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California GAMA Special Study:Archival Data Conversion & Upload

A. Visser, G. Eppich, R. Bibby, M. Singleton, D. Hillegonds, J. Moran, B. Esser

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GAMA: AMBIENT GROUNDWATER
MONITORING & ASSESSMENT PROGRAM
SPECIAL STUDY

California GAMA Special Study:
Archival Noble Gas and Tritium Data Conversion & Upload

By Ate Visser, Gary R. Eppich, Richard K. Bibby, Michael J. Singleton, Darren J. Hillegonds, Jean E. Moran, and Bradley K. Esser*

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

Prepared in cooperation with the
California State Water Resources Control Board
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California GAMA Special Study: Archival Data Conversion & Upload (LLNL-TR- 650040)

Ate Visser, Gary R. Eppich, Richard K. Bibby, Michael J. Singleton, Darren J. Hillegonds, Jean E. Moran*, and Bradley K. Esser
*Lawrence Livermore National Laboratory, *California State University-East Bay*
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Executive Summary

LLNL has uploaded over 3000 tritium analyses and over 4000 noble gas analyses to the GeoTracker GAMA database. Data preparation included:

- Cross-checking of GAMA project data in the LLNL database against reported data
- Associating GAMA project data with published technical reports or articles
- Associating LLNL analytes and analytical protocols with existing electronic deliverable format (EDF) parameters
- Obtaining electronic deliverable format (EDF) parameters for non-standard LLNL analytes and analytical protocols
- Electronically reporting quality control data with associated control limits via the EDF control limit (EDFCL) file for LLNL analytical protocols
- Transforming archival GAMA project data into electronic data deliverables

Contents

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Noble gases and tritium as groundwater tracers

Dissolved noble gases (helium, neon, argon, krypton and xenon) in groundwater provide a snapshot of groundwater recharge conditions. Noble gases are transported conservatively in saturated media, providing a long term record. Altitude and temperature control noble gas solubility. Water level fluctuations cause bubble entrainment in the unsaturated zone and noble gas super-saturation, known as excess air. These properties make dissolved noble gases especially well-suited to examining recharge processes and groundwater transport [Manning and Caine, 2007; Plummer et al., 2001; Manning and Solomon, 2005; Rademacher et al., 2001, 2005; Singleton and Moran, 2010].

The primary sources of noble gases dissolved in natural waters are equilibration of water with the atmosphere and the decay of several radioactive isotopes (Ozima and Podosek, 2002; Porcelli et al., 2002). The abundances of the heavier noble gases (Ne, Ar, Kr, Xe) in groundwater are due primarily to atmospheric equilibration of water during groundwater recharge and excess air formation, and their elemental abundances are directly related to the temperature and altitude of the groundwater recharge location.

Helium isotopes (^{3}He and ^{4}He) in groundwater are derived from several different sources: equilibration with the atmosphere (^{3}He and ^{4}He), excess air from bubble entrainment in the unsaturated zone (^{3}He and ^{4}He), nuclear fission of ^{6}Li (nucleogenic ^{3}He) associated with the production of ^{4}He by U-Th decay (radiogenic ^{4}He)(Schlosser et al., 1989), mantle helium (^{3}He and ^{4}He) and tritium decay (tritiogenic ^{3}He). The abundances of the helium isotopes are directly related to the age of the sample – the time since last contact with the atmosphere.

When combined with measurements of tritium, helium isotopes provide a means of quantifying the apparent ^{3}H/^{3}He groundwater subsurface residence time, or groundwater age, over a time scale of about 55 years. Radiogenic helium is also a tracer for groundwater age, typically in the range of 10^3 to 10^6 years (Marine, 1979).

Upload of tritium and noble gas concentrations to the GAMA GeoTracker database

The Noble Gas Mass Spectrometer facility at LLNL has been operational for over fifteen years. During that time, over four thousand noble gas analyses and over three thousand tritium analyses have been performed on groundwater samples from the state of California. These data have been compiled, verified and uploaded to the State's GeoTracker GAMA Groundwater Information System. The analytical protocols of the uploaded data – the concentration of tritium and the concentrations of dissolved noble gases and isotope ratio of dissolved helium – have been associated with new and existing electronic deliverable format (EDF) parameters in the GeoTracker GAMA Groundwater Information System (Table 1). In summary, 3154 samples have been analyzed for tritium and 4187 samples have been analyzed for noble gases. For 2870 of these samples, both a tritium and a noble gas analysis are available.

Table 1: List of analytes and associated EDF parameters

Analyte	Analyte Code	Unit	Extraction Method Code	Analytical Method Code	Analyses (#)
3H	**H-3**	pCi/L	NONE	**3HE_ACC**	**3154**
	Tritium (Hydrogen 3)		No extraction required for this method	Tritium by helium-3 accumulation (LLNL-TM-623415)	
3He/4He	**3HE/4HE**	atom ratio	NONE	**NG_IRMS**	**4181**
	Helium-3 /Helium-4		No extraction required for this method	Noble gas isotope ratio mass spectrometry (LLNL-TM-623335)	
4He	**4HE**	cm^3STP/g	NONE	**NG_IRMS**	**4159**
	Helium-4		No extraction required for this method	Noble gas isotope ratio mass spectrometry (LLNL-TM-623335)	
Ne	**NE**	cm^3STP/g	NONE	**NG_IRMS**	**4145**
	Neon		No extraction required for this method	Noble gas isotope ratio mass spectrometry (LLNL-TM-623335)	
Ar	**AR**	cm^3STP/g	NONE	**NG_IRMS**	**4098**
	Argon		No extraction required for this method	Noble gas isotope ratio mass spectrometry (LLNL-TM-623335)	
Kr	**KR**	cm^3STP/g	NONE	**NG_IRMS**	**4128**
	Krypton		No extraction required for this method	Noble gas isotope ratio mass spectrometry (LLNL-TM-623335)	
Xe	**XE**	cm^3STP/g	NONE	**NG_IRMS**	**3922**
	Xenon		No extraction required for this method	Noble gas isotope ratio mass spectrometry (LLNL-TM-623335)	

cm^3STP/g: Cubic centimeter of gas, at standard temperature and pressure (0°C, 1 bar) per gram of water sample.

pCi/L: Picocuries per liter of water sample. 3.2 pCi/L corresponds to 1 tritium unit (TU), defined as a tritium:hydrogen (^3H:^1H) atom ratio of 1:10^{18}.

The remainder of this report describes the various projects for which the samples were collected and analyzed. The majority of the samples were collected and analyzed for various parts of the GAMA Program. The technical reports and scientific publications in which portions of the tritium and noble gas data were previously reported are briefly discussed. The data verification steps are presented. The sample collection and analysis protocols are described in detail in Visser et al. (2013a; 2013b). All uploaded analyses meet minimum data quality objectives and QA/QC as outlined in these SOPs.

This task addresses LLNL isotopic data that was generated to support the GAMA California Aquifer Susceptibility, Priority Basin and Domestic Well Projects. The dataset, hereafter referred to as “GAMA project data" includes the isotopic composition of water and nitrate, and tritium and noble gas concentrations.

Summary of projects

1. The California GAMA and CAS Programs

In response to concerns expressed by the California Legislature and the citizenry of the State of California, the State Water Resources Control Board (SWRCB), implemented the Groundwater Ambient Monitoring and Assessment (GAMA) Program to assess groundwater quality, and provide a predictive capability for identifying areas that are vulnerable to contamination. Under various aspects of the GAMA program, LLNL has completed 2881 tritium analyses and 3954 noble gas analyses (Table 2). In addition, 227 tritium analyses and 273 noble gas analyses are reported that were performed under various LLNL funded projects.

Table 2: Number of uploaded noble gas and tritium analyses per GAMA project and LLNL funded projects.

Group	Noble Gas[1]	Tritium
SWRCB CAS and GAMA Programs	**3954**	**2881**
California Aquifer Susceptibility (CAS)	1069	1073
GAMA Special Studies	255	269
GAMA Priority Basin	2334	1539
GAMA Priority Basin Trend	195	-
GAMA Shallow Aquifer Assessment	101	-
LLNL funded	**227**	**273**
Total	**4181**	**3154**

[1] Noble gas analyses include concentrations for the noble gases (He, Ne, Ar, Kr, Xe) and the isotopic composition of helium ($^3He/^4He$).

A. The California Aquifer Susceptibility (CAS) Project

The California Aquifer Susceptibility (CAS) assessment was performed from 2000 to 2003 in collaboration with the U.S. Geological Survey (USGS) and Lawrence Livermore National Laboratory (LLNL). The primary objective of the California Aquifer Susceptibility (CAS) project (under the GAMA Program) is to assess water quality and to predict the relative susceptibility to contamination of groundwater resources throughout the state of California (Figure 1). Detailed information on the CAS project can be found at [Water Board GAMA website](). This effort was the foundation for the GAMA Priority Basin Project.

Two types of groundwater tests were performed in the assessment: age-dating and low-level VOC analyses. Age-dating (tritium-helium analysis) was used to provide information on the presence of young groundwater and low level VOC analysis is used as an "early warning" for potential contamination. Over 1,000 Public Drinking water wells were sampled during CAS and analyzed for tritium and dissolved noble gas concentrations (Table 3).

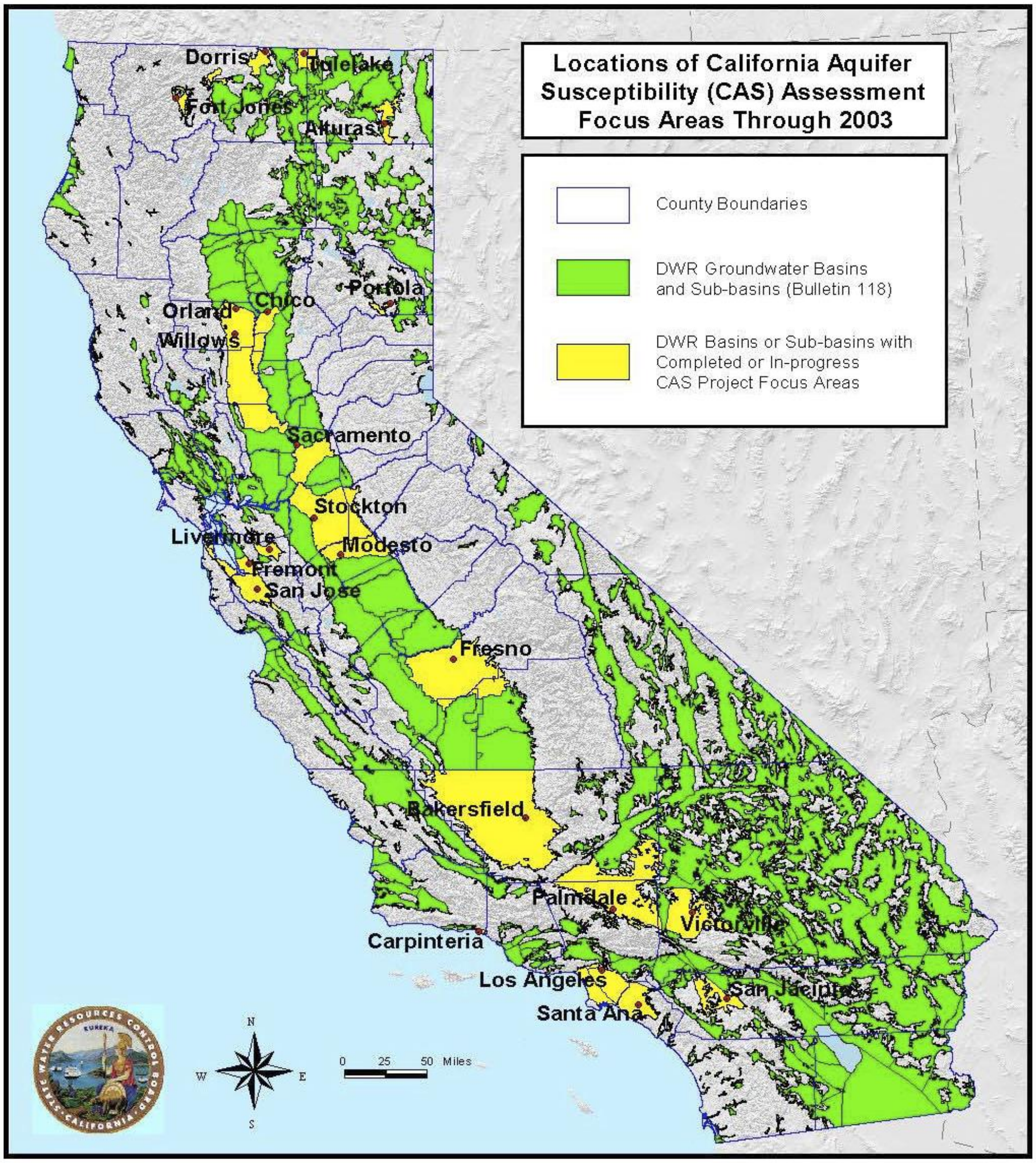

Figure 1: Map of California Aquifer Susceptibility Focus areas in 2003.

Table 3: Summary of California Aquifer Susceptibility program effort

Year	Geographic Area	Noble gas analyses	Tritium analyses	Report
2000	Los Angeles County Orange County (LA/Santa Ana)	214	195	cas_llnl_la_orange.pdf (Hudson et al., 2002)
2001	Alameda County	36	41	cas_llnl_alameda.pdf (Moran et al., 2002a)
2001	Santa Barbara County (Carpinteria)	4	4	
2001	Riverside County (San Jacinto)	26	18	san_jacinto_wrir024243.pdf (Hamlin et al., 2002)
2001/ 2002	Fresno County Stanislaus County (Modesto)	85	89	cas_usgs_modesto_fresno.pdf (Wright et al., 2004)
2001/ 2002	Santa Clara County San Mateo County	207	210	cas_llnl_santaclara_sanmateo.pdf (Moran et al., 2002b)
2001/ 2002	Sacramento County	126	126	cas_llnl_sac.pdf (Moran et al., 2003)
2001/ 2002	San Joaquin County	103	107	
2003	Butte County (Chico) Glenn County Modoc County Siskiyou County Plumas County Shasta County	148	163	cas_llnl_no_sacval_volcanics.pdf (Moran et al., 2005c)
2002/ 2003	San Bernardino County (Victorville)	32	33	usgs_antelope_mojave.pdf (Densmore et al., 2005)
2002/ 2003	Los Angeles County (Antelope Valley / Palmdale)			usgs_antelope_mojave.pdf (Densmore et al., 2005)
2002/ 2003	Kern County (Bakersfield)	43	43	cas_llnl_bakersfield.pdf (Moran et al., 2005b)
	Other CAS samples	45	44	
Total		1069	1073	

[1] Noble gas analyses include concentrations for the noble gases (He, Ne, Ar, Kr, Xe) and the isotopic composition of helium ($^3He/^4He$).

All reports can be at http://www.waterboards.ca.gov/water_issues/programs/gama/docs/

B. The California GAMA Priority Basin (PB) Project

The Groundwater Quality Monitoring Act of 2001 (Water Code Sections 10780-10782.3) otherwise known as AB 599 resulted in a publicly accepted plan to monitor and assess the quality of all priority groundwater basins that account for over 90% of all groundwater used in the state. The plan prioritizes groundwater basins for assessment based on groundwater use across the state. The GAMA Priority Basin Project monitors groundwater for a dozens of chemicals at very low detection limits, including emerging contaminants. Monitoring and assessments are on a ten-year cycle, with trend monitoring more frequent. The State Water Board is collaborating with the U.S. Geological Survey (USGS) and Lawrence Livermore National Laboratory (LLNL) to implement the Priority Basin Project. From 2004 to 2012, the GAMA Program's Priority Basin Project focused on assessing groundwater resources used for public drinking-water supplies (Figure 2). More than 2,000 public-supply wells were sampled by U.S. Geological Survey (USGS) for this effort.

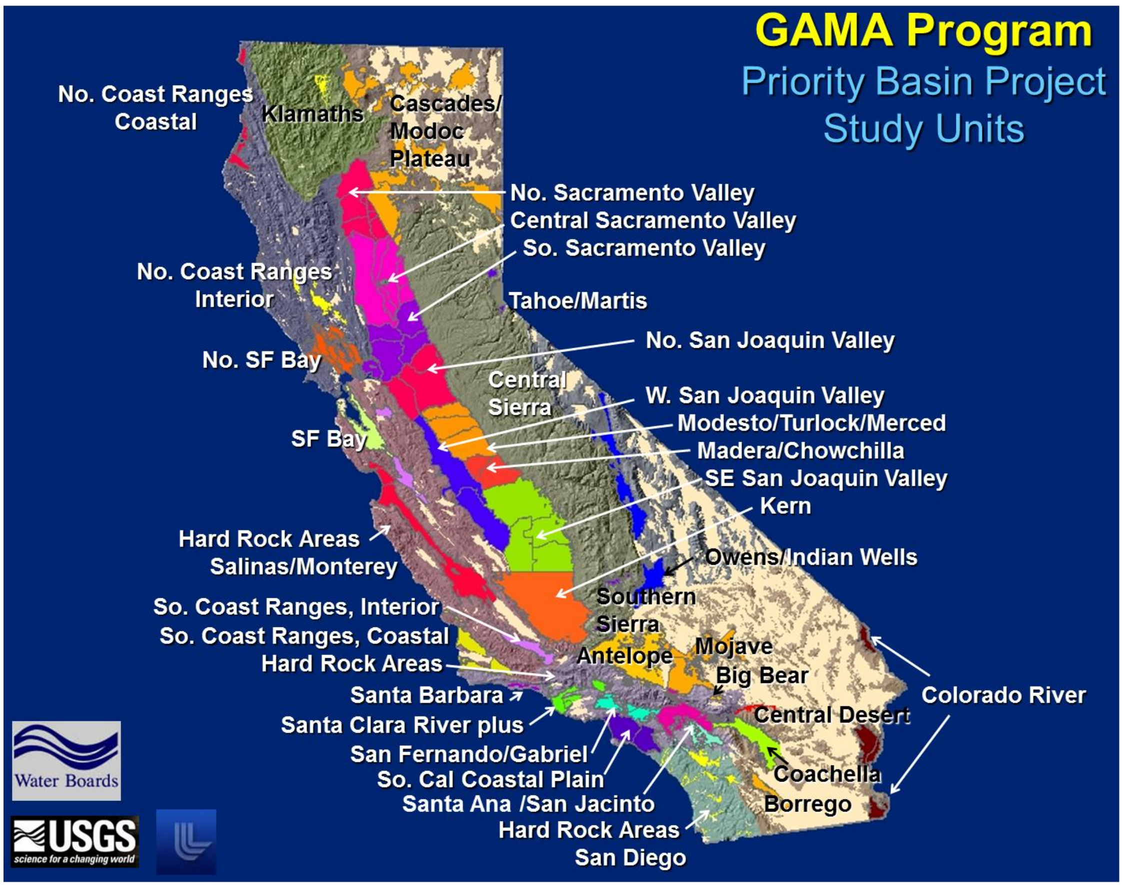

Figure 2: Map of GAMA Priority Basin Project (Source: USGS)

Noble gas concentrations and the helium isotope ratio have been measured in 2051 samples from the Priority Basin Project (Table 4a,b). The complete noble gas suite (concentrations and helium isotope ratio) is available for 2003 samples, the remaining 48 lack one or more noble gas concentrations due to instrument failure. Priority Basin noble gas data constitute nearly half of the entire data upload, against 2136 samples from other projects. These include CAS, and Priority Basin Trends sampling. Noble gas analyses are completed for all 37 Study Units. The data has been reported for 17 Study Units in various USGS Data Series Reports. Noble gas data for 20 Study Units have not been reported in the DSR.

Table 4a: GAMA Priority Basin Provinces and Study Units.

Province Label	Province	Study Unit Label	Study Unit
BR	Basin & Range	**OWENS**	Owens/Indian Wells
CV	Central Valley	**CE**	Central Eastside San Joaquin Valley
CV	Central Valley	**KERN**	Kern
CV	Central Valley	**MADCHOW**	Madera-Chowchilla
CV	Central Valley	**MIDSAC**	Central Sacramento Valley
CV	Central Valley	**NSAC**	Northern Sacramento Valley
CV	Central Valley	**NSJV**	Northern San Joaquin Basin
CV	Central Valley	**SESJV**	Southeast San Joaquin Valley
CV	Central Valley	**SSAC**	Southern Sacramento Valley
CV	Central Valley	**WSJV**	Western San Joaquin Basin
D	Desert	**ANT**	Antelope Valley
D	Desert	**CLUB**	Borrego, Central Desert, Low Use Basins
D	Desert	**COA**	Coachella
D	Desert	**COLOR**	Colorado
D	Desert	**MOJO**	Mojave
KM	Klamath Mountains	**KLAM**	Klamath Basin
MPC	Modoc Plateau & Cascades	**CAMP**	Cascades & Modoc Plateau (all units)
NCR	Northern Coast Ranges	**NOCO**	North Coast Ranges
NCR	Northern Coast Ranges	**NSF**	North San Francisco Bay
SCR	Southern Coast Ranges	**MS**	Monterey Bay / Salinas
SCR	Southern Coast Ranges	**SCHDRK**	Santa Cruz Mountains
SCR	Southern Coast Ranges	**SCRC**	South Coast Range – Coastal
SCR	Southern Coast Ranges	**SCRI**	South Coast Range – Interior
SCR	Southern Coast Ranges	**SF**	San Francisco Bay
SD	San Diego	**SD**	San Diego
SD	San Diego	**SDHDRK**	San Diego Mountains
SN	Sierra Nevada	**CENSI**	Central Sierras
SN	Sierra Nevada	**SIERRA**	Sierran Regional
SN	Sierra Nevada	**SOSA**	Southern Sierras
SN	Sierra Nevada	**T**	Tahoe / Martis
TPR	Transverse & Peninsular Range	**Bear**	Big Bear Basin
TPR	Transverse & Peninsular Range	**CLAB**	Coastal Los Angeles Basin
TPR	Transverse & Peninsular Range	**SBB**	Santa Barbara Basin
TPR	Transverse & Peninsular Range	**SCRV**	Santa Clara River Valley
TPR	Transverse & Peninsular Range	**SGHDRK**	San Gabriel Mountains
TPR	Transverse & Peninsular Range	**ULAB**	San Gabriel / San Fernando
TPR	Transverse & Peninsular Range	**USAW**	Santa Ana Basin

Table 4b: Number of noble gas analyses uploaded for Priority Basin Study Units.

Province	Study Unit	^{3}H	$^{3}He/^{4}He$	^{4}He	Ne	Ar	Kr	Xe	All NGs	Any NG	DSR Nr.	NG data in DSR?
BR	OWENS	73	73	71	71	71	71	71	71	73	427	no
CV	CE	73	75	75	75	74	75	75	74	75	325	yes[2]
CV	KERN	46	45	45	45	42	45	45	42	45	337	yes[1]
CV	MADCHOW	20	34	34	34	34	34	34	34	34	455	no
CV	MIDSAC	105	101	101	100	99	101	100	99	101	385	no
CV	NSAC	65	64	64	64	64	64	64	64	64	452	yes[2]
CV	NSJV	26	15	15	15	15	15	15	15	15	196	yes[1]
CV	SESJV	96	101	101	101	95	101	101	95	101	351	yes[1]
CV	SSAC	41	42	42	39	37	42	42	37	42	285	yes[1]
CV	WSJV	0	49	49	49	47	48	47	47	49	706	no
D	ANT	49	55	54	55	54	55	55	53	55	479	no
D	CLUB	27	50	50	50	50	50	50	50	50	659	no
D	COA	35	31	31	31	31	31	31	31	31	373	no
D	COLOR	8	27	27	27	27	27	27	27	27	474	no
D	MOJO	53	54	54	54	54	54	54	54	54	440	no
KM	KLAM	0	47	47	47	47	47	47	47	47	803	yes
MPC	CAMP	0	88	88	88	87	88	88	87	88	688	no
NCR	NOCO	0	55	54	54	51	53	53	50	55	609	no
NCR	NSF	86	97	96	97	92	97	97	92	97	167	yes[1]
SCR	MS	96	92	92	92	90	92	92	90	92	258	yes[1]
SCR	SCHDRK	0	24	24	24	24	24	24	24	24	874	yes
SCR	SCRC	20	65	65	65	62	62	62	62	65	504	no
SCR	SCRI	13	54	54	54	54	54	54	54	54	463	no
SCR	SF	24	79	79	79	78	79	79	78	79	396	yes[2]
SD	SD	56	64	61	64	64	64	64	61	64	129	yes[1]
SD	SDHDRK	0	43	43	42	43	42	42	42	43	874	yes
SN	CENSI	30	28	28	28	28	28	28	28	28	335	no
SN	SIERRA	15	77	76	76	76	76	76	76	77	534	no
SN	SOSA	47	47	47	47	47	47	47	47	47	301	no
SN	T	32	47	47	47	47	47	47	47	47	432	no
TPR	Bear	0	38	38	38	38	38	38	38	38	747	no
TPR	CLAB	69	62	62	62	62	62	62	62	62	387	no
TPR	SBB	0	24	24	23	23	23	23	22	24	742	no
TPR	SCRV	51	49	49	49	49	49	49	49	49	408	yes[2]
TPR	SGHDRK	0	33	33	33	33	33	33	33	33	874	yes
TPR	ULAB	22	24	24	24	24	24	24	24	24	356	yes[1]
TPR	USAW	99	98	98	98	97	98	98	97	98	404	yes[2]
Priority Basin Total		1377	2051	2042	2041	2010	2040	2038	2003	2051		

Notes on Noble Gas data in DSR reports:
1: no pipette recalibration was needed (8 Study Areas).
2: a correction was needed, the data reported in the DSR is incorrect (5 Study Areas).

Tritium concentrations have been measured in 1377 samples from the Priority Basin Project (Table 4a, b). Priority Basin tritium data constitute nearly half of the entire data upload, against 1806 samples from other projects. These include CAS, and Priority Basin Trends sampling.

In September 2011, a calibration drift was discovered cumulating over 5 years. The corrective action taken was re-evaluation of all noble gas concentrations measured over that period. The corrected noble gas concentrations (2126 samples) have been reported to the USGS on 29 March 2012 and 26 April 2012. The correction factor varies between 0.9% and 10.7%. Most study units have been analyzed within a short time span. Some later analysis dates refer to re-analyses of samples. The USGS publications (Data Series Reports) reporting noble gas data on these study units contain biased noble gas concentration data. The data presented in this upload contains the recalibrated data.

C. The California GAMA Priority Basin Trends (PBT) Project

To establish trends in groundwater quality, a selection of 10% of the wells is revisited after 10 years under the Priority Basin Trends program. Noble gas concentrations have been analyzed in 195 PBT samples.

D. The California GAMA Shallow Aquifer Assessment Project

Starting in 2012, the GAMA Priority Basin Project began an assessment of water resources in shallow aquifers in California. These shallow aquifers provide water for domestic and small community-supply wells, which are often drilled to shallower depths in the groundwater system than public-supply wells. Shallow aquifers are of interest because shallow groundwater may respond more quickly and be more susceptible to contamination from human activities at the land surface, than the deeper aquifers. Noble gas concentrations have been analyzed in 101 SAA samples.

E. The California GAMA Special Studies (SS) Program

Within the framework of the GAMA program, Lawrence Livermore National Laboratory (LLNL) has conducted several groundwater special studies covering nitrate, wastewater, and groundwater recharge. A number of these studies have relied on the tritium and noble gas data that are uploaded (Table 5). Other studies have examined the same samples for other water quality aspects (nitrate, waste water indicators, isotopes), without evaluating the tritium and noble gas data.

One Special Study for which no new analyses were performed is nevertheless relevant to the interpretation of tritium, noble gas and tritium-helium ages: it presents investigation of the simulation of groundwater age and deconvolution methods to interpret tritium-helium data (Carle et al., 2010).

Table 5 Number of uploaded noble gas and tritium analyses from Special Studies

Special Study Data	Title	Noble Gas[1]	Tritium	Report
Salinas	California GAMA Special Study: Nitrate Fate and Transport in the Salinas Valley	28	40	(Moran et al., 2011)
Tulare	California GAMA Domestic Wells: Nitrate and Water Isotopic Data for Tulare County	-	-	(Singleton et al., 2010b)
Ripon	California GAMA Special Study: An isotopic and dissolved gas investigation of nitrate source and transport to a public supply well in California's Central Valley	16	17	(Singleton et al., 2010a)
SEWD Morada	Tracking Water Quality Changes during Groundwater Banking at Two Sites in San Joaquin County	11	15	(Moran et al., 2009)
SEWD	California GAMA Special Study: Ion exchange and trace element surface complexation reactions associated with applied recharge of low TDS water in the San Joaquin Valley, California	30	32	(McNab Jr et al., 2010)
GAMA-Chico GAMA-WW	Fate and Transport of Wastewater Indicators: Results from Ambient Groundwater and from Groundwater Directly Influenced by Wastewater	38	30	(Moran et al., 2006)
SONOMA	California GAMA Special Study: Interpretation of Isotopic Data in the Sonoma Valley, California (posted 11/08/12)	10	10	(Moran et al., 2010)
SEPTIC		32	23	No report
OCWD		69	68	No report
Rialto-Colton	Perchlorate migration within Rialto-Colton and adjacent basins. Collaboration with USGS. http://ca.water.usgs.gov/projects/rialto_colton.html	21	31	No report
Total		**255**	**269**	

[1]: Noble gas analyses include concentrations for the noble gases (He, Ne, Ar, Kr, Xe) and the isotopic composition of helium ($^3He/^4He$).

SWRCB GAMA Groundwater Reports: See Groundwater Reports on GAMA Program website (www.waterboards.ca.gov/water_issues/programs/gama/)

2. LLNL projects with funding from other sources

Tritium and noble gas analyses performed for Livermore funded studies have also been uploaded to GeoTracker GAMA database (Table 6). These include 227 noble gas analyses and 273 tritium analyses from two projects: Laboratory Directed Research and Development towards sources of nitrate and transport of nitrate in groundwater (NO3 LDRD) and the climate vulnerability of a high elevation basin (Squaw Valley).

Two additional scientific papers were based on the LLNL database of noble gas concentrations, discussing the impact of artificial recharge on dissolved noble gases (Cey et al., 2008) and evaluating noble gas recharge temperatures in a shallow unconfined aquifer (Cey et al., 2009).

Table 6: Number of uploaded noble gas and tritium analyses from LLNL funded projects

Project	Reports	Noble Gas[1]	Tritium
NO3 LDRD[2]	Nitrate Biogeochemistry and Reactive Transport in California Groundwater: LDRD Final Report (Esser et al., 2006)	**171**	**214**
	Sources and Transport of Nitrate in Shallow groundwater in the Llagas Basin of Santa Clara County, California (Moran et al., 2005d)	55	57
	Sources and transport of nitrate in groundwater in the Livermore Valley Basin, California (Moran et al., 2005a)	33	35
	Sources of groundwater nitrate revealed using residence time and isotope methods (Moore et al., 2006)	23	23
	Impact of Dairy Operations on Groundwater Quality (Esser et al., 2009)	34	45
	Fate and transport of wastewater indicators: Results from ambient groundwater and from groundwater directly influenced by wastewater (Moran et al., 2006)	74	103
Squaw	Dissolved noble gas and isotopic tracers reveal vulnerability of groundwater in a small, high-elevation catchment to predicted climate changes (Singleton and Moran, 2010)	**56**	**59**
Total		**227**	**273**

[1]: Noble gas analyses include concentrations for the noble gases (He, Ne, Ar, Kr, Xe) and the isotopic composition of helium ($^3He/^4He$).

[2]: Numbers in bold represent the total number of analyses performed related to LDRD project. Data presented in reports overlap and the sum of the number of analyses per report does not add up to total number of analyses.

Data verification

3. Noble gas concentrations

Noble gases in groundwater (except helium) are entirely from atmospheric origin. The composition of the noble gas concentrations are controlled by the noble gas abundances in the atmosphere, air pressure (recharge altitude) and temperature dependent solubility. The differences in noble gas solubility result in specific (temperature dependent) noble gas concentration ratios. Water table fluctuations cause air entrapment in the unsaturated zone, leading to excess dissolution of noble gases with an atmospheric abundance signature. As a result of these processes, the concentrations of noble gases (except helium) are constrained and consistent with each other.
The quality of the measured noble gas data is checked by comparing the measured concentrations with solubility concentrations and realistic excess air amounts for the given recharge altitude and a fitted recharge temperature. If the measured concentrations of noble gases in the sample are improbable, a duplicate sample is measured.

F. Outlier removal

The data was analyzed for outliers in two ways: (1) outliers within the distribution of the specific noble gas concentrations, and (2) groups of outliers with respect to the concentrations of other noble gases. A summary of excluded values is presented in Table 7.
Selection criteria for outliers within the noble gas concentration distribution were subjectively formulated the high and low end of the distribution. The criterion for high value outliers was that the value was 25% larger than the next smaller value. This criterion was only applied to the 0.1% of the distribution. The criterion for low value outliers was that the measured concentration was less than 1% of the median concentration.
Groups of outliers with respect to the concentrations of other noble gases were derived from visual inspection of figures plotting concentrations of each noble gas against the concentration of all other noble gases. Two groups of outlying data that that could be attributed to one of the noble gases were removed. In both cases the argon concentration was anomalous.

Table 7: Summary of outliers

Reason	Number	Reason	Number	Reason	Number
Low ^{4}He[1]	9	**High ^{4}He[1]**	4	**Bad Xe[2]**	153
Low Ne[1]	13	**High Ne[1]**	4	**High Ar[2]**	26
Low Ar[1]	9	**High Ar[1]**	13	**Low Ar[2]**	14
Low Kr[1]	7	**High Kr[1]**	3		
Low Xe[1]	10	**High Xe[1]**	3	**Total**	212

[1]: outliers within the distribution of the specific noble gas
[2]: outliers with respect to the concentrations of other noble gases.

A total of 212 measurements were removed as outliers. Most of them (n=153) contained anomalous xenon data, all measured between 3/2/2004 and 5/14/2004. Other outliers do not show any temporal correlations.

The remaining dataset still shows a number of outliers, compared to expected noble gas concentrations. In Figure 3, noble gas concentrations are plotted against each other on property-property plots. Solubility-controlled air-water equilibrium concentrations are plotted in blue, for temperatures ranging from 0°C (highest concentration) to 35°C (lowest concentration). Addition of 0.05 cm^3STP/g of unfractionated excess air (equivalent to ΔNe = 450%) is shown in purple lines for each 5°C increment.

The noble gas concentrations in samples included in the trapezoid described by the equilibrium concentrations plus excess air are what is expected in environmental samples. The same simulated equilibrium concentrations are expected for helium without the addition of terrigenic or tritiogenic helium. Samples outside of these trapezoids are outliers that have not been removed. Further removal of outliers requires assumptions on the likelihood of fractionation of excess air and possible degassing of groundwater within the aquifer.

Histograms of the uploaded noble gas data show that the data are not normally distributed (Figure 4). A Shapiro-Wilk Normality test was performed (Table 8) and all distributions are significantly different from Normal (the probability that these distributions are normal is extremely low).

Table 8: Shapiro-Wilk Normality test of uploaded noble gas data.

Analyte	Shapiro-Wilk W-value	Probability
$^3He/^4He$	0.73	<0.0001
^{4}Helium	0.31	<0.0001
Neon	0.33	<0.0001
Argon	0.79	<0.0001
Krypton	0.45	<0.0001
Xenon	0.69	<0.0001

Because none of the noble gas concentration distributions are normal, outlier tests based on the normality assumption cannot be performed. The data will likely contain measured values that are improbable, based on the currently accepted models for noble gas dissolution. No further efforts to remove data were made, to avoid constraining the data to currently accepted models. If a subset of the data is used, a critical evaluation of the subset is recommended.

4. Tritium Concentrations

Tritium concentrations are reported with their respective propagated measurement uncertainty. The laboratory quality criterion is that the propagated uncertainty at the time of sampling shall be less than the square root of the quadratic sum of 1 pCi/L plus 5% of the tritium activity at the time of sampling. While 123 of 3154 samples (4%) do not meet the laboratory quality criterion, these samples have been reported nevertheless. If the calculated tritium concentration is less than zero due to blank subtraction and/or air contamination correction, the reported value is zero. Because the sources of measurement uncertainty are variable, the propagated uncertainty varies between samples and it is not possible to assign a single detection limit to the tritium data set as a whole. The propagated uncertainty should be considered the detection limit for tritium concentrations less than the uncertainty (n=359). It is up to the user of the data to judge whether the measured tritium concentrations constitutes detection, according to an appropriate confidence level.

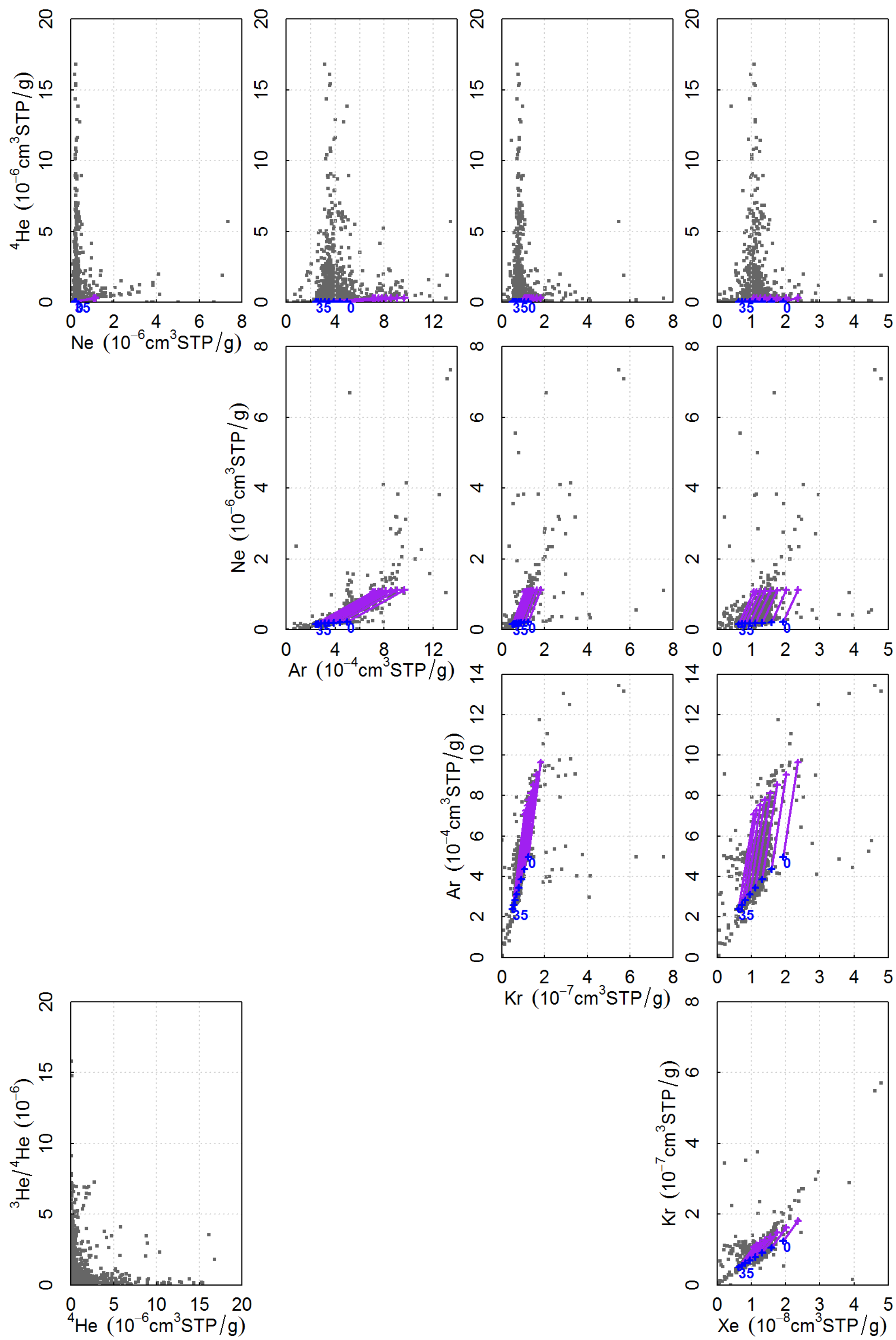

Figure 3: Measured and expected noble gas concentrations for LLNL sample analyses uploaded to the Geotracker GAMA Groundwater Information System. Each plot is one analyte against another analyte for all noble gas analyses uploaded to the database. Measured concentrations are shown in gray; thermodynamic equilibrium concentrations are shown in blue for temperatures from 0-35°C, and the addition of up to of 0.5 cm3 STP/g of unfractionated excess air is shown in purple. See text for further explanation.

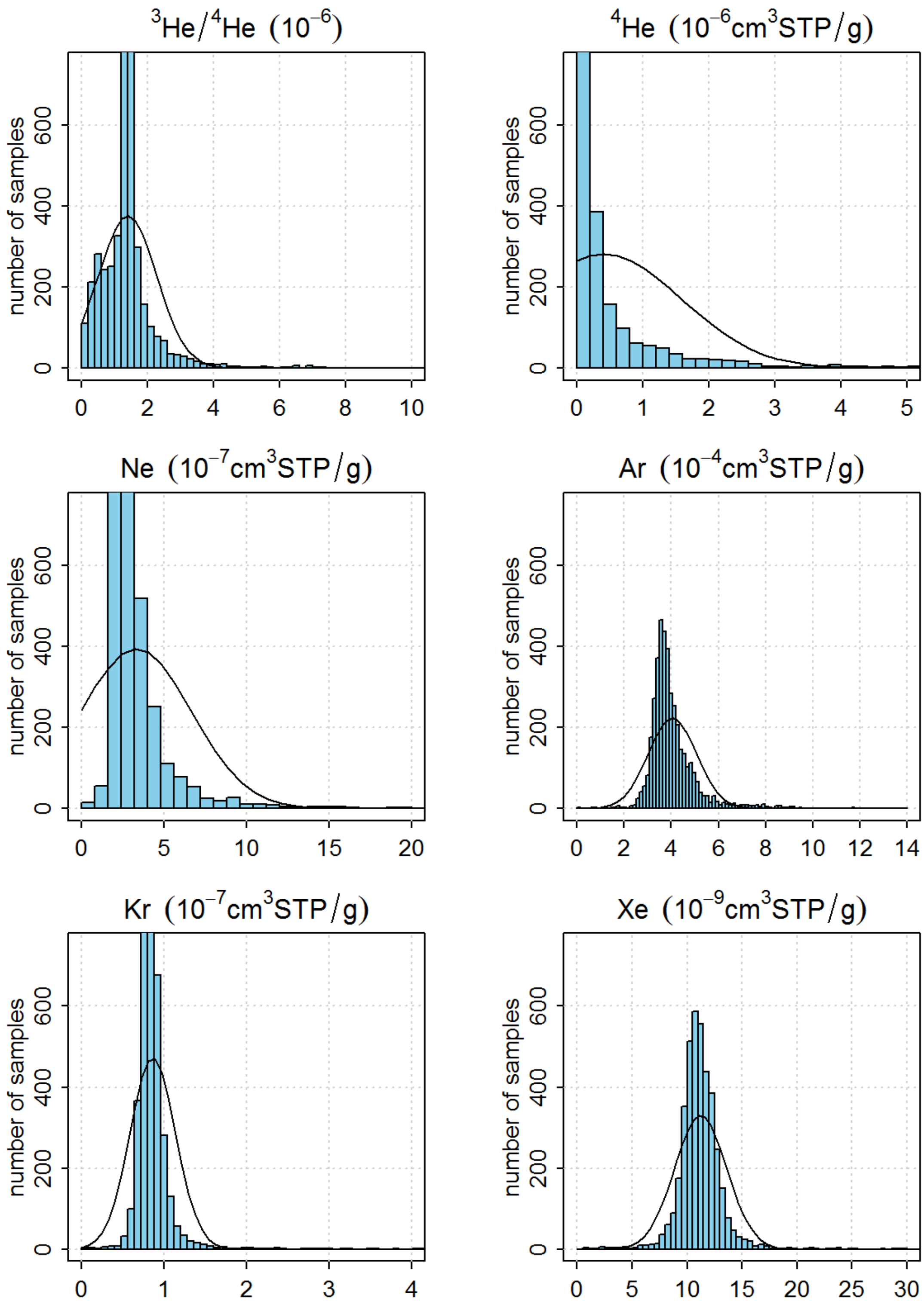

Figure 4: Histograms of noble gas measurements ($^3He/^4He$, ^4He, Ne, Ar, Kr, and Xe) uploaded to Geotracker GAMA Geographical Information System. A normal distribution with the same mean and standard deviation is shown.

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References

Carle, S.F., Moran, J.E., Esser, B.K., 2010. California GAMA Special Study:Groundwater Age Simulation and Deconvolution Methods for Interpretation of ^{3}H-^{3}He Data Lawrence Livermore National Laboratory, LLNL-TR-425141.

Cey, B.D., Hudson, G.B., Moran, J.E., Scanlon, B.R., 2008. Impact of Artificial Recharge on Dissolved Noble Gases in Groundwater in California. Environ. Sci. Technol. 42, 1017-1023.

Cey, B.D., Hudson, G.B., Moran, J.E., Scanlon, B.R., 2009. Evaluation of Noble Gas Recharge Temperatures in a Shallow Unconfined Aquifer. Ground Water 47, 646-659.

Densmore, J.N., Belitz, K., Wright, M.T., Dawson, B., 2005. Evaluation of Volatile Organic Compounds in Two Mojave Desert Basins - Mojave River and Antelope Valley - in San Bernardino, Los Angeles, and Kern Counties, California, June-October 2002. USGS Scientific Investigations Report 2004-5248, p. 40.

Esser, B.K., Beller, H.R., Carle, S.F., Cey, B., Hudson, G.B., Leif, R.N., Letain, T.E., Moody-Bartel, C., Moore, K.B., McNab, W., Moran, J.E., Tompson, A., 2006. Nitrate Biogeochemistry and Reactive Transport in California Groundwater: LDRD Final Report. Lawrence Livermore National Laboratory, p. 209.

Esser, B.K., Beller, H.R., Carle, S.F., Hudson, G.B., Kane, S.R., Leif, R.N., LeTain, T.E., McNab, W.M., Moran, J.E., 2009. California GAMA Program: Impact of dairy operations on groundwater quality. Lawrence Livermore National Laboratory, p. 100.

Hamlin, S.N., Belitz, K., Kraja, S., Dawson, B., 2002. Ground-Water Quality in the Santa Ana Watershed, California: Overview and Data Summary. USGA Water-Resources Investigations Report 02-4243, p. 55.

Hudson, G.B., Moran, J.E., Eaton Gail, F., 2002. Interpretation of Tritium-^{3}Helium Groundwater Ages and Associated Dissolved Noble Gas Results from Public Water Supply Wells in the Los Angeles Physiographic Basin. Lawrence Livermore National Laboratory, UCRL-AR-151447, p. 24.

Marine, I.W., 1979. The use of naturally occurring helium to estimate groundwater velocities for studies of geologic storage of radioactive waste. Water Resources Research 15, 1130-1136.

McNab Jr, W.W., Singleton, M.J., Moran, J.E., Esser, B.K., 2010. California GAMA Special Study: Ion exchange and trace element surface complexation reactions associated with applied recharge of low-TDS water in the San Joaquin Valley, California. Lawrence Livermore National Laboratory LLNL-TR-450392, p. 15.

Moore, K.B., Ekwurzel, B., Esser, B.K., Hudson, G.B., Moran, J.E., 2006. Sources of groundwater nitrate revealed using residence time and isotope methods. Applied Geochemistry 21, 1016-1029.

Moran, J.E., Beller, H., Eaton, G.F., Ekwurzel, B.E., Esser, B.K., Hu, Q., Hudson, G.B., Leif, R., McNab, W., Moody-Bartel, C., 2005a. California GAMA program: Sources and transport of nitrate in groundwater in the Livermore Valley Basin, California. Lawrence Livermore National Laboratory, UCRL-TR-217189, p. 30.

Moran, J.E., Beller, H.R., Leif, R., Singleton, M.J., 2006. California GAMA Program: Fate and transport of wastewater indicators: Results from ambient groundwater and from groundwater directly influenced by wastewater. Lawrence Livermore National Laboratory, UCRL-TR-222531, p. 58.

Moran, J.E., Carle, S.F., Esser, B.K., 2010. California GAMA Special Study: Interpretation of Isotopic Data in the Sonoma Valley, California. Lawrence Livermore National Laboratory LLNL-TR-427958, p. 31.

Moran, J.E., Esser, B.K., Hillegonds, D., Holtz, M., Roberts, S.K., Singleton, M.J., Visser, A., 2011. California GAMA Special Study: Nitrate Fate and Transport in the Salinas Valley. Lawrence Livermore National Laboratory, LLNL-TR-484186.

Moran, J.E., Hudson, G.B., Eaton Gail, F., Leif, R., 2002a. A Contamination Vulnerability Assessment for the Livermore-Amador and Niles Cone Groundwater Basins. Lawrence Livermore National Laboratory, UCRL-AR-148831, p. 25.

Moran, J.E., Hudson, G.B., Eaton, G.F., Leif, R., 2002b. A Contamination Vulnerability Assessment for the Santa Clara and San Mateo County Groundwater Basins. Lawrence Livermore National Laboratory, UCRL-TR-201929, p. 49.

Moran, J.E., Hudson, G.B., Eaton, G.F., Leif, R., 2003. A Contamination Vulnerability Assessment for the Sacramento Area Groundwater Basin. Lawrence Livermore National Laboratory, UCRL-TR-203258, p. 45.

Moran, J.E., Hudson, G.B., Eaton, G.F., Leif, R., 2005b. California GAMA Program: A Contamination Vulnerability Assessment for the Bakersfield Area Lawrence Livermore National Laboratory, UCRL-TR-208179, p. 34.

Moran, J.E., Hudson, G.B., Eaton, G.F., Leif, R., 2005c. Results for the Sacramento Valley and Volcanic Provinces of Northern California. Lawrence Livermore National Laboratory, UCRL-TR-209191, p. 71.

Moran, J.E., McNab, W.W., Esser, B.E., Hudson, G.B., 2005d. California GAMA program: Sources and transport of nitrate in shallow groundwater in the Llagas Basin of Santa Clara County, California. Lawrence Livermore National Laboratory, UCRL-TR-213705, p. 37.

Moran, J.E., Singleton, M.J., McNab, W.M., Leif, R., Esser, B.K., 2009. California GAMA Program: Tracking Water Quality Changes During Groundwater Banking at Two Sites in San Joaquin County. Lawrence Livermore National Laboratory LLNL-TR-412861, p. 79.

Schlosser, P., Stute, M., Sonntag, C., Munnich, K.O., 1989. Tritiogenic ^{3}He in Shallow Groundwater. Earth and Planetary Science Letters 94, 245-256.

Singleton, M.J., Moran, J.E., 2010. Dissolved noble gas and isotopic tracers reveal vulnerability of groundwater in a small, high-elevation catchment to predicted climate changes. Water Resour. Res. 46, W00F06.

Singleton, M.J., Moran, J.E., Esser, B.K., Roberts, S.K., Hillegonds, D.J., 2010a. California GAMA Special Study: An isotopic and dissolved gas investigation of nitrate source and transport to a public supply well in Califonia's Central Valley. Lawrence Livermore National Laboratory LLNL-TR-427957, p. 32.

Singleton, M.J., Roberts, S.K., Esser, B.K., 2010b. California GAMA Domestic Wells: Nitrate and Water Isotopic Data for Tulare County. Lawrence Livermore National Laboratory LLNL-TR-450497-Draft p. 47.

Visser, A., Hillegonds, D., Esser, B.K., 2013a. Collection and Analysis of Groundwater for Determination of Noble Gas Abundance and Helium Isotopic Composition (SOP-NGMS-122 revision 5). Lawrence Livermore National Laboratory NGMS Standard Operating Procedure (LLNL-TM-623335), p. 15.

Visser, A., Hillegonds, D., Esser, B.K., 2013b. Collection and Analysis of Groundwater for Determination of Tritium by Helium-3 Accumulation (SOP-NGMS-121 revision 5). Lawrence Livermore National Laboratory NGMS Standard Operating Procedure (LLNL-TM-623415), p. 9.

Wright, M.T., Belitz, K., Johnson, T., 2004. Assessing the Susceptibility to Contamination of Two Aquifer Systems Used for Public Water Supply in the Modesto and Fresno Metropolitan Areas, California, 2001 and 2002. USGS Scientific Investigations Report 2004–5149, p. 35.

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