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ORIGINAL ARTICLE

Water quality and hydrogeochemistry of a basin and range watershed in a semi-arid region of northern New Mexico

Benjamin Linhoff[1,2] · Patrick Longmire[1,3] · Michael Rearick[1] · Denis McQuillan[4] · George Perkins[1]

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Abstract Hundreds of domestic wells in northern New Mexico, have concentrations of U, As, and NO_3^- that exceed the Environmental Protection Agency's (EPA) maximum contaminant level (MCL) for drinking water consumption. As part of a case study in groundwater quality, we collected groundwater samples from 749 domestic wells throughout the eastern half of the Española Basin. All water samples were analyzed for major ions, trace metals, and alkalinity. Selected samples were also analyzed for stable isotopes of O, H, and N. Of the wells we measured, 15, 173, and 99 had respective NO_3^-, U, and As concentrations that exceeded the EPA's MCL. Total dissolved solids (TDS), U, and HCO_3^- were elevated in the Sangre de Cristo mountain block and around the town of Nambé. Our findings suggest that roll-front U deposits and devitrification of volcanic ash result in elevated U near Nambé, while weathering of granitic rocks accounts for high U in the mountain block. Arsenic concentrations were high in much of the study area with the exception of the Santa Fe metro region and the mountain block. Elevated As concentrations can be explained by devitrification of volcanic ash, anion exchange with clays, and mixing with hydrothermal fluids. In wells with high NO_3^- concentrations, analysis of N isotopes are consistent with contamination from domestic wastewater effluent. Our findings suggest that the geochemistry of the region is largely influenced by local geology while groundwater contamination from domestic water treatment and wastewater effluent is an emerging issue.

Keywords Uranium · Arsenic · Groundwater · Geochemistry · Water quality

✉ Benjamin Linhoff
blinhoff@whoi.edu

[1] Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[2] Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, 266 Woods Hole Road, MS 25, Woods Hole, MA 02543, USA

[3] NM Environment Department, DOE Oversight Bureau, PO Box 1663, MS M894, Los Alamos, NM 87544, USA

[4] New Mexico Environment Department, Harold Runnels Building, 1190 St. Francis Dr. Suite N4050, Santa Fe, NM 87505, USA

Introduction

Hundreds of domestic wells used for drinking water in Española Basin in northern New Mexico have high concentrations of potentially hazardous chemical constituents. This region includes the towns of Nambé, Española, Los Alamos, as well as the state capital city of Santa Fe (Fig. 1). In particular, elevated concentrations of U and As are common. Because domestic wells are not regulated and testing is the responsibility of the well owner, many wells have never been tested for common contaminants such as U, As, F^- or NO_3^-. Furthermore, many residents in this area are unaware of the potential health hazards associated with their well water.

This study investigated in detail the hydrogeochemistry and the geographic distribution of water quality of the eastern side of the Española Basin. Two major water fairs were conducted—the first in 2004 focused on the region around Nambé, NM, and the second in 2009 focused on Santa Fe, NM and the surrounding region. In both of these water fairs, residents served by private water supply wells were encouraged, through a news release, to call the New

Mexico Environment Department (NMED) and request that their well be tested free of cost. During the 2004 Nambé Water Fair, 264 wells were tested while 485 wells were tested during the 2009 water fair, for a total of 749 wells. In addition to the wells, two streams were sampled during the summer of 2009 in the high Sangre de Cristo mountain block at elevations >3000 m.

Geologic Setting

The Española Basin is a west-tilted half graben within the Rio Grande Rift in northern New Mexico (Fig. 1). It is approximately 19 miles wide, bound to the west by the Jemez Mountains and to the east by the Sangre de Cristo Mountains. The western slopes of the Sangre de Cristo Mountains are composed of Precambrian granitic igneous and high-grade metamorphic rocks locally overlain by Pennsylvanian limestone, sandstone and shale. The Miocene Tesuque Formation makes up the bulk of the basin fill, a 2000–2500 m thick sequence of alluvial fan sediments primarily derived by erosion of these lithologies and the Sangre de Cristo Mountains (Kuhle and Smith 2001).

The Tesuque Formation includes alluvial-fluvial and lacustrine deposits with numerous inter bedded ash-fall tuff layers (Cavazza 1986). The overall composition of the Tesuque Formation is fairly similar throughout the central

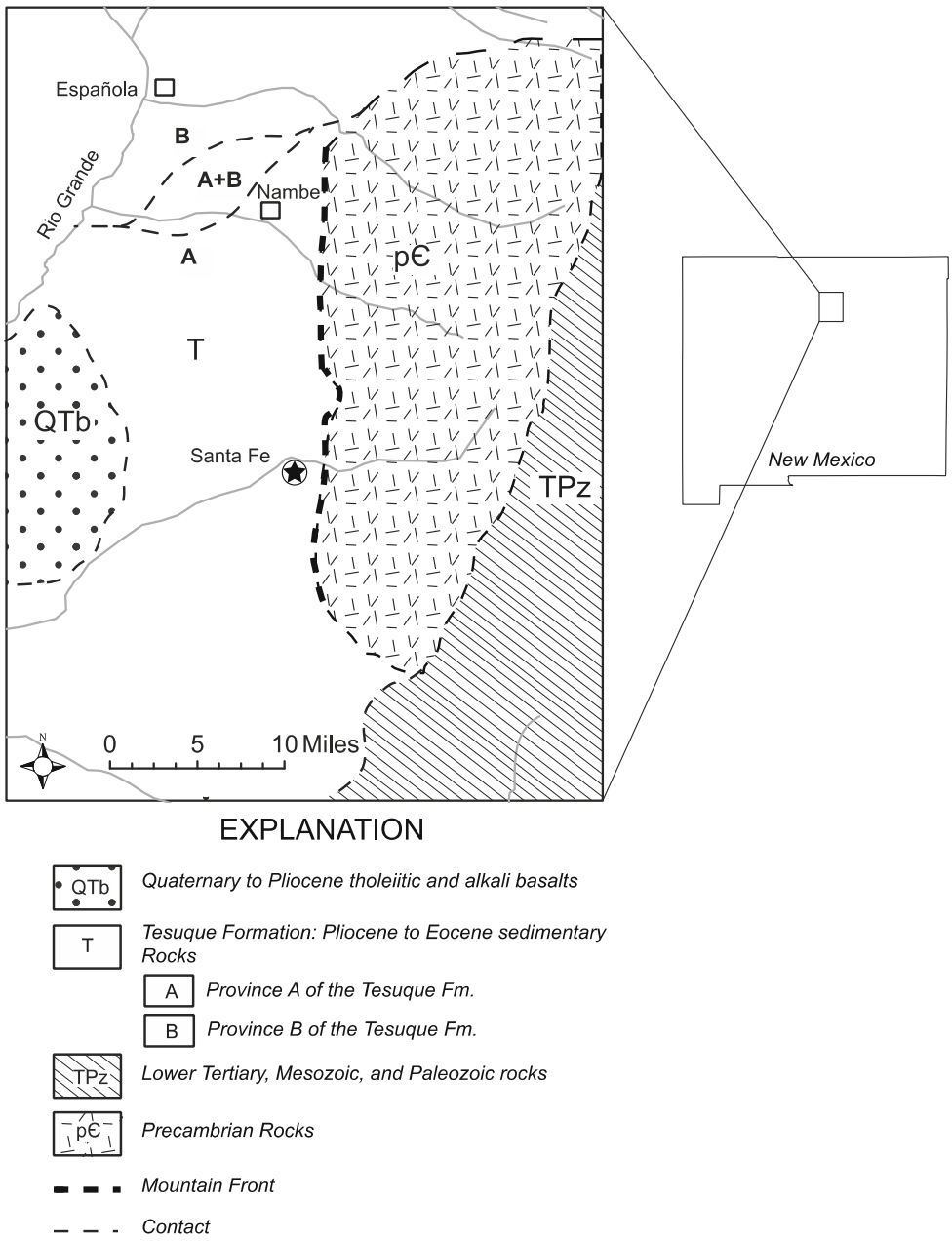

Fig. 1 Map of New Mexico showing the location of the Española Basin and a simplified geology map of Española Basin based on Manning (2009)

Española Basin. However, within the sampled region there are two distinct sedimentary provinces present within the Tesuque Formation: Province A in the eastern, central, and southern portion, and Province B in the northwest and northern portion of the field area, including the Nambé River valley (Fig. 1). Province A is characterized by plutonic and metamorphic detritus derived by erosion of the Precambrian Santa Fe Block of the Sangre de Cristo Mountains. Province B is characterized by minor but distinctive volcaniclastic and sedimentaclastic detritus (Cavazza 1986). The source for Province B is possibly in the area of the Taos Plateau and the Latir volcanic field north of the field area. There is also a narrow intermediate area between Province A and B that represents a hybrid of the two (Fig. 1). In the hills north of the town of Nambé several small, laterally discontinuous, roll-front U deposits have been mapped (Koning 2003; Fig. 1). Quaternary alluvium fills all of the river drainages throughout the field area, including the valleys of the Nambé, Santa Fe, En Medio, and Chimayo rivers.

Hydrogeology of Española Basin

The hydrogeology of the Española Basin is complex, typical of basin range watersheds. In general, groundwater and streams flow from high elevations in the Sangre de Cristo Mountains and the Jemez Mountains to the Rio Grande (Keating et al. 2003; Manning 2009). Streams flowing from the Sangre de Cristo mountain block to the basin are gaining in their upper reaches and are losing in the valley (Manning 2009). Similarly, stream flow is generally perennial in the upper reaches and ephemeral in the lower sections. High evaporation and thick unsaturated zones prevent most direct aquifer recharge from rainfall in the basin. However, seasonal stream flow from snowmelt and sporadic summer monsoons result in infrequent but focused recharge events.

Because of the generally impermeable bedrock and the steep topography in the mountain block, groundwater flow in this region likely follows local topography and discharges to mountain streams. This results in little direct groundwater flow from the Mountain Block Aquifer to the Tesuque Formation Aquifer in the valley below the Sangre de Cristo Mountains. Instead, Keating et al. (2003) suggested that recharge to the basin likely occurs at the mountain block-basin boundary and through basin floor recharge. This is facilitated by the break in topography between the steep mountain block and the basin valley, and the change from low porosity in the Precambrian gneiss and granites in the mountain block to the higher porosity of the Tesuque Formation's sandstones and volcaniclastics (Fig. 1). Major faults at this contact (Koning 2003) may also provide a pathway for recharge to the Tesuque Formation Aquifer allowing dilute mountain stream water to recharge at this point.

The Tesuque Formation is the principal aquifer through much of the studied area, excluding wells located in the Sangre de Cristo mountain block. Groundwater in the Tesuque Formation is typically produced at depths greater than 60 m, although the depth to the water table is highly variable (based on interviews with well owners). Using mass-balance calculations of chloride concentrations in the unsaturated zone, Anderholm (1994) determined that most recharge occurs in and around arroyos while very little to no recharge occurs outside of arroyos in the Española Basin valley. In the same study, analysis of $\delta^{18}O$ and $\delta^{2}H$ isotopes showed that recharge in the arroyos occurs during winter precipitation and spring snowmelt from the Sangre de Cristo Mountains.

Methods

Sampling

The location of each wellhead sampled for this study was recorded using a global positioning system (GPS). Sampling teams endeavored to collect groundwater samples from outdoor frost-free spigots prior to any water treatment devices. In addition to the 749 groundwater samples collected, two streamwater samples were collected from >3000 m in the Sangre de Cristo mountain block during the summer of 2009. Unstable field parameters including pH and specific conductivity were measured in situ through probe methods. Water samples were collected in 250 mL low density polyethylene (LDPE) bottles (Nalgene Nunc International Inc.) and were refrigerated at 4 °C prior to chemical analysis at Los Alamos National Laboratory (LANL). ArcGIS software (version 9.0) was used to plot all sample locations and resolve spatial trends in groundwater chemistry. ArcGIS was further used to differentiate regions of elevated concentrations of all metals and anions and correlate water chemistry to local geology.

Statistical analyses

Statistical analyses were completed using the software package R (The R Project for Statistical Computing http://www.r-project.org). Principle component analysis (PCA) was performed to reduce the dimensionality of the data set using the method described by Husson et al. (2010). Prior to PCA, all data were scaled to unit variance. Spearman's rank correlation coefficient (ρ) was calculated for 21 parameters to help determine the sources of ions and their relationships (Table 2). Spearman's rank correlation coefficient does not require data to be normally distributed as

does the more commonly used Pearson's r (Helsel and Hirsch, 2002), and also allows for multiple detection limits (Helsel et al. 2005). Prior to this calculation, non-detects were changed to equal the detection limit.

Chemical analyses

Major cations and trace metals were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) utilizing EPA methods 200.7 and 200.8. The specific systems utilized were a Perkin Elmer Optima 2100 DV and an Elan 6100. Ultra high-purity nitric acid (Fisher Trace Metal Grade) was used in sample and calibration preparation prior to sample analysis. Internal standards (Sc, Ge, Bi, and In) were added to both samples and standards to correct for matrix effects which can result in differing sample introduction rates. Some samples were diluted prior to analysis to minimize matrix effects as well as to allow the analytes of interest to remain within the linear dynamic range of the calibration. Standard Reference Material (SRM) 1643e Trace Elements in Water was used to check the accuracy of the multi-element calibrations. Typical ICP parameters were: 1300 W forward power, 15 mL/min cooling gas, 0.2 mL/min auxiliary flow; 0.8 mL/min nebulizer flow; and 1.5 mL/min sample uptake. Inorganic anion samples were analyzed by ion chromatography (IC) following EPA method 300 on a Dionex DX-600 system. Alkalinity measurements were made following EPA method 310.1 which is a titrimetric analysis with an end-point of pH = 4.5. Charge balance calculations were performed for all waters. Cation and anion analyses were repeated for waters with charge balance errors greater than ten percent though greater than 90 % of waters had errors less than five percent.

Fifty groundwater samples from throughout the field area as well as the two stream water samples from Sangre de Cristo mountain block were selected for $\delta^{18}O$ and $\delta^{2}H$ measurements. Stable O and H isotopes were measured in continuous flow mode using a GV Instruments Isoprime isotope ratio mass spectrometer (GV Instruments, Manchester, UK). All stable isotope ratios are reported in the standard δ-notation as the per mil deviation (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}O$ and $\delta^{2}H$. $\delta^{18}O$ and $\delta^{2}H$ values were calibrated using in-house standards calibrated to IAEA standards V-SMOW, SLAP and GISP. $\delta^{18}O$ was measured through analysis of CO_2 equilibrated with 400 µl water on a GV Instruments Multiflow peripheral instrument in an adaptation of Craig (1957). $\delta^{2}H$ was measured using chromium reduction from water using a GV Instruments Eurovector Elemental Analyzer. Analytical linearity was monitored and corrected for by analyzing standards after every five samples for both methods. Analytical precision on an in-house standard was <±0.16 ‰ for $\delta^{18}O$ and <±0.99 ‰ on replicate analyses for $\delta^{2}H$.

Twenty-one groundwater samples were analyzed for aqueous NO_3^- concentrations as well as N, and O isotope ratios (in NO_3^-) using a modified version of the microbial denitrification technique described by Casciotti et al. (2002) and Sigman et al. (2001) using *Pseudomonas aurofaciens* (ATCC 13985). Stable N and O isotope compositions were measured for N_2O in continuous flow mode using a GV Instruments Isoprime isotope ratio mass spectrometer (GV Instruments, Manchester, UK). Analytical linearity was monitored and corrected for by analyzing standards after every five samples. An analysis blank, consisting of the identical tryptic soy broth and NaOH solution used for samples was used in the blank correction procedure. All stable isotope ratios are reported in the standard δ -notation as the per mil deviation (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) for $\delta^{18}O$ and atmospheric N_2 for $\delta^{15}N$. A calibration curve for $\delta^{15}N$ was constructed using analyses of IAEA-NO-3 and USGS32 ($\delta^{15}N_{air}$ = 4.7 and 180 ‰ vs. atmospheric N_2, respectively). $\delta^{18}O$ values were calibrated using analyses of IAEA-NO-3 and USGS34 ($\delta^{18}O$ = 25.6 and −30.9 ‰ vs. VSMOW, respectively). Analytical precision of ±0.25 ‰ for $\delta^{15}N$ and ±0.90 ‰ for $\delta^{18}O$ (in NO_3^-) were routinely measured.

Results

Basic statistical analyses including mean, median, and standard deviation for 21 physical and chemical parameters are listed in Table 1. While not administered to the private domestic supply wells used for this study, both the EPA and the New Mexico Water Quality Control Commission (WQCC) have established enforceable numerical standards to protect human health, and are listed in Table 1 to assess the suitability of the well water for domestic supply. With regard to constituents that create aesthetic nuisances, but do not threaten human health, WQCC standards are enforceable while EPA standards are not.

pH varied between 5.8 and 9.6 while the majority of groundwaters were slightly alkaline (median pH = 7.8; Tables 1). The spatial distributions of total dissolved solids (TDS), As, and U are shown in Fig. 2. Constituents generally congruent with the spatial distribution of TDS were alkalinity, Cl^-, Na, and Ca. The majority of groundwaters with U concentrations over the EPA's MCL (30 µg/L) were within Nambé and the Mountain Block Aquifer (Fig. 2). In the town of Nambé, mean U concentrations were over 100 µg/L with one sample exceeding 1800 µg/L.

Table 1 Summary of basic statistics of each parameter

Parameter	Units	*n*	Mean	Median	std dev	Range	EPA MCL	WQCC Standard
Alkalinity	meq/L	749	202	181	107	15–1953	–	–
As	μg/L	742	5.5	2.9	7.8	<0.2–89.5	10	–
B	μg/L	738	98	58	140	<2–1822	–	–
Ba	μg/L	730	120	100	110	<1–1420	2	–
Br	mg/L	686	0.2	0.1	0.3	<0.01–2.47	–	–
Ca	mg/L	749	57	44	55	0.01–649	–	–
Cl	mg/L	749	36	14	114	0.8–1639	–	250
F	mg/L	746	0.7	0.5	0.6	<0.01–6.5	4	2.0
Fe	μg/L	320	292	34	1820	<10–26000	–	0.3
HCO_3	mg/L	749	236	207	128	18.3–2383	–	–
K	mg/L	749	8	2	40	0.1–532	–	–
Li	μg/L	749	57	25	97	1–915	–	–
Mg	mg/L	735	11	6	16	<0.01–164	–	–
Mn	μg/L	224	44	5	149	<1–1394	–	0.05
Mo	μg/L	544	5	2	12	<1–136	–	–
Na	mg/L	749	64	28	163	0.4–3154	–	–
NO_2 (as NO_2)	mg/L	10	0.3	0.1	0.4	<0.01–1.06	3.3	–
NO_3 (as NO_3)	mg/L	639	9	6	13	<0.01–191	44	–
pH		749	7.9	7.8	0.3	5.8–9.6	–	6.5–8.5
PO_4	mg/L	151	0.15	0.03	1.03	<0.01–12.7	–	–
SiO_2	mg/L	749	25	23	11	1.0–94	–	–
SO_4	mg/L	749	77	30	299	0.5–7050	–	250
Sr	mg/L	744	0.6	0.4	0.9	<0.001–10	–	–
U	μg/L	688	44	6	131	<0.2–1820	30	–
V	μg/L	701	11	6	22	<1–373	–	–
TDS	mg/L	749	525	402	614	7–11351	–	500
Cl/Br	mg/L	686	218	123	429	12–9397	–	–
Na/Ca	mol	749	14	1	82	0.1–1363	–	–

Fluoride concentrations varied between <1 and 6.5 mg/L (median = 0.5 mg/L). The majority of groundwaters with As and F^- concentrations over the EPA's MCL (As = 10 μg/L; F^- = 4 mg/L) were in the Tesuque Formation including the southwest, west and northern parts of the field area (Fig. 2). Concentrations of other potentially hazardous constituents including Be, Cd, Cr, Pb, Hg, Ra, and Tl were not detected in any well at concentrations exceeding the limits set by the EPA or WQCC. There was significant spatial variation in NO_3^- concentrations in groundwaters throughout the study area. Nitrate concentrations varied from <0.01 to 191 mg/L (as NO_3; Table 1), and 15 wells had NO_3^- concentrations greater than the EPA MCL of 44 mg/L (as NO_3).

$\delta^{15}N$ in NO_3^- was positive and correlated to $\delta^{18}O$ in NO_3^- ($\rho = 0.64$, $p < 0.001$; Fig. 3) while $\delta^{15}N$ was not correlated to NO_3^- concentrations (Fig. 3). The local meteoric water line from samples selected for $\delta^{18}O$ and δ^2H analysis was $\delta^2H = 7.714\ \delta^{18}O + 0.95$ (Fig. 3). This is offset from the global meteoric water line which is $\delta^2H = 8\ \delta^{18}O + 10$ (Gat 1996). Heavier $\delta^{18}O$ and $\delta\ ^2H$ values were generally found in the mountain block at higher elevations, while the Tesuque Formation waters showed more variation (Fig. 3). Mean $\delta^{18}O$ and δ^2H values in the Tesuque Formation Aquifer were −11.1 and −84.2 ‰ respectively while in the Sangre de Cristo mountain block mean $\delta^{18}O$ and δ^2H values were −10.6 and −81.2 ‰ respectively. Two stream water samples taken in the Sangre de Cristo Mountains had mean $\delta^{18}O$ and δ^2H values of −12.2 and −89.3 ‰ respectively.

Some residents have installed anion exchange and reverse osmosis systems to decrease U and other hazardous constituents in their drinking water. Water softeners have also been installed in many residences through the region. Analytical results suggested that 15 groundwater samples had undergone either softening or reverse osmosis treatment prior to sample collection, and this was confirmed through interviews with the well users. Because test results

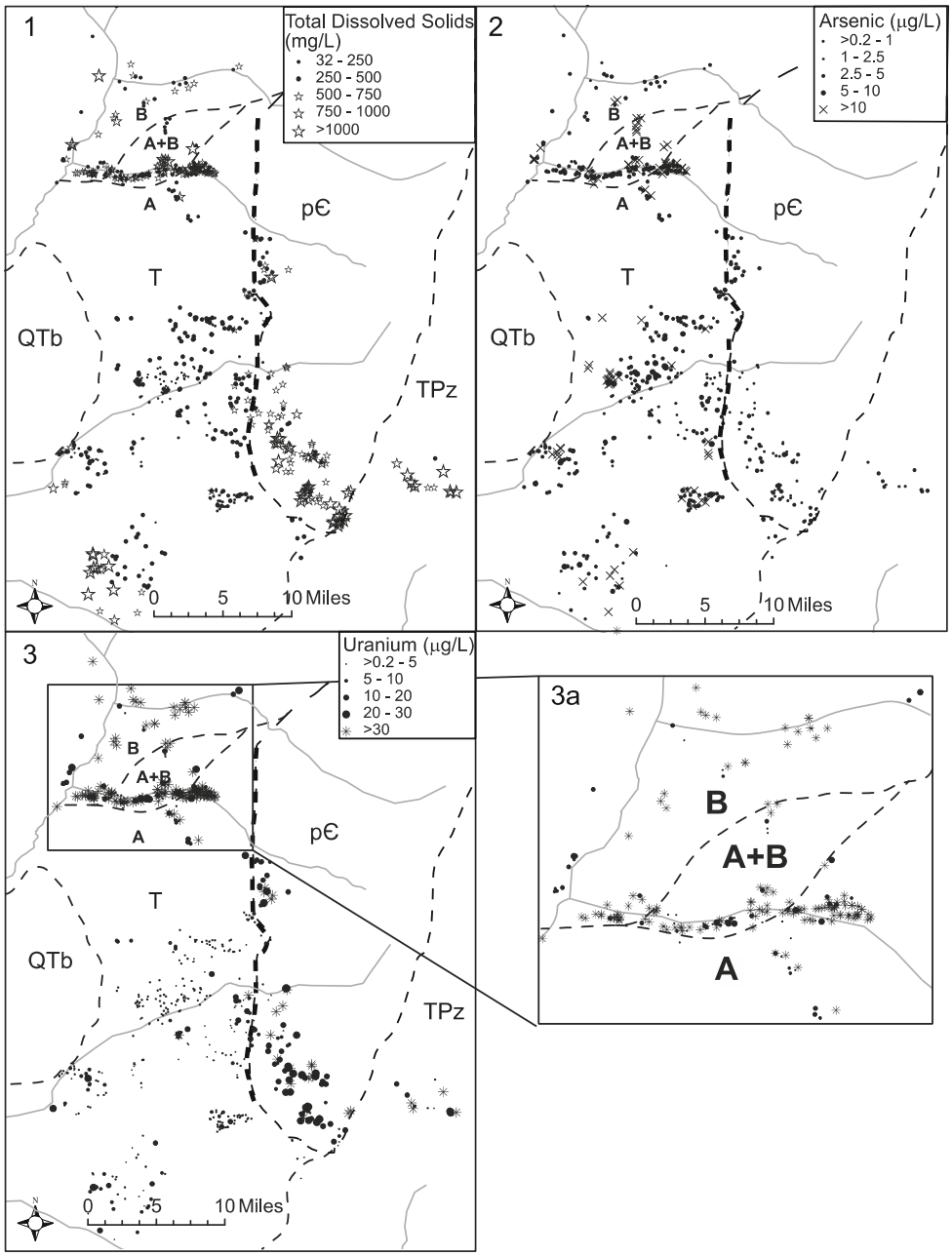

Fig. 2 Geological maps of Española Basin showing distribution of concentrations of TDS (map 1), As (map 2) and U (map 3 and 3a) in groundwaters through the Española Basin

for these samples are not representative of the natural chemical quality of the aquifer, they were not used for the assessment of groundwater quality and are not discussed here.

Thirty-five percent of the wells tested contained SO_4^{2-}, Cl^-, and/or TDS at concentrations exceeding limits set by the WQCC to protect against aesthetic problems, but did not contain constituents at concentrations posing health hazards. Many wells, particularly in the Canoncito-Glorieta area and along Highway 14 (the region southeast of Santa Fe), contained high concentrations of SO_4^{2-} and/or TDS. Cl/Br ratios were positively correlated to increasing Cl^- in the mountain block and in the Nambé region (Fig. 7). There was no correlation found anywhere between the Cl/Br ratio and TDS, U, NO_3^-, K, or As.

Results of the PCA analysis are presented graphically in Fig. 4 where the length of the arrow represents the relative importance of the associated parameter in determining the distribution of samples. Based on this analysis, Dimension One (28 % of data variability) is most significantly correlated to TDS, Na and Mg; Dimension Two (14 % of data variability) is most significantly correlated to As, F and pH; and Dimension Three is most significantly correlated to U and SiO_2 (8 % of data variability). Results from Spearman rank correlation coefficient calculations are summarized in Table 2. Correlations shown in bold in Table 2 have p values <0.001.

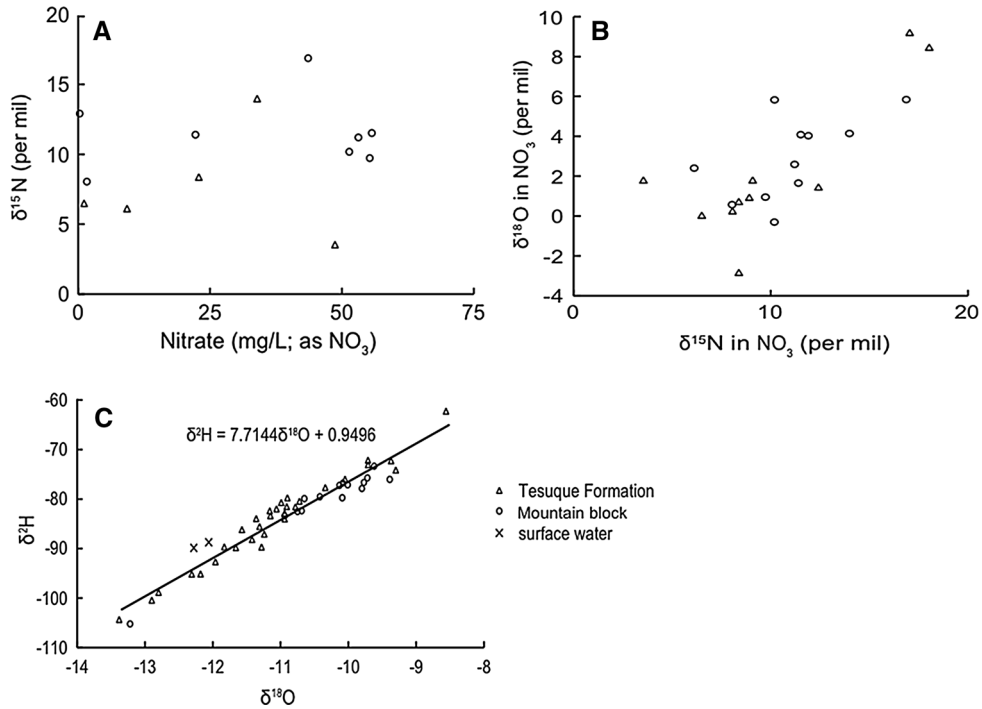

Fig. 3 Bivariate plots showing $\delta^{15}N$ vs. NO_3^- (**a**), $\delta^{18}O$ in NO_3^- vs. $\delta^{15}N$ in NO_3^- (**b**), and the local meteoric water line (**c**)

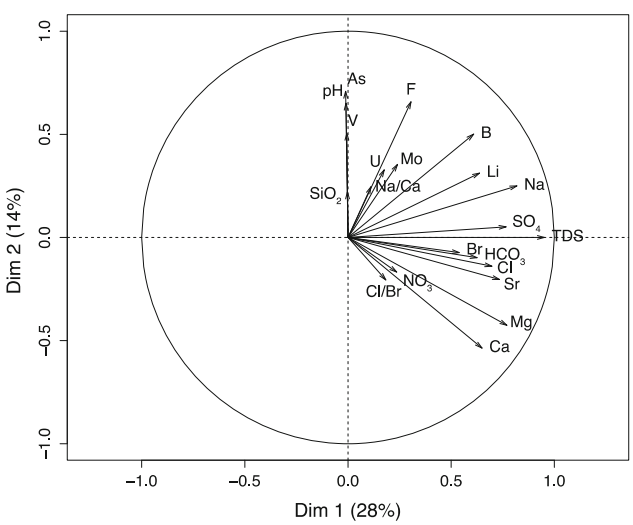

Fig. 4 Graphical representation of the principle component analysis (PAC) of chemical constituents in groundwater. The two dimensions of the PCA plot represent 42 % of the data variability; the first dimension contributes 28 % and the second contributes 14 %

Discussion

Mountain block aquifer

Wells in the Sangre de Cristo mountain block are set in highly fractured gneiss and granite in the Precambrian Santa Fe Block of the Sangre de Cristo Mountains (Fig. 1). Groundwater in this region is characterized by elevated HCO_3^-, Ca, TDS, U, heavier $\delta^{18}O$ and $\delta^{2}H$, and is typically Ca + Mg : HCO_3^- type water (Figs. 2, 5). The mean molar ratio of Ca : HCO_3^- of groundwaters in the mountain block was 0.5 suggesting dissolution of carbonate minerals is a major factor controlling of the region's groundwater chemistry (Stumm and Morgan 2012). The carbonate source could be Pennsylvanian limestone, which stratigraphically overlays the Precambrian granites and gneisses in the mountain block (Koning 2003). However, this unit is absent in the Española Basin except for a small local outcrop east of the Santa Fe metro area (Koning 2003). A second source of carbonate weathering may be trace calcite veins within the granitic bedrock similar to other watersheds (Blum et al. 1998).

Tesuque formation aquifer

All wells sampled west of the Sangre de Cristo mountain block are situated in the Tesuque Formation Aquifer or in Quaternary alluvial fill overlaying the Tesuque Formation (Fig. 1). This region includes groundwaters in the Santa Fe metro area and the region surrounding the town of Nambé. Wells in the Tesuque Formation Aquifer had varying TDS and many of the wells had As concentrations over the EPA MCL (>10 μg/L; Fig. 2). The age of groundwaters in the Tesuque Formation increases moving away from the mountain block and many are likely Pliestocene in age (>11,550 BP; Manning 2009). In general, TDS and As concentrations increased with distance from the Sangre de Cristo Mountains (Fig. 2). In contrast to the Mountain Block Aquifer, within the Tesuque Formation Aquifer

groundwaters were mixed Ca + Na : HCO_3^- and Na + K : HCO_3^- type groundwaters (Fig. 5).

Santa Fe metro area

Wells within the Santa Fe metro area are set in Quaternary alluvium and the Upper Tesuque Aquifer; groundwater depth varies from approximately 15-60 m in the Santa Fe metro area (Anderhold 1994). The groundwater in this area is younger than the surrounding Tesuque Formation Aquifer (Manning 2009), and generally has lower TDS with no chemical constituents exceeding an EPA MCL (Fig. 2). We offer several explanations for the more dilute groundwaters in the metro area. First, stream loss from the Santa Fe River may account for the more dilute wells surrounding the river. However, because the Santa Fe River is a major source for drinking water for the city of Santa Fe, release of the river is highly regulated with above ground flow occurring only in the spring. Therefore, the Santa Fe River's affect on nearby groundwater may be less pronounced presently than in historical times. Like most cities, recharge to the underlying aquifer is likely augmented by leaking municipal water systems (Lerner 2002). This additional recharge within the city of Santa Fe may account for the generally more dilute groundwaters in this region.

Nambé region

Groundwaters in the northern portion of the field area near the town of Nambé are geochemically distinct from waters in the rest of the Tesuque Formation Aquifer. Most of these groundwaters are situated in Province B of the Tesuque Formation and as such are influenced by a higher percentage of volcaniclastics than groundwaters in the rest of the Española Basin (Fig. 1). Groundwaters in the Nambé region generally had significantly elevated concentrations of U, As, TDS and HCO_3^- and most groundwaters were Na + K:HCO_3^- type waters. Notably, the highest concentrations of U and As observed in this study were found in this area with median U concentration of 60 μg/L in the town of Nambé. Based on interviews with well owners regarding the depth of their wells, the highest concentrations of U in this region were found in shallow wells in the Quaternary alluvium or in the Upper Tesuque Formation while deeper wells were generally more dilute. Uranium roll-front ore deposits in the hills north of the town of Nambé and volcaniclastics of Province B of the Tesuque Formation (Cavazza 1986) are potential sources for the high U in the region's groundwater. Furthermore, the high concentration of HCO_3^- found in this region likely compels the formation of stable uranyl-carbonato complexes that increase U mobility (Langmuir 1978).

Geochemistry

The vast majority of groundwaters contained redox sensitive constituents such as U, SO_4^{2-} and NO_3^- while less than half of the sampled waters had detectable amounts of Fe and Mn. Median Fe and Mn concentrations were low (34 and 5 μg/L respectively) and only 10 of the 749 groundwater samples had detectable levels of NO_2^- (Table 1). Consequently, we interpret the majority of groundwaters sampled for this study as being oxic.

Waters with high concentrations of F^- typically had low concentrations of Ca suggesting transport through cation exchanging clays (Chae et al. 2006). In support of this conclusion, the PCA analysis (Fig. 4) shows F^- plots on the opposite side of Ca and there is a positive relationship between the ratio of Na/Ca and F^- (Fig. 4). According to spearman's rank correlation coefficients, F^- is most closely related to B ($\rho = 0.61$), As ($\rho = 0.44$), and pH ($\rho = 0.40$).

The source of SO_4^{2-} was explored in Fig. 6 by comparing the elemental ratio of SO_4/Cl with TDS. Groundwaters with a high SO_4/Cl ratio likely have a gypsum source while groundwaters with a low SO_4/Cl ratio likely have a brine water source. In this study, both high and low SO_4/Cl ratios were observed with increasing TDS (Fig. 6). While gypsum may be a source of some SO_4^{2-} in this region, domestic wastewater and water treatment effluent likely explains the low SO_4/Cl ratios in many groundwaters.

The most important factors that control As mobility are redox conditions and pH (Wang et al. 2009). The basic pH of waters in oxic conditions promotes the desorption of As(V) and other oxyanion-forming elements from metal oxides because of the changing surface charge as pH increases (Wang et al. 2009). In this study, high As concentrations were related to basic pH (Figs. 4, 7) and may be sourced from the volcanic material found in the Tesuque Formation (Cavazza 1986). Interestingly, elevated concentrations of As were found at a similar distance from the Sangre de Cristo mountain block in the Tesuque Formation Aquifer (Fig. 2). This trend may suggest these groundwaters are of similar age or set in a similar lithology. Arsenic concentrations are most closely related to V ($\rho = 0.54$), F ($\rho = 0.44$), and pH ($\rho = 0.39$), conditions typical of watersheds influenced by volcanic material (Scanlon et al. 2009).

Uranium concentrations in the Tesuque Formation Aquifer (outside the region surrounding the town of Nambé) were typically low. Most groundwaters in the

Table 2 Results of Spearman's rank correlation coefficient (ρ)

	As	B	Br	Ca	Cl	F	HCO_3	Li	Mg	Mo	Na	NO_3^-	pH	SiO_2	SO_4	Sr	U	V	TDS	Cl/Br	Na/Ca
As	1	**0.24**	−0.04	**−0.27**	−0.04	**0.44**	−0.07	0.12	**−0.19**	**0.16**	0.09	−0.07	**0.39**	**0.14**	−0.02	−0.11	**0.15**	**0.54**	−0.03	−0.09	0.10
B	**0.24**	1	0.34	0.08	**0.33**	**0.61**	**0.30**	**0.42**	**0.25**	**0.31**	**0.59**	0.02	**0.24**	0.02	**0.47**	**0.35**	0.12	**0.24**	**0.54**	0.03	0.12
Br	−0.04	**0.34**	1	**0.44**	**0.50**	**0.27**	**0.39**	**0.18**	**0.52**	0.12	**0.32**	**0.28**	−0.10	−0.11	**0.32**	**0.24**	−0.02	0.00	**0.45**	−0.09	0.07
Ca	**−0.27**	0.08	**0.44**	1	**0.50**	−0.07	**0.41**	**0.18**	**0.83**	−0.01	**0.21**	**0.30**	**−0.27**	−0.01	**0.42**	**0.69**	0.04	−0.17	**0.55**	**0.22**	−0.15
Cl	−0.04	**0.33**	**0.50**	**0.50**	1	0.11	**0.48**	**0.29**	**0.63**	0.09	**0.56**	**0.23**	−0.08	−0.05	**0.31**	**0.35**	0.01	−0.02	**0.67**	**0.24**	**0.28**
F	**0.44**	0.61	**0.27**	−0.07	0.11	1	0.07	**0.21**	0.06	**0.24**	**0.29**	−0.07	**0.40**	0.12	**0.22**	0.10	0.13	**0.29**	**0.23**	−0.10	**0.16**
HCO_3	−0.07	**0.30**	**0.39**	**0.41**	**0.48**	0.07	1	**0.40**	**0.56**	0.08	**0.43**	**0.24**	−0.02	0.10	**0.16**	**0.35**	**0.17**	0.01	**0.57**	0.23	0.08
Li	**0.12**	**0.42**	**0.18**	**0.18**	**0.29**	**0.21**	**0.40**	1	**0.25**	**0.43**	**0.61**	**0.21**	**0.21**	0.17	**0.49**	**0.44**	**0.48**	−0.03	**0.58**	0.07	0.00
Mg	**−0.19**	**0.25**	**0.52**	**0.83**	**0.63**	0.06	**0.56**	**0.25**	1	0.01	**0.40**	**0.27**	**−0.24**	**−0.14**	**0.47**	**0.70**	−0.05	−0.07	**0.67**	0.22	−0.08
Mo	**0.16**	**0.31**	0.12	−0.01	0.09	**0.24**	0.08	**0.43**	0.01	1	**0.17**	**0.24**	0.14	0.04	0.13	0.13	**0.40**	0.04	**0.15**	0.04	0.01
Na	0.09	**0.59**	**0.32**	**0.21**	**0.56**	**0.29**	**0.43**	**0.61**	**0.40**	0.17	1	0.02	0.11	−0.02	**0.83**	**0.45**	**0.16**	0.06	**0.91**	0.09	**0.20**
NO_3	−0.07	0.02	**0.28**	**0.30**	**0.23**	−0.07	**0.24**	**0.21**	**0.27**	**0.24**	0.02	1	−0.05	0.03	0.01	0.14	0.09	−0.05	**0.15**	**0.15**	−0.02
pH	**0.39**	**0.24**	−0.10	**−0.27**	−0.08	**0.40**	−0.02	**0.21**	**−0.24**	0.14	0.11	−0.05	1	0.13	−0.03	−0.10	**0.18**	**0.29**	−0.02	−0.07	0.11
SiO_2	**0.14**	0.02	−0.11	−0.01	−0.05	0.12	0.10	**0.17**	−0.14	0.04	−0.02	0.03	0.13	1	−0.10	0.03	**0.35**	−0.07	−0.02	−0.01	−0.10
SO_4	−0.02	**0.47**	**0.32**	**0.42**	**0.31**	**0.22**	**0.16**	**0.49**	**0.47**	0.13	**0.83**	0.01	−0.03	−0.10	1	**0.61**	0.08	−0.03	**0.86**	0.05	0.06
Sr	−0.11	**0.35**	**0.24**	**0.69**	**0.35**	0.10	**0.35**	**0.44**	**0.70**	0.13	**0.45**	0.14	−0.10	0.03	**0.61**	1	0.11	−0.08	**0.65**	0.13	−0.07
U	**0.15**	0.12	−0.02	0.04	0.01	0.13	**0.17**	**0.48**	−0.05	**0.40**	**0.16**	0.09	**0.18**	**0.35**	0.08	0.11	1	0.00	0.14	0.01	−0.02
V	**0.54**	**0.24**	0.00	**−0.17**	−0.02	**0.29**	0.01	−0.03	−0.07	0.04	0.06	−0.05	**0.29**	−0.07	−0.03	−0.08	0.00	1	−0.02	−0.06	0.14
TDS	−0.03	**0.54**	**0.45**	**0.55**	**0.67**	**0.23**	**0.57**	**0.58**	**0.67**	0.15	**0.91**	**0.15**	−0.02	−0.02	**0.86**	**0.65**	0.14	−0.02	1	**0.16**	0.17
Cl/Br	−0.09	0.03	−0.09	**0.22**	**0.24**	−0.10	**0.23**	0.07	**0.22**	0.04	0.09	**0.15**	−0.07	−0.01	0.05	0.13	0.01	−0.06	**0.16**	1	−0.04
Na/Ca	0.10	0.12	0.07	**−0.15**	**0.28**	**0.16**	0.08	0.00	−0.08	0.01	**0.20**	−0.02	0.11	−0.10	0.06	−0.07	−0.02	**0.14**	**0.17**	−0.04	1

Bold values represent correlations with $p < 0.001$

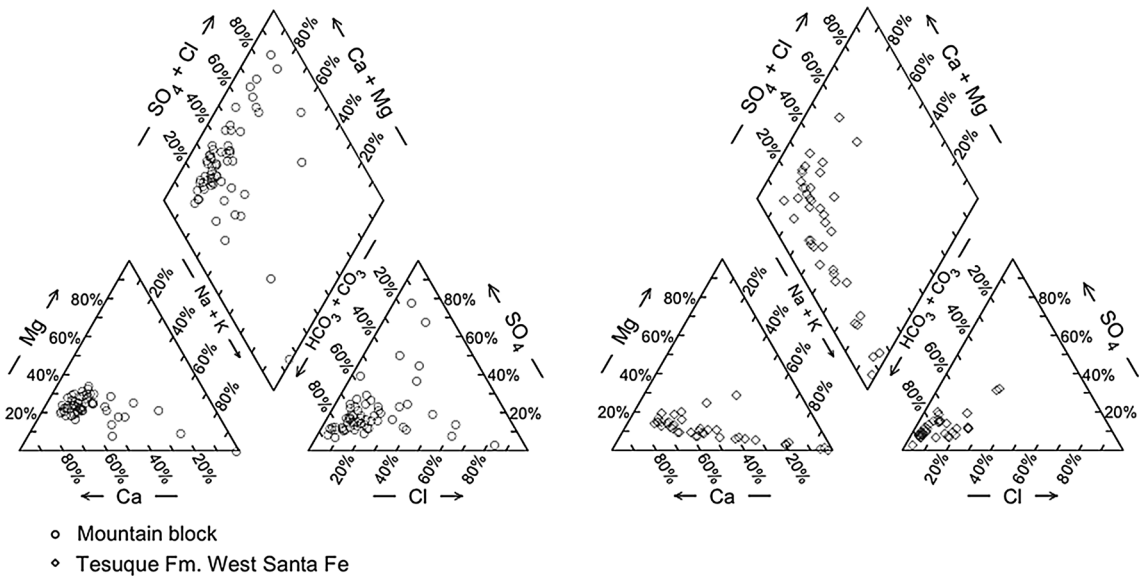

Fig. 5 Piper Diagrams of showing groundwaters in the Sangre de Cristo mountain block and representative wells from the Tesuque Formation west of Santa Fe

Tesuque Formation Aquifer (excluding the region around Nambé) were Ca + Na:HCO_3^- type waters. Uranium in the mountain block is most likely derived from relatively U-rich granitic rocks in the Santa Fe block of the Sangre de Cristo Mountains. The high concentrations of U in the groundwater can be explained by HCO_3^- and U forming highly stable uranyl-carbonato complexes allowing U to behave conservatively in the aquifer (Langmuir 1978). While there was a significant correlation between U and HCO_3^- in the Mountain Block Aquifer (Fig. 7), the spearman's correlation coeffeficient between U and HCO_3^- of all groundwaters sampled was only 0.17 (Table 2). Of all groundwaters sampled, U was most strongly correlated to Li ($\rho = 0.48$), Mo ($\rho = 0.40$) and SiO_2 ($\rho = 0.35$). These correlations suggest potential influence from hydrothermal waters similar to observations by Von Strandmann et al. (2006). High concentrations of HCO_3^- in the Mountain Block Aquifer and the aquifer's granitic composition makes groundwaters in this region especially prone to elevated U concentrations.

Interpretations of $\delta^{18}O$ and δ^2H

Lighter $\delta^{18}O$ and δ^2H values in water are typically associated with recharge at higher elevations, colder climates and precipitation farther from the ocean (Gat 1996). In contrast, heavier $\delta^{18}O$ and δ^2H values are consistent with warmer climates, precipitation at lower elevation, and recharge closer to the ocean. However in our study area, wells in the Tesuque Formation Aquifer have both the isotopically lightest and heaviest $\delta^{18}O$ and δ^2H values, while wells in the Sangre de Cristo mountain block generally have heavier $\delta^{18}O$ and δ^2H values (Fig. 3c).

In the Tesuque Formation Aquifer, Manning (2009) found a relationship between lighter $\delta^{18}O$ and δ^2H values and increasing depth. Furthermore, deeper groundwaters were correlated to low ^{14}C activities suggesting many deep groundwaters were recharged during the Pleistocene (Manning 2009). While we were unable to obtain reliable depth information from the domestic wells and did not attempt to date the groundwater, it is likely that many of the lighter $\delta^{18}O$ and δ^2H values in the Tesuque Formation Aquifer were from Pleistocene age groundwater. Streams originating high in the Sangre de Cristo Mountains and recharging through the numerous arroyos in the valley (or at the mountain block-valley contact) are another potential source of isotopically light water to the Tesuque Formation Aquifer. However, the two surface water samples from the high Sangre de Cristo Mountains were not the isotopcially lightest samples analyzed (Fig. 3c), suggesting modern day recharge from higher elevations is not the source for the lightest $\delta^{18}O$ and δ^2H groundwaters. However, as these stream samples were collected in the summer, $\delta^{18}O$ and δ^2H values we measured may not be representative of values measured during other times of the year (Wang et al. 2014).

Relatively heavier $\delta^{18}O$ and δ^2H values in the Sangre de Cristo mountain block could be caused by either modern day recharge or evaporation of surface waters before recharge. Substantial evaporation before recharge in the mountain block seems unlikely, as the area is generally tree

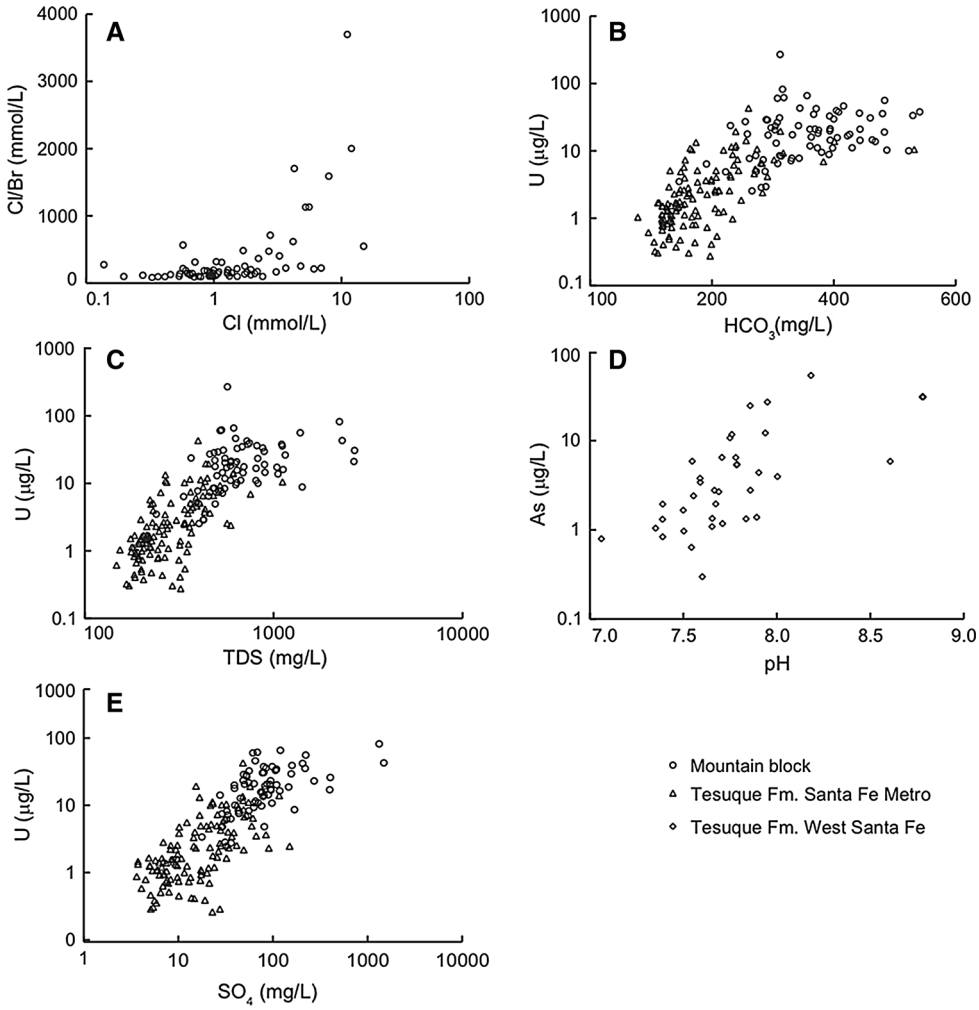

Fig. 6 Bivariant plots of waters in the Sangre de Cristo mountain block and wells in the Tesuque Formation in the Santa Fe metro area and the region west of Santa Fe. Plot A shows Cl/Br ratios vs. Cl concentrations in the mountain block. Plot B shows U vs. HCO_3^- in the mountain block and the Tesuque Formation. Plot C shows U vs. TDS in the mountain block and Tesuque Formation. Plot D shows As vs. pH in the region west of the Santa Fe metro area in the Tesuque Formation. Plot E shows the correlation between U and SO_4^- in the mountain block and the Tesuque Formation Aquifer

covered and most of the domestic wells are on steep slopes that are not conducive to extensive evaporation.

Anthropogenic Impacts

Disposal of brine waste from domestic water treatment is an emerging issue in the Española Basin. Wastewater from water treatment devices is discharged to on-site septic systems and leach fields that can contaminate the groundwater supply (Vengosh and Pankratov 1998). Domestic wastewater contains elevated chloride and reduced nitrogen species, the latter of which oxidizes to nitrate in oxidizing groundwater. Water softener exchanges divalent ("hardness") cations (Ca^{2+}, Mg^{2+}, Sr^{2+}) with monovalent ("soft") Na^+ or K^+, depending on the salt used to regenerate the softener. Consequently, softener regeneration waste contains the divalent cations removed during the softening process. Figure 4, showing the graphical results of the PCA analysis, shows that the divalent cations Ca^{2+}, Mg^{2+}, and Sr^{2+} group with NO_3^- and Cl/Br. This implies a relationship between these components and suggests that domestic wastewater is a source of high NO_3^- contamination. Furthermore, the Cl/Br ratio increased with Cl^- concentration in the mountain block (Fig. 7a), indicating possible influence from brine discharge from water home water treatment or road salts (Davis et al. 1998). Additionally, groundwaters with both high Cl/Br ratios and high $\delta^{15}N$ values were likely contaminated by septic tank effluent.

The positive correlation between $\delta^{15}N$ and $\delta^{18}O$ in NO_3^- (Fig. 3b; $\rho = 0.64$, $p < 0.001$) is indicative of denitrification occurring from excess organic matter infiltrating groundwater (Aravena et al. 1993). We interpret wells with high concentrations of NO_3^- ($NO_3^- > 5$ mg/L as NO_3^-) as being contaminated by wastewater effluent. Other significant correlations ($p < 0.001$) were found between NO_3^- constituents associated with water treatment systems, notably Br ($\rho = 0.28$), Ca ($\rho = 0.3$), Cl ($\rho = 0.23$), and Mg ($\rho = 0.27$). Further implying a non-geological source for high NO_3^- concentrations, there was no spatial distribution pattern to elevated concentrations of NO_3^- in the studied area.

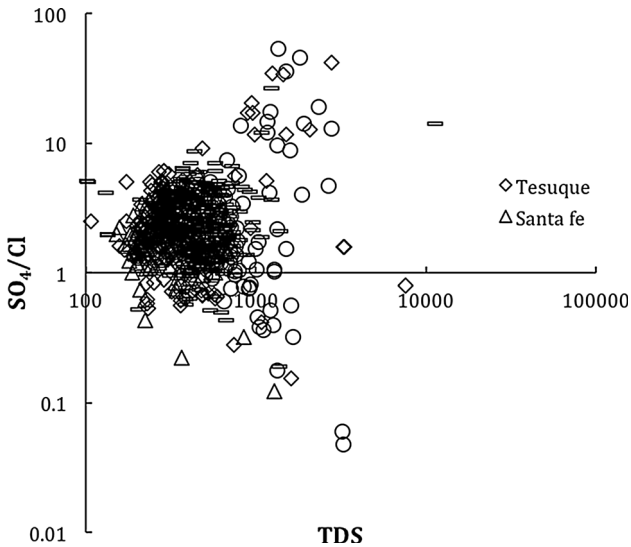

Fig. 7 SO_4/Cl ratio versus TDS. Groundwaters with high SO_4/Cl ratio likely have a gypsum source while waters with low SO_4/Cl ratios likely have a brine or evaporite source. The sources of low SO_4^{2-} within the Española Basin is likely contamination from domestic wastewater and water treatment effluent

Summary

Groundwater quality in the Española Basin is largely controlled by the region's geology while contamination from domestic wastewater and water treatment effluent is an emerging issue. With the exception of the Santa Fe metro area, which in general was more dilute, groundwater in most of the Española Basin had relatively high TDS that was coincident with elevated HCO_3^-, Cl^-, and Na. The fractured granites and gneisses in the Sangre de Cristo Mountains and the sediments of the Tesuque Formation form two geochemically distinct aquifers. High concentrations of U are common in the Sangre de Cristo mountain block likely due to weathering of granitic rocks within the watershed. Our results suggest that elevated As concentrations in the Tesuque Formation Aquifer are likely caused by devitrification of volcanic ash, anion exchange with clays, and mixing with hydrothermal fluids. In the region around the town of Nambé, U, As, and TDS were particularly elevated with many wells exceeding the EPA's MCL for As and U. Roll-front U deposits and devitrification of volcanic ash may supply excess U and As around Nambé. Contamination from domestic wastewater and water treatment effluent impact many wells within the Española Basin as evidenced by elevated concentrations of NO_3^- and high Cl/Br ratios.

Based on our observations, we recommend domestic well owners in the Española Basin test their well water for potentially hazardous chemical constituents including U, As, and F^-. Furthermore, because of the high number of wells in the region contaminated by domestic wastewater and water treatment effluent, we recommend additional testing for NO_3^- and that new septic systems follow guidelines outlined by NMED.

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References

Anderholm SK (1994) Ground-water recharge near Santa Fe, north-central New Mexico. US Geological Survey

Aravena R, Evans ML, Cherry JA (1993) Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. Groundwater 31:180–186

Blum JD, Gazis CA, Jacobson AD, Chamberlain CP (1998) Carbonate versus silicate weathering in the Raikhot watershed within the High Himalayan Crystalline Series. Geology. doi:10.1130/0091-7613(1998)026<0411

Casciotti KL, Sigman DM, Hastings MG et al (2002) Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Anal Chem 74:4905–4912. doi:10.1021/Ac020113w

Cavazza W (1986) Miocene sediment dispersal in the central Española basin, Rio Grande rift, New Mexico, USA. Sediment Geol 51:119–135

Chae GT, Yun S, Kwon M et al (2006) Batch dissolution of granite and biotite in water: implication for fluorine geochemistry in groundwater. Geochemical Journal-Japan- 40:95

Craig H (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. Geochim Cosmochim Acta 12:133–149

Crossey LJ, Karlstrom KE, Springer AE et al (2009) Degassing of mantle-derived CO_2 and He from springs in the southern Colorado Plateau region-Neotectonic connections and implications for groundwater systems. Geol Soc Am Bull 121:1034–1053

Davis SN, Whittemore DO, Fabryka-Martin J (1998) Uses of chloride/bromide ratios in studies of potable water. Groundwater 36:338–350

Gat JR (1996) Oxygen and hydrogen isotopes in the hydrologic cycle. Annu Rev Earth Planet Sci 24:225–262

Helsel D, Hirsch R (2002) Statistical methods in water resources, Techniques of Water-Resources Investigations of the United States Geological Survey. Book 4, Hydrologic Analysis and Interpretation. Chapter A3. US Geol Survey 1–524

Helsel DR et al (2005) Nondetects and data analysis. Statistics for censored environmental data. Wiley-Interscience, USA

Husson F, Lê S, Pagès J (2010) Exploratory multivariate analysis by example using R. CRC press

Keating EH, Vesselinov VV, Kwicklis E, Lu Z (2003) Coupling Basin- and Site-Scale Inverse Models of the Española Aquifer. Ground Water 41:200–211. doi:10.1111/j.1745-6584.2003.tb02583.x

Keating EH, Fessenden J, Kanjorski N et al (2010) The impact of CO_2 on shallow groundwater chemistry: observations at a natural

analog site and implications for carbon sequestration. Environ Earth Sci 60:521–536

Koning DJ (2003) Geologic map of the Chimayo 7.5-minute quadrangle

Kuhle A, Smith GA (2001) Alluvial-slope deposition of the skull ridge member of the Tesuque formation, Española Basin, New Mexico. New Mex Geol 23:30–37

Langmuir D (1978) Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim Cosmochim Acta 42:547–569

Lerner DN (2002) Identifying and quantifying urban recharge: a review. Hydrogeol J 10:143–152

Manning AH (2009) Ground-water temperature, noble gas, and carbon isotope data from the Española Basin, New Mexico. U.S. Geological Survey, USA

Scanlon BR, Nicot JP, Reedy RC et al (2009) Elevated naturally occurring arsenic in a semiarid oxidizing system, Southern High Plains aquifer, Texas, USA. Appl Geochem 24:2061–2071

Sigman DM, Casciotti KL, Andreani M et al (2001) A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Anal Chem 73:4145–4153

Stumm W, Morgan JJ (2012) Aquatic chemistry: chemical equilibria and rates in natural waters. Wiley

Vengosh A, Pankratov I (1998) Chloride/bromide and chloride/fluoride ratios of domestic sewage effluents and associated contaminated ground water. Ground Water 36:815–824. doi:10.1111/j.1745-6584.1998.tb02200.x

Von Strandmann PAEP, Burton KW, James RH et al (2006) Riverine behaviour of uranium and lithium isotopes in an actively glaciated basaltic terrain. Earth Planet Sci Lett 251:134–147. doi:10.1016/j.epsl.2006.09.001

Wang Y, Shvartsev SL, Su C (2009) Genesis of arsenic/fluoride-enriched soda water: a case study at Datong, northern China. Appl Geochemistry 24:641–649

Wang Y, Chen Y, Li W (2014) Temporal and spatial variation of water stable isotopes (^{18}O and ^{2}H) in the Kaidu River basin, Northwestern China. Hydrol Process 28:653–661. doi:10.1002/hyp.9622