Leachability of Natural Perchlorate from Soil within the Sierra de los Valles, New Mexico

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ABSTRACT

Meltwater from the 2009-2010 snowpack season was allowed to percolate through soil-core columns collected in a high mountainous, small catchment basin located in the Sierra de Los Valles, New Mexico. Leaching tests were performed to determine if naturally occurring perchlorate in soil could be solubilized by the meltwater at detectable concentrations greater than the analytical detection limit of 0.50 nM (0.05 µg/L) using liquid chromatography-mass spectrometry/mass spectrometry. Soil cores and snowpack-meltwater samples were collected at an elevation of 2835 m asl. Soil cores were collected in December 2009 and snowpack samples were collected in March 2010. The first set of cores was collected along the southwest-facing slope of the basin with the second set collected down-slope of the first set and near the drainage area. Cores collected along the slope represent approximately 57 cm of soil with 3 to 5 cm of weathered volcanics. The drainage cores represent approximately 61 cm of organic-rich soil. Samples were collected at a location that is considered to be an area of active groundwater recharge to bedrock. Historical snowpack data for the study area suggest that approximately 55 mL of meltwater passing through the core column reflects an average infiltration without evapotranspiration. Volumes of leachate obtained from the drainage and slope cores were 78 and 55 mL, respectively, and analyzed for low-level perchlorate. Analyses of major ions and trace elements were also performed on the acidic leachate samples. Natural perchlorate was detected in the slope and drainage leachate samples at 2.72 and 23.13 nM (0.27 and 2.3 µg/L), respectively. These results suggest that natural perchlorate becomes mobile as snowmelt reacts with soil within the recharge area of the mountain block and that the ubiquitous presence of natural perchlorate in the local groundwater system may be a result of this process. Other soluble oxyanions (nitrate, oxalate, phosphate, and sulfate) and trace elements (aluminum, barium, boron, iron, manganese, nickel, and zinc) associated with mineral dissolution were also detected at varying concentrations in the leachate samples.

EXPERIMENTAL PROCEDURES

The bottom ends of the acetate liners containing unconsolidated core were packed with silica hair and covered with fiberglass mesh secured by a stainless steel hose clamp. The liners were then clamped vertically to a ring stand. For the slope core liner, an inverted 4-L low density polyethylene container, previously rinsed with deionized water, provided a reservoir for the snow sample. The reservoir container was covered with aluminum foil to prevent air-borne particulate matter from contaminating the snow sample. A very small (<0.05 mm) hole punched into the lid of the reservoir container allowed melting snow to drip into the upper end of the liner containing unconsolidated slope core. The apparatus was placed in a refrigerator cooled to approximately 3°C. A polypropylene beaker was placed below the bottom end of the liner to collect leachate. The experimental procedure for the drainage core was similar to that of the slope core except that a 4-L reservoir containing snow was not used during the experiment. Snow was allowed to melt in the refrigerator. The snow meltwater was poured directly into liners containing non-packed and packed unconsolidated drainage core material.

Local precipitation records for the seasonal snowpack deposited in the study area suggest that 55 mL of melt water migrating through the slope core liner would represent an average annual volume of infiltrating meltwater under natural conditions. It was assumed that a greater amount of snowpack (e.g., drifts and less evaporation) would occur in the drainage area and therefore, 78 mL of melt water was passed through the drainage core liner.

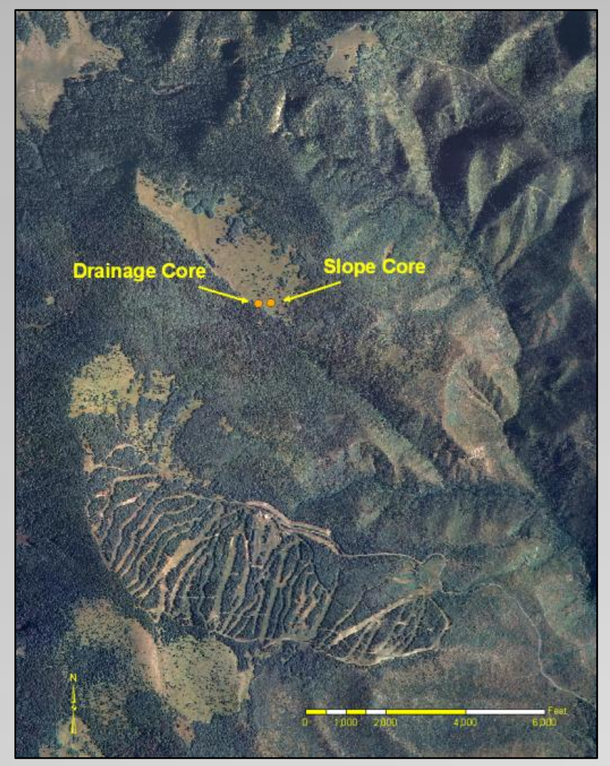
One leachate test was performed on the slope core liner with 55 mL meltwater infiltrating through the liner. Approximately 4.5 hours were required to collect 55 mL of leachate fluid from the slope core liner.

Two leachate tests were conducted on two liners containing drainage core material. The core in the first liner was treated equally to that of the slope core where meltwater was allowed to infiltrate downward under gravity and leachate was collected in a beaker prior to chemical analyses. Approximately 16.5 hours were required to collect 78 mL of leachate fluid. Core material within the second liner was tamped tightly to maximize the surface-area contact and increase the residence time between the meltwater and core material. It took approximately 96 hours to collect 78 mL of leachate fluid migrating through the packed drainage core liner. Once 78 mL were collected from the second liner, an additional 50 mL of leachate were collected to determine if additional meltwater infiltrating through the packed liner would result in a change in solute concentrations.

FIELD PROCEDURES

Core and snowpack samples were collected within the upper reach of the Los Alamos Canyon watershed at approximately 2835 meters (m) above sea level – see aerial photo to the right. Soil and snowpack samples were collected at the same locations. Soil cores were collected in December 2009, when soil moisture was assumed to be at a minimum. The first set of cores ("slope core") was collected along the southwest-facing slope of the drainage. The second set of cores ("drainage core") was collected within the drainage. Three cores were collected at each site. Cores were collected using a 68 cm long soil-recovery probe. A 61 cm long (2.4 mm diameter) acetate plastic liner set within the probe was used to capture core material. The probe was introduced into soil-bedrock via the force of a slide hammer. Approximately 57 cm of soil were collected at the slope site; 61 cm of soil were collected at the drainage site. Compaction during the sampling process resulted in approximately 50%, on average, reduction in core length. The lower 3 – 5 cm portions of the slope cores represent weathered and non-weathered bedrock; the remaining core was visually characterized as being a poorly developed soil with low organic content. The drainage core contained a much darker and well-developed soil with higher organic content; bedrock was not encountered at the drainage site. Augering at the drainage core location positioned the bedrock at about 200 cm below ground surface. Within an hour after collection, the core samples were placed and stored in a freezer at the NMED DOE OB Los Alamos site office.

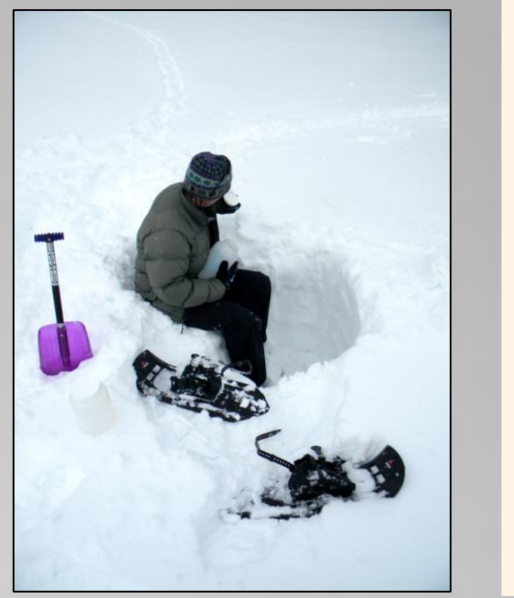
Snowpack samples, collected at the same location as the core samples, were collected on March 1, 2010 – see aerial photo to the right. At each site, the 2009 – 2010 snowpack was sampled to capture a profile representing the snowpack season. The snowpack was collected using sterilized, pre-packaged plastic scoops. Aliquots of the snowpack profile at each site were placed in two clean 2-L plastic containers and kept frozen in the NMED DOE OB freezer.



Core and snowpack sampling locations

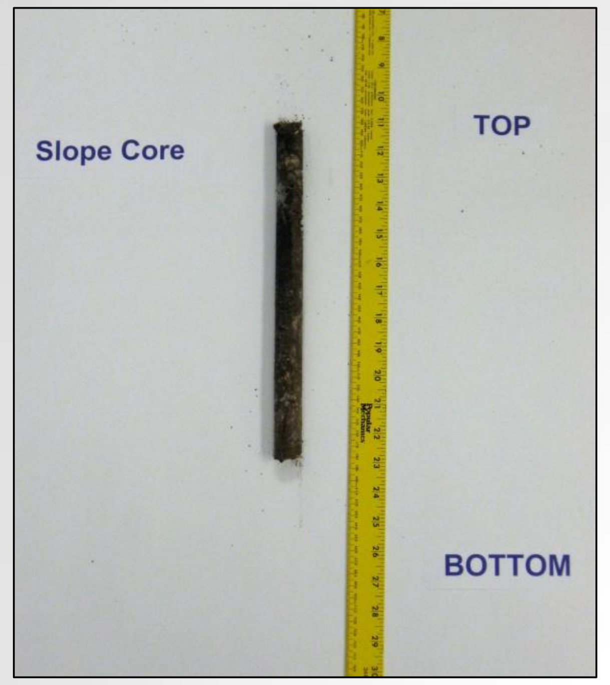
NMED scientist sets core driver for removal of drainage soil core

NMED staff prepare to collect soil core on slope location



NMED scientist collects snowpack at drainage/slope location

Core column apparatus with leachate collector



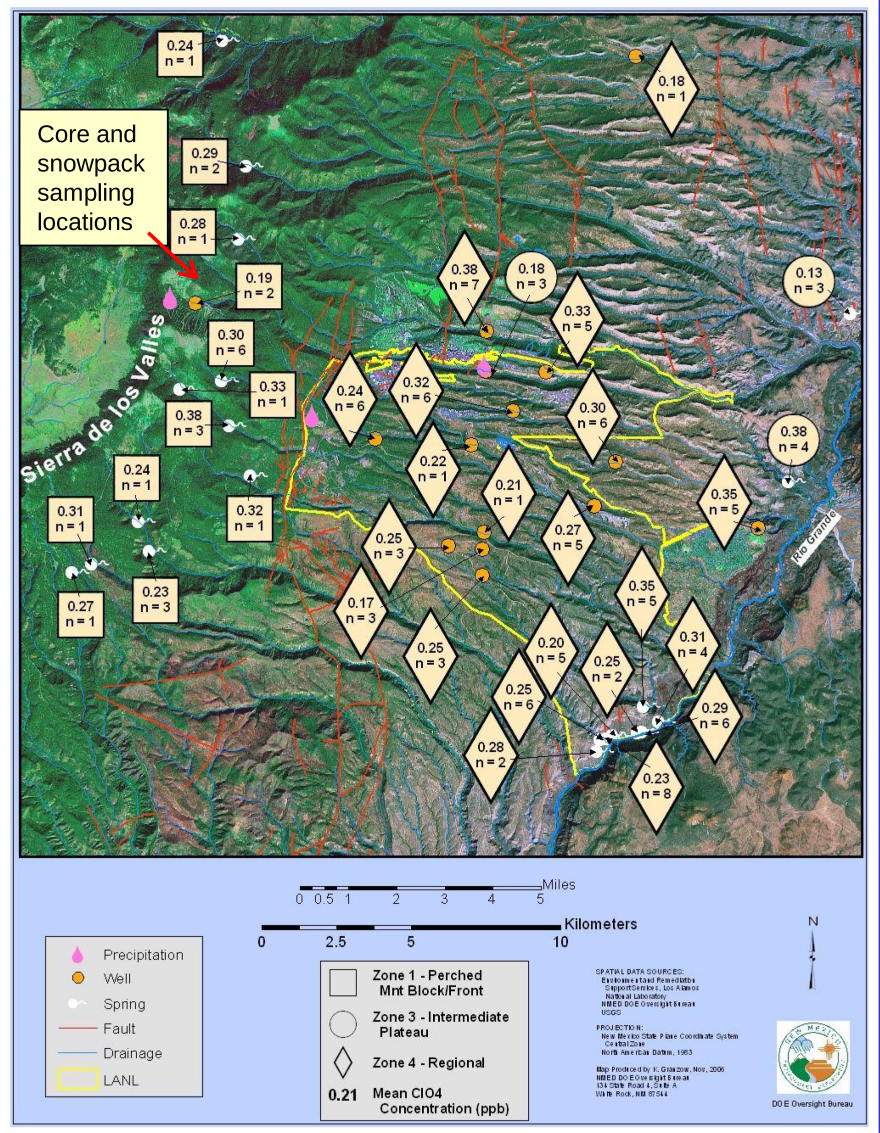
Slope core

Leachate apparatus

PURPOSE AND BACKGROUND

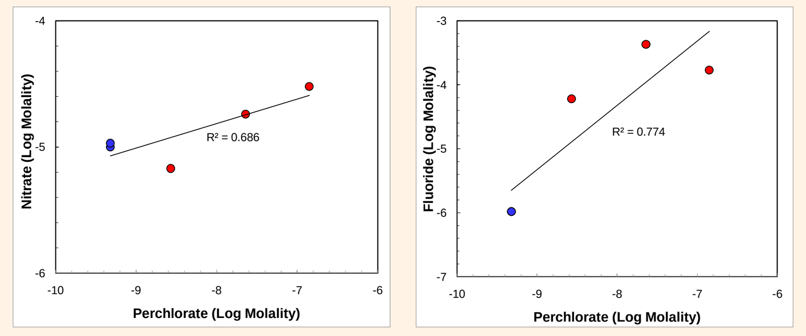
The purpose of this study is to determine if naturally occurring perchlorate could be leached from mountainous soils with melt water from 2009 – 2010 snowpack. The study area is located in the primary recharge zone of the Sierra de los Valles, New Mexico. (See map to the right)

The ubiquitous presence of naturally occurring perchlorate in groundwater at Los Alamos, New Mexico and surrounding areas is well documented (Dale, et al., 2008). Dale et al. (2008) report that background perchlorate concentrations range from 0.09 to 0.45 µg/L with a mean of 0.27 µg/L (2 sigma +/- 0.07; n = 121). Perchlorate concentrations in groundwater discharging in the recharge area within the Sierra de los Valles are virtually the same as in the deep regional groundwater, with a mean of 0.28 µg/L for the recharge waters and 0.27 µg/L for the regional aquifer (see figure showing Los Alamos mean background values). However, as shown on the figure illustrating perchlorate concentration versus percent modern carbon, the concentration of perchlorate is likely to be influenced by paleoclimate changes that took place during the Holocene Epoch. The current conceptual model for the presence and behavior of naturally occurring perchlorate in groundwater at Los Alamos suggests that perchlorate likely originates as a natural component of wet atmospheric deposition as proposed by Rajagopalan, et al. (2009), followed by deposition and entrainment in thin land-surface soil horizons. The enrichment of perchlorate in soil horizons may occur as the oxyanion is deposited during episodic summer monsoon rains in the high-elevation recharge areas followed by intermittent drying periods. Soluble perchlorate is initially stored in soil horizons followed by downward movement within the vadose zone facilitated by snowmelt infiltration.



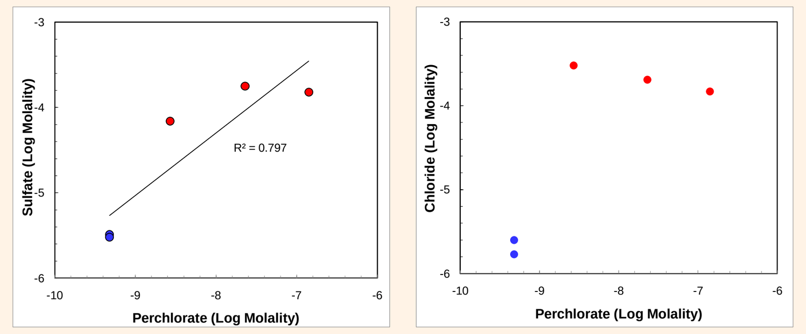
Los Alamos area mean background perchlorate values

Perchlorate Versus Nitrate and Fluoride Concentrations in Snowpack and Core Leachate Samples, Los Alamos, New Mexico



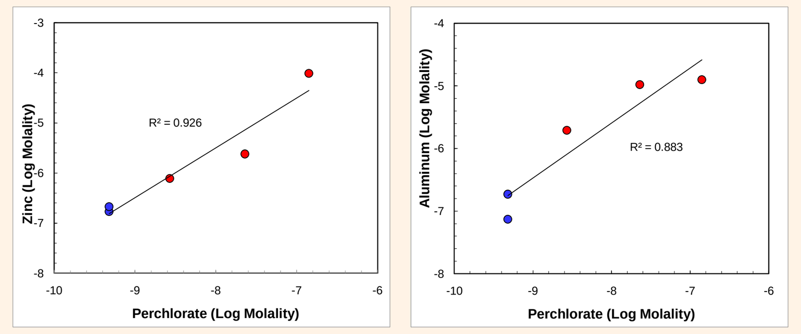
These two figures show perchlorate versus nitrate concentrations and perchlorate versus fluoride concentrations in snowpack and core leachate samples collected in the Jemez Mountains, New Mexico. Perchlorate, nitrate, and fluoride are soluble anions that are easily leached from the core using snowpack water. Blue – snowpack melt Red - leachate

Perchlorate Versus Sulfate and Chloride Concentrations in Snowpack and Core Leachate Samples, Los Alamos, New Mexico



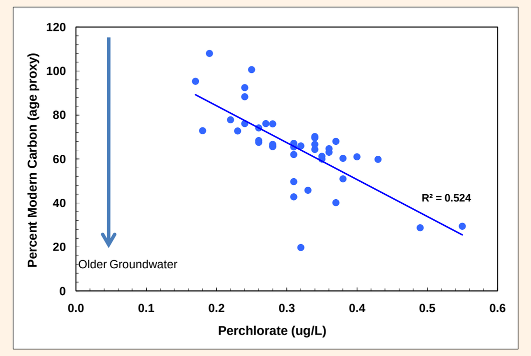
These two figures show perchlorate versus sulfate concentrations and perchlorate versus chloride concentrations in snowpack and core leachate samples collected in the Jemez Mountains, New Mexico. Perchlorate, sulfate, and chloride are soluble anions that are easily leached from the core using snowpack water. Based on analytical results for the leachate samples, chloride concentrations slightly decrease with increasing perchlorate. Blue – snowpack melt Red - leachate

Perchlorate Versus Zinc and Aluminum Concentrations in Snowpack and Core Leachate Samples, Los Alamos, New Mexico



These two figures show perchlorate versus zinc concentrations and perchlorate versus aluminum concentrations in snowpack and core leachate samples collected in the Jemez Mountains, New Mexico. Perchlorate, zinc, and aluminum are soluble species that are moderately leached from the core using snowpack water characterized by acidic pH values (6.0 and 5.5). Blue – snowpack melt Red - leachate

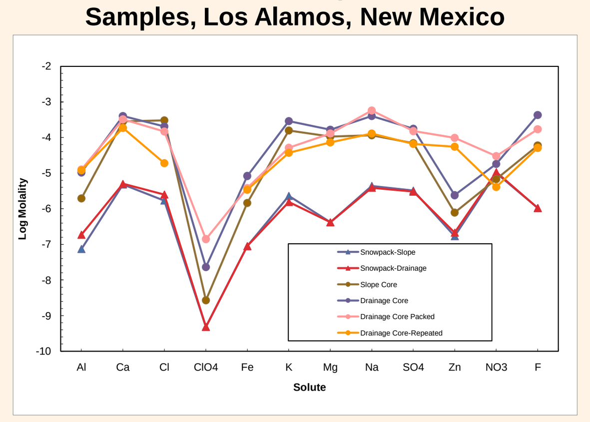
Perchlorate Versus Percent Modern Carbon (^{14}C) for Modern and Submodern Age Groundwater, Los Alamos, New Mexico



Plot illustrating the relationship between percent modern carbon (radiocarbon) versus perchlorate concentration. The data set represents results from the sampling of 42 wells and springs with unadjusted radiocarbon ages ranging from less than 5 years to greater than 13,000 years (Dale, et al., 2010).

Perchlorate data source: RACER database (www.racerdat.com)
Percent Modern Carbon (radiocarbon) data source: Dale, et al., 2010

Solute Concentrations in Snowpack and Core Leachate Samples, Los Alamos, New Mexico



This figure shows selected background solute concentrations in snowpack and core leachate samples collected in the Jemez Mountains, New Mexico. Concentrations of perchlorate are the lowest (0.048 ppb, log molality = -9.32) in the snowpack samples and the highest in leachate sample from the packed drainage core (up to 14 ppb, log molality = -6.85). Other solutes shown in the above figure also occur at higher concentrations in the leachate samples, showing variable leachability.

CONCLUSIONS

It appears that naturally occurring perchlorate in the groundwater system at Los Alamos, New Mexico is initially leached during recharge within the mountain-block recharge area. An atmospheric origin for perchlorate, as proposed by Rajagopalan, et al., 2009, is applicable to this study.

Concentrations of perchlorate are the lowest (0.048 ppb, log molality = -9.32) in the snowpack samples and the highest in the one leachate sample from the tamped drainage core (14 ppb, log molality = -6.85). Other solutes occur at higher concentrations in the leachate samples compared to snowpack and show variable leachability.

Perchlorate, chloride, fluoride, nitrate, and sulfate are soluble anions that are easily leached from core material using snowpack water.

Perchlorate, aluminum, and zinc correlate with each other in the leachate samples. This suggests that these two metals are stable as soluble species that are moderately leached from the core using snowpack water characterized by acidic pH values (5.5 and 6.0).

Detectable concentrations of aluminum, boron, manganese, nickel, silicon, and zinc in the snowpack may be attributable to atmospheric deposition of combusted fossil fuels and/or resuspended dust particles (soluble and/or colloidal) reflecting the local soils and bedrock.

Station	Field pH (S.U.) Melt Water	Low-Level ClO4 LC-MS/MS (ug/L or ppb)	Reporting Limit	Method Detection Limit	Al ppm	B ppm	Ba ppm	Ca ppm	Cl ppm	F ppm	Fe ppm	K ppm	Mg ppm	Mn ppm	Na ppm	Ni ppm	NO3 ppm	Oxalate ppm	pH (SU)	PO4 ppm	Si ppm	SiO2 ppm calc	SO4 ppm	Zn ppm
Slope Core	Not applicable	**0.27**	0.05	0.01	0.052	0.102	0.095	11.38	10.50	1.14	0.08	6.13	2.57	0.014	2.62	0.033	0.42	0.07	Not measured	0.22	1.67	3.58	6.59	0.050
Drainage Core	Not applicable	**2.3**	0.05	0.01	0.284	0.256	0.099	16.06	7.22	8.05	0.46	11.36	3.94	0.039	9.18	0.023	1.12	0.05	Not measured	<0.01	6.08	13.02	17.02	0.155
Drainage Core Packed	Not applicable	**14**	0.05	0.01	0.341	0.507	0.097	13.06	5.28	3.19	0.21	1.98	3.09	0.028	13.16	0.033	1.89	0.03	Not measured	0.31	14.62	31.28	14.62	6.28
Drainage Core Packed Extended Leachate	Not applicable	Not analyzed	Not analyzed	Not analyzed	0.325	0.124	0.063	7.48	0.68	0.98	0.19	1.45	1.73	0.020	2.94	0.019	0.25	<0.01	Not measured	0.04	11.10	23.74	6.41	3.57
Snowpack melt at slope core site (1)	6.0	**0.048**	0.05	0.01	0.002	0.006	<0.001	0.19	0.06	0.02	<0.01	0.09	0.01	0.004	0.10	0.003	0.62	0.02	6.59	<0.01	0.04	0.08	0.31	0.011
Snowpack melt at drainage core site (2)	5.55	**0.048**	0.05	0.01	0.005	0.012	<0.001	0.20	0.09	0.02	<0.01	0.06	0.01	0.004	0.09	0.003	0.66	0.01	7.42	<0.01	0.04	0.08	0.29	0.014
Meltwater equipment blank - composited from (1) and (2)	Not applicable	**0.048**	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not measured	Not analyzed	Not analyzed	Not analyzed	Not analyzed	Not analyzed

REFERENCES CITED

Dale, M., Granzow, K., Longmire, P., Englert, D., Rearick, M., and Perkins, G., 2008, Naturally Occurring Perchlorate in Ground Water, Northern Rio Grande Basin, New Mexico: New Mexico Environment Department, Department of Energy Oversight Bureau.

Dale, M.R., Longmire, P., Granzow, K.P., Martinez, D., Perkins, C.A., Rearick, M.S., and Perkins, G., 2010, Radiocarbon Dating and Paleohydrology of Regional Aquifer Groundwater Beneath the Pajarito Plateau, New Mexico: 2010 NGWA Ground Water Summit and 2010 Ground Water Protection Council Spring Meeting, Denver, CO (Poster).

Rajagopalan, S., Anderson, T., Cox, S., Harvey, G., Cheng, Q., and Jackson, A.W., 2009, Perchlorate in Wet Deposition Across North America: Environmental Science and Technology, Vo. 43., p. 616 – 622, doi: 10.1021/es801737u.