gas molecules have the same mass (for example, both CO ($CO_2$ fragment) and $N_2$ have mass 28), O ($O_2$ and $H_2O$ fragment) and $CH_4$ have mass 16). Also, the mass filter shows interference on neighboring m/z ratios (for example, $N_2$ (28) causes a signal on m/z 27 and 29, typically at 1% of the m/z 28 signal). For these interferences, a correction needs to be applied, affecting the detection limit of rare gases with mass spectra abundant gases. For methane, the $CH_3$ fragment of the $CH_4$ molecule is measured without interference on m/z 15, because the m/z 16 signal of O is overwhelming. Ionization of $C_2H_6$ causes fragments with masses 28 (45%) and 27 (15%) to be more abundant than the original molecule (30, 12.3%). Initially, m/z 27 was chosen because of the higher abundance, correcting for $N_2$ interference. Additional tests showed that the signal of the entire molecule at m/z 30 did not suffer from interferences and allowed for a much lower detection limit.

## 6.5 System Calibration

### 6.5.1 Nitrogen

Nitrogen ($N_2$) is measured on m/z 28. Calibration mixtures were made by mixing 0, 1 or 2 aliquots of pure $N_2$ with 2, 3 or 4 aliquots of air, obtaining $N_2$/Ar ratios between 83.5 (air) and 197. Nine calibration mixtures were analyzed in sets together with four air standards (2 aliquots of air) and two blanks, replicating a NGMS analysis run. Four calibration runs were performed. The instrument sensitivity to $N_2$, relative to Ar, was calibrated to the "2x air std" measurements, by minimizing the root mean squared errors between measured and atmospheric $N_2$/Ar ratios. The $N_2$/Ar sensitivity ratio is 1.335. The calibrated $N_2$/Ar sensitivity ratio was then used to predict $N_2$/Ar ratios of mixtures of pure $N_2$ with air to evaluate the accuracy of the system at other ratios (Figure A3a). Errors between predicted and actual ratios vary from -5.2 (-6.2%) at 83 to +8 (4.0%) at 197 (Figure A3b). The errors show a small upward trend with increasing $N_2$/Ar ratios indicating the $N_2$/Ar response is slightly non-linear. The root of the mean squared relative errors (RMSRE) of non-standard gas mixtures is 2.8%.

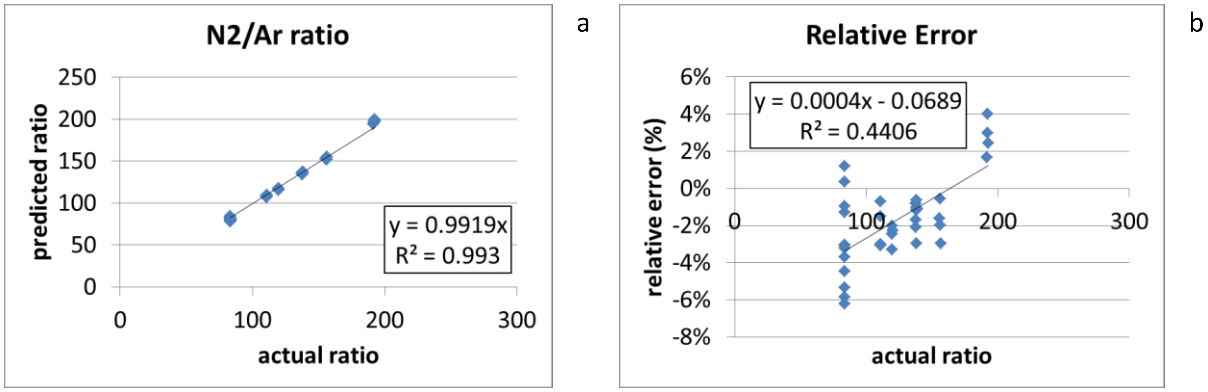

**Figure A3: Calibrated measurements of $N_2$/Ar ratios (left) and error structure (right).**

$N_2$/Ar ratios in groundwater are expected to vary between 38 and 50, due to variations in recharge temperature (10°C - 25°C) and excess air (0%-100% ΔNe). $N_2$ concentrations vary between $1.2 \times 10^{-2}$ cm3STP/g (25°C, 0% ΔNe) and $2.4 \times 10^{-2}$ cm3STP/g (10°C, 100% ΔNe). A 3% relative error on a typical groundwater concentration corresponds to an uncertainty of $3.5 \times 10^{-4}$ - $7 \times 10^{-4}$ cm3STP/g, equivalent to an uncertainty of 2-4 mg $NO_3$/L denitrified to $N_2$. The detection limit for excess nitrogen from denitrification at 95% probability is 3-6 mg/L nitrate, depending on the recharge temperature and excess air composition of the sample.

### 6.5.2 Carbon dioxide calibration

$CO_2$ is measured at m/z 44, with no interference. The $CO_2$/Ar sensitivity ratio was calibrated against 28 gas mixtures with $CO_2$/Ar ratios between 2.5 and 353. $CO_2$/Ar ratios in groundwater are expected to be above 40 due to the high solubility of $CO_2$ and dissociation into carbonic acid. The sample preparation procedure (freezing the water under vacuum) will liberate all $CO_2$ species ($CO_2$, $H_2CO_3$, $HCO_3$, $CO_3$) and the $CO_2$ measurement will equal the total dissolved inorganic carbon (DIC) concentration. $CO_2$/Ar ratios were obtained by mixing aliquots of $CO_2$ and air at ratios between 2:1 and 1:2. Because the pure $CO_2$ reservoir was small, the pressure decreased by a factor of 50 due to repeatedly taking aliquots, and a wide range of $CO_2$/Ar ratios was obtained.

A $CO_2$/Ar sensitivity ratio of 1.284 was obtained by minimizing the root mean squared error (RMSE) between measured and known $CO_2$/Ar ratios of all 28 mixtures (Figure A4a). The relative error varies between +3% at $CO_2$/Ar ratios above 100, to -9% at ratios below 10 (Figure A4b). The absolute error increases with $CO_2$/Ar ratio. The overall RMSRE was 5%, but this metric decreased with increasing $CO_2$/Ar ratio. A linear regression between the squared error (SE) and the $CO_2$/Ar ratio provided an adequate description of the error structure. The regression slope is 0.03, and the measurement uncertainty is given by the equation $\sigma_{CO2/Ar} = \surd\ (0.03 \times CO_2/Ar)$. This results in a relative error of 5% at a ratio of 10, decreasing to 2% at a ratio of 100. At typical ratios in groundwater between 40 and 100, the measurement uncertainty is below 3%.

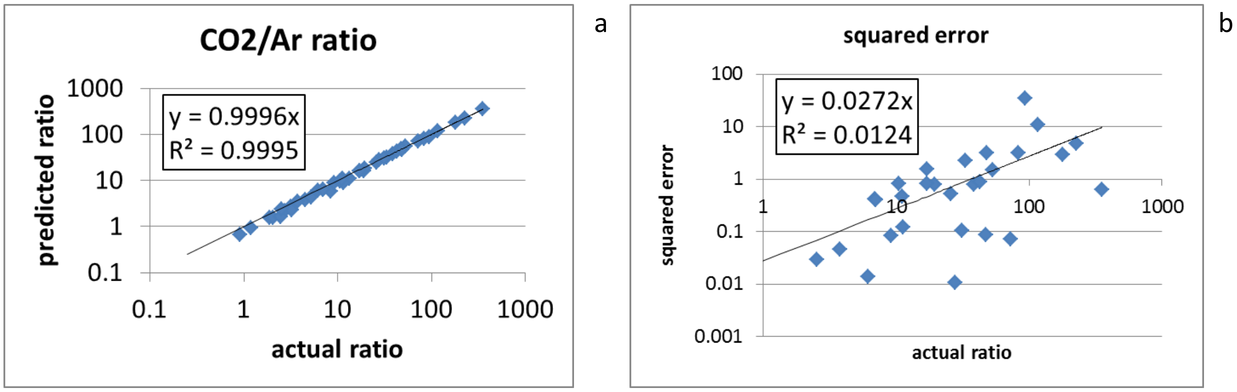

**Figure A4: Calibrated measurements of $CO_2$/Ar ratios (left) and error structure (right).**

The magnitude of the interference on m/z 28 by a CO fragment of $CO_2$ was evaluated by a linear regression between m/z 28 and 44 signals of pure $CO_2$ gas aliquots at various pressures. A slope of 0.0816 was found. With $CO_2/N_2$ ratios in groundwater samples between 1 and 2.5, a correction of 8% to 20% due to the $CO_2$ interference is necessary (Figure A5).

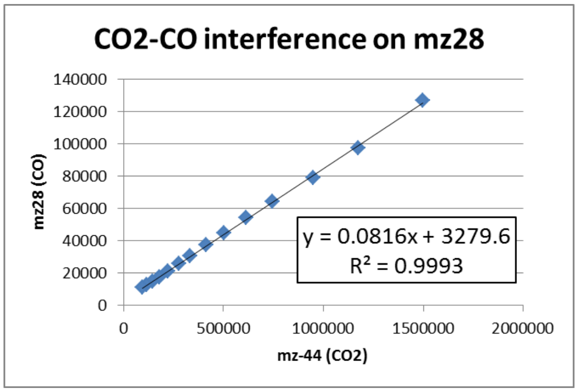

**Figure A5: Interference of CO, a fragment of $CO_2$, on nitrogen measurements at m/z 28.**

### 6.5.3 Methane and Ethane

Methane is measured on m/z 15, a $CH_3$ fragment of $CH_4$, because of interferences with O fragments of $H_2O$ at m/z 16. $CH_4$/Ar and $C_2H_6$/Ar sensitivity ratios were calibrated using 119 mixtures of natural gas and air. The natural gas composition, provided by PG&E, contains 95% $CH_4$, 3.8% $C_2H_6$, and less than 1% of $N_2$, $CO_2$ or $C_3H_8$. $CH_4$/Ar ratios in the calibration gas mixtures varied from 0.18 to 106, by mixing aliquots of natural gas and air at ratio between 1:2 and 2:1 with decreasing pressures in the small natural gas reservoir. $CH_4$/Ar ratios in groundwater are expected to vary from 0 to over 100. The EPA action level for methane in groundwater is 10 mg $CH_4$/L, due to the risk of explosion of exsolved gas rather than health concerns. The action level is equal to 0.014 $cm^3$STP/g, or $CH_4$/Ar ratios between 23 and 47, depending on the Ar concentration in groundwater, typically varying between 3 and 6 × 10-4 $cm^4$STP/g.

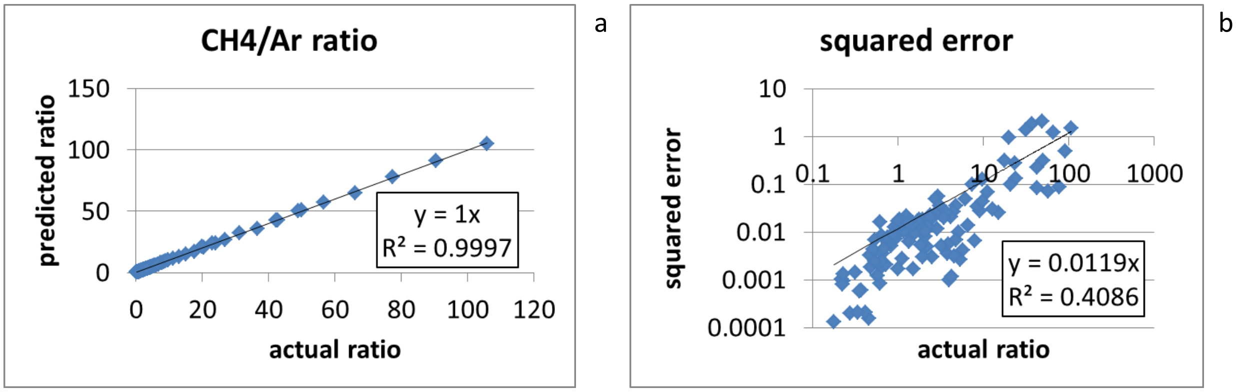

**Figure A6: Calibrated measurements of $CH_4$/Ar ratios (left) and error structure (right).**

The $CH_4$/Ar sensitivity ratio was estimated to be 1.76, by minimizing the RMSE between measured and known $CH_4$/Ar ratios (Figure A6a). Note that this relates to the sensitivity to the $CH_3$ fragment, which constitutes only 40% of the gas fragments after ionization of $CH_4$. ($CH_4$ constitutes 46%). The relative error between measured and known $CH_4$/Ar ratios varies from ±5% at ratios above 10, to ±15% at ratios below 1 (Figure A6b). The error structure was approximated by linear regression between the squared error and the ratio. The regression slope (0.012) results in a predicted measurement uncertainty of $\sigma_{CH4/Ar} = \surd\ (0.012 \times CH_4/Ar)$. The predicted relative measurement uncertainty decreases from 11% at a $CH_4$/Ar ratios of 1, to 3.5% at a ratio of 10, to 1.1% at a ratio of 100.

The $CH_4$ detection limit is determined by the variation of the $CH_4$/Ar signal of air standards, containing no methane. The $CH_4$/Ar air standard signal has a mean of 0.026 and a standard deviation of 0.020. Considering the sensitivity ratio, the 2 σ detection limit raising the $CH_4$/Ar ratio significantly above the background is 0.06. With Ar concentrations in groundwater varying between 3 and 6 × 10-4 $cm^4$STP/g, the methane detection limit is 14-27 µg $CH_4$/L, 370-714 times lower than the EPA action limit. In practice, a detection limit of 0.5 mg $CH_4$/L (20 times below the EPA action level) is realistic.

Detection of ethane in the presence of nitrogen (m/z 28) is challenging due to the overlap of the 28 peak on 27. To calibrate the $C_2H_6$ sensitivity, the $N_2$ interference was first quantified as the ratio of the 27/40 signal over the 28/40 signal, measured in $N_2$-air calibration mixtures. The mean and standard deviation of the 27/40 over 28/40 ratio are 0.0116 and 0.0018. $C_2H_6$ can be detected if the 27/40 signal is above 0.015 times the 28/40 signal (mean interference plus 2 σ). Eight of the 119 natural gas-air mixtures show detectable levels of $C_2H_6$, with $CH_4$/Ar ratios varying between 43 and 106. The $C_2H_6$/Ar sensitivity ratio was estimated to be 4.08, by minimizing the RMSE between measured and known $C_2H_6$/Ar ratios (Figure A7). The RMSRE for $C_2H_6$/Ar is 8.1%. The detection limit is approximately 2% of the $N_2$ concentration and varies between 0.24 and 0.60 mg $C_2H_6$/L, depending on the $N_2$ concentration in groundwater, typically between 0.011 and 0.028 $cm^3$STP/g. $C_2H_6$ can be detected on m/z 27 if groundwater is contaminated with natural gas and the methane concentration is above 3-8 mg $CH_4$/L (assuming 4% $C_2H_6$ in natural gas). This level is close to the EPA action limit and does not allow for early detection and attribution of natural gas in groundwater. Therefore, the ethane signal on m/z 30 was also investigated.

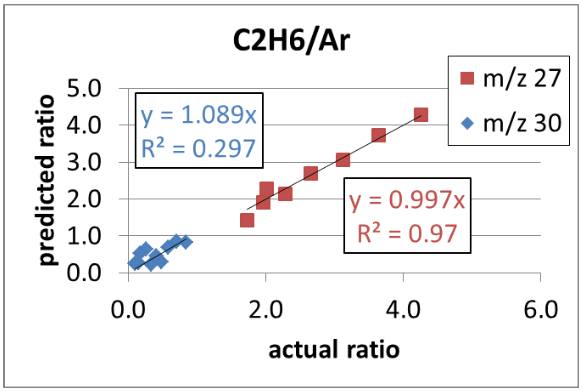

**Figure A7: Calibrated measurements of ethane on m/z 27, suffering from interference by $N_2$, and m/z 30.**

Gas mixtures of natural gas and air (n=24) with $CH_4$/Ar ratios below 2.5 were analyzed to study the detection limit of $C_2H_6$ on m/z 30. Positive detection of $C_2H_6$ is achieved if the measured signal is 2 standard deviations (σ = 0.02) above the average (µ = 0.009) of the 30/40 signal of the air standards. Considering the $C_2H_6$/Ar sensitivity ratio (5.22) and typical Ar concentrations (3-6 × $10^{-4}$ cm4STP/g), the detection limit for $C_2H_6$ is 80-160 µg $C_2H_6$ /L, equivalent to 1-2 mg $CH_4$ /L of natural gas. This level is 5-10 times below the EPA action limit and allows for early attribution of detected methane in groundwater to natural gas or biogenic sources.