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Environmental Contamination and Toxicology

Mercury Concentrations in Groundwater Collected from Wells on and near the Nevada Test Site, USA

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Groundwater from southern Nevada has been studied extensively and characterized chemically on a number of occasions due to its proximity to the Nevada Test Site (NTS), Yucca Mountain, and Death Valley National Park (e.g., Winograd and Eakin 1964; Dudley and Larson 1976; White and Chuma 1987; Farnham et al. 2000; Stetzenbach et al. 2001). The NTS is of interest because a number of nuclear devices were detonated within its boundaries at or below the water table; Yucca Mountain is relevant because it is the proposed geologic repository for storage of the nation's high-level nuclear waste; and Death Valley National Park because there exist numerous natural springs throughout the Park. Many of these more recent studies have taken advantage of inductively coupled plasma mass spectrometry (ICPMS) to determine concentrations of trace (μg/L) and ultra-trace (ng/L) elements. The technique, developed in the mid-1980's, is ideally suited for groundwater analyses because of its low detection limits and multi-element capabilities. The data generated by ICPMS for southern Nevada groundwater has proved useful in evaluating groundwater sources and flow histories, including mixing patterns (e.g., Johannesson et al. 1997a,b). Noticeable absent from all these studies is the element mercury. This is understandable considering the difficulty in reliably determining mercury at ng/L levels, typically found for groundwater away from point sources of mercury. Problems with determining mercury at these levels include sample contamination, mercury is ubiquitous at low-levels, and relatively poor detection limits by ICPMS due to mercury's poor ionization in the plasma.

Currently, we are engaged in analysis of groundwater collected from a network of wells on and near the NTS, as part of the Nye County Early Warning Drilling Program (NCEWDP). The purpose is to establish a groundwater monitoring system to protect the residents of Nye County in Amargosa and Pahrump Valleys against potential radionuclide contamination from activities at Yucca Mountain and past nuclear weapons testing on the NTS. The program is also intended to provide hydrologic information in one of the least understood hydrogeologic systems in the vicinity of Yucca Mountain. We have taken this opportunity to collect additional groundwater samples from wells on- and adjacent to- the NTS, using ultra-clean sampling techniques, to reliably determine mercury for the first

time using cold vapor atomic fluorescence spectrometry (CVAFS). This single element technique uses dual gold trapping for preconcentration and can provide sub-ng/L detection capability. The mercury data is of interest 1) to understand the role of groundwater in aquatic mercury cycling in desert environments (Springs and adjacent wetlands are utilized extensively by wildlife in the region), 2) to see if there has been any contamination from numerous mines scattered throughout the region which used mercury in their operations, 3) because additional data on the aquifer may prove useful in deciphering the groundwater flow system and 4) the data may serve as baseline information for future studies.

MATERIALS AND METHODS

Groundwater samples were collected approximately 190 km northwest of Las Vegas, Nevada in Amargosa Valley and Crater Flat (Fig. 1). Specific sample information, including the depth and lithology of the screened interval where samples were obtained, are given in Table 1. In addition, samples were collected from two springs (Crystal and Ash) located within the regional aquifer but along a different flow path than the groundwater samples. The hydrogeologic setting of the study area has been described in detail elsewhere (e.g., Blankennagel and Weir 1973; Johannesson et al. 1999). In short, regional groundwater is believed to flow generally from north to south, with a significant portion eventually flowing southwest toward Death Valley. Some important recharge zones include the mountains and basins in north-central Nevada and the Spring and Sheep mountains in the south. Major discharges occur at springs in Ash Meadows National Wildlife Refuge, Death Valley National Park, and along the Muddy River north-east of Las Vegas, Nevada. The geology consists of Precambrian through Paleozoic sedimentary carbonate rocks (mostly of marine origin) underlying volcanic rocks (rhyolitic and quartz latitic) and basin-fill alluvial and lacustrine sediments. Each of these units contain groundwater and represent the principal aquifers for the region.

Samples were collected during August and September of 2002 using the ultra-clean sampling technique described by Stetzenbach et al. (1994), with slight modifications. Groundwater was collected in 125 ml PFA-Teflon bottles which were previously soaked in 20% nitric acid followed by 20% hydrochloric acid and rinsed with deionized water (>18.2 MΩ). Groundwater was collected after the well was flushed with at least 3 well volumes and there was stabilization of pH, temperature, and conductivity. Samples were collected both unfiltered and filtered (0.45 μm; Gelman Sciences groundwater filters). The filters were placed directly on the pump outlet tubing and water was allowed to pass through the filter for at least one minute prior to collection. In addition, separate samples were collected in Nalgene bottles for field measurements (pH, conductivity, temperature, and alkalinity) using standard techniques. For the springs, the water was pumped from the source using a peristaltic pump equipped with acid-washed Teflon tubing. The spring water samples were not filtered and field measurements

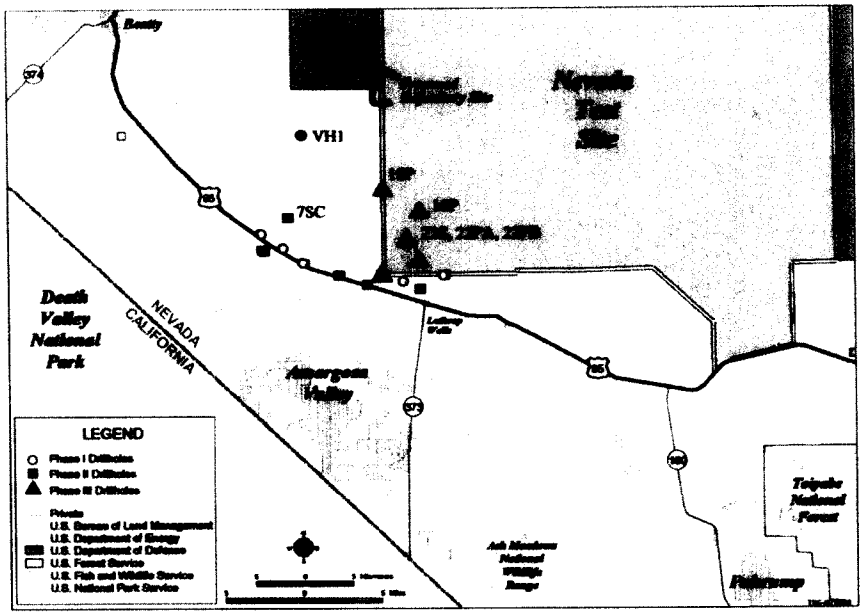

Figure 1. Regional map of study area showing the sampled wells and the proposed Yucca Mountain repository site (used with permission from Nye County). Well VH1 is not part of the NCEWDP.

were not taken. Samples were sealed in polyethylene bags and transported on ice to the laboratory. The samples were then preserved in a laminar flow hood by adding concentrated hydrochloric acid (obtained sub-boiled distilled in quartz from Seastar, Inc.) to obtain a 0.05% solution. All samples were stored at 4°C and analyzed within 28 days of collection.

Samples were analyzed by CVAFS using a Tekran Model 2600 (Toronto, CA) and following U.S. EPA Method 1631 (U.S. EPA 2001). Briefly, the sample is pumped from a 50 mL polyethylene centrifuge tube and combined with a solution containing $SnCl_2$ in a liquid-gas separater, where Sn^{+2} acts to reduce the oxidized mercury species to elemental mercury and the mercury vapor is introduced into the instrument via an argon flow. Subsequently, the mercury is preconcentrated twice on dual gold traps before being evolved in a pulse via rapid heating and detected in an atomic fluorescence spectrometer. The instrument was calibrated (r^2 >0.995) with dilutions of a NIST-traceable Hg standard solution (AccuTrace, New Haven, CT, USA). Analysis of a certified reference material (SRM 1641d "Mercury in Water") demonstrated the accuracy of the method and verified that the instrument remained calibrated during the analyses. Recoveries for the reference material (n=5) and spiked samples (n=5) averaged 94% and 92%,

Table 1. Sample dates, locations, depths and lithologies of screened (collection) zones.

NCEWDP Wells Sampled	Location	Date	Depth (m)	Lithology
7SC (Zone 1)	36° 43' 31.812" 116° 33' 25.439"	9/13/02	24 - 27	Silty sand with gravel; valley fill - alluvium
7SC (Zone 2)	"	"	55 - 64	Ashfall tuff - feldspar, quartz, biotite
7SC (Zone 3)	"	"	82 - 113	Silty sandy clay - tertiary valley fill
10P (Zone 1)*	36° 43' 48.874" 116° 24' 20.362"	8/27/02	202 - 214	Silty sand with gravel; valley fill - alluvium
10P (Zone 2)	"	"	244 - 262	Volcanic conglomerate with ashflow clasts
18P	36° 45' 04.797" 116° 26' 50.340"	8/26/02	255 - 270	Ashflow tuff - feldspar, quartz, biotite
22PA (Zone 1)	36° 42' 15.712" 116° 25' 06.581"	8/28/02	159 - 177	Silty sand with gravel; valley fill - alluvium
22PA (Zone 2)	"	8/28/02	202 - 232	"
22PB (Zone1)*	36° 42' 15.665" 116° 25' 05.863"	8/29/02	269 - 299	"
22PB (Zone 2)	"	8/30/02	348 - 360	Volcanic conglomerate
22S (Zone 1)	36° 42' 15.132" 116° 25' 06.636"	9/11/02	159 - 177	Silty sand with gravel; valley fill - alluvium
22S (Zone 2)	"	9/10/02	202 - 232	"
22S (Zone 3)	"	"	269 - 299	"
22S (Zone 4)	"	9/9/02	348 - 360	Volcanic conglomerate
VH-1	36° 47' 32" 116° 33' 07"	9/18/02	no screen pump at 212	Pyroclastic flow tuffs

* Samples collected in duplicate.

respectively. Various blanks were analyzed and indicated that there was minimal contamination associated with the reagents, filter, and field operations. In addition, wash water blanks were analyzed periodically and confirmed that mercury was not being carried over between samples. The relative percent difference (RPD) for duplicate measurements averaged 5.6% and ranged from 0.6 to 20%. Field duplicates varied by a slightly greater margin (mean RPD = 18%; range 11 to 30%) but were still respectable for ng/L levels. The method detection limit was estimated at 0.2 ng/L (3 sigma criteria).

RESULTS AND DISCUSSION

Concentrations of mercury in the groundwater and results for typical water quality measurements are given in Table 2. From the field data it is evident that the water samples are fairly uniform with respect to pH, conductivity, temperature, and alkalinity. The water was slightly basic (mean pH of 8.1), relatively warm (mean temperature of 31.6°C), with a moderate salt content (mean conductivity of 0.39 μSm/cm), and with some acid-neutralizing capacity (mean alkalinity of 130 mg/L). Mercury concentrations differed between the unfiltered (total mercury) and filtered (dissolved mercury) samples (Fig. 2). For the unfiltered samples, concentrations averaged 11.9 ± 10.7 ng/L and ranged from 0.4 to 36.7 ng/L. For the filtered samples, concentrations averaged 5.4 ± 4.3 ng/L, about half of that of the unfiltered samples, and ranged from below the detection limit to 15.7 ng/L. Concentrations of mercury were lower in the filtered samples versus their unfiltered counterpart in all cases but one when they were essentially identical. These differences indicate that a substantial percentage of the mercury in the raw groundwater is associated with the particle phase, which is not uncommon for a number of trace elements that adsorb to particle surfaces. The unfiltered data were also more variable than the filtered data, probably due to differing levels of suspended solids. Unfortunately, we did not measure suspended solids in these samples to be sure. Although species in filtered samples (<0.45μm) are sometimes considered "dissolved", it should be kept in mind that particles below this cutoff exist (e.g., colloids) and can influence concentrations and transport properties.

Overall, the concentrations found in this study compare favorably to the very low concentrations observed in groundwater collected elsewhere using ultra-clean techniques and away from any known point sources (Krabbenhoft and Babiarz 1992; Lindqvist et al. 1991). The low mercury concentrations indicate that there has been no impact from mining operations in the area and that mercury-bearing minerals are probably not present. The concentrations are also below those of concern for wildlife using the numerous artesian spring-fed wetlands in the region. Analyses of water from two springs (Crystal and Ash Springs) within the southern Nevada regional aquifer indicated mercury concentrations remain low in these surface waters 1.9 and 28.4 ng/L, respectively. The higher level in Ash Spring may be due to the greater amount of organic matter found in the pool compared to Crystal Spring. Organic matter is well known to complex mercury and these samples were not filtered. While these levels are still low, it would be of interest to measure mercury in some of the larger springs used extensively by wildlife, such as nearby Ash Meadows. It is possible the high evaporation rate due to the desert climate may concentrate the mercury in the water and that given the right conditions sulftate-reducing bacteria may convert the inorganic mercury to the more bioaccumulatable methyl-mercury form. Ash Spring is typically warmer than Crystal Spring.

Table 2. Mercury concentrations and field data for groundwater from the NTS.

Sample	Mercury (ng/L)				pH	Conduct. (mS/cm)	Temp. (°C)	Alkalin. (mg/L)
	unfiltered	RPD	filtered[b]	RPD				
7SC (Zone 1)	3.8	4.4	<DL	-	7.3	0.95	34.1	306
7SC (Zone 2)	4.9	1.6	<DL	4.2	7.1	0.97	25.2	331
7SC (Zone 3)	0.4	89.6[c]	<DL	-	7.6	1.02	27.7	422
10P (Zone 1)	4.2	2.6	1.7	11.7	7.8	0.30	33.9	111
10P (Zone 1)[a]	3.7	4.9	1.9	2.2	7.8	0.30	31.3	110
10P (Zone 2)	6.3	3.8	2.4	3.9	7.8	0.29	31.2	108
18P	3.6	3.7	3.2	8.9	8.2	0.35	34.9	142
22PA (Zone 1)	26.9	2.5	5.2	4.4	7.6	0.29	30.3	105
22PA (Zone 2)	5.2	4.4	1.0	-	7.4	0.29	31.3	107
22PB (Zone 1)	14.4	0.9	9.9	7.6	8.0	0.16	30.8	125
22PB (Zone 1)[a]	12.0	5.6	7.3	3.5	8.0	0.16	30.1	127
22PB (Zone 2)	15.0	4.7	15.7	0.6	7.9	0.34	35.0	131
22S (Zone 1)	26.7	6.7	7.8	2.8	7.7	0.29	28.6	108
22S (Zone 2)	18.4	1.6	9.3	12.4	8.0	0.28	29.0	115
22S (Zone 3)	36.7	4.6	2.3	3.5	7.9	0.29	28.2	114
22S (Zone 4)	0.5	20.0	<DL	-	8.2	0.29	29.4	114
VH1	20.3	12.2	2.5	10.0	8.1	0.39	31.6	130
Mean:	11.9	5.3	5.4	5.8	8.1	0.39	31.6	130
Median:	6.3	4.4	3.2	4.2	7.8	0.29	30.8	115
Minimum:	0.4	0.9	<DL	0.6	7.1	0.16	25.2	105
Maximum:	36.7	20.0	15.7	12.4	8.2	1.02	35	422

[a] Denotes field duplicate. [b] Filters used were 0.45μm. [c] Not included in summary statistics. <DL = below detection limit, estimated at 0.22 ng/L; RPD = Relative Percent Difference of duplicate analyses.

There appears to be no significant correlation for mercury concentrations with depth and lithology. For example, the concentration for mercury in the unfiltered samples from well 22S initially decreases from 26.7 to 18.4 ng/L from zone 1 (159-177 m) to zone 2 (202-232 m), then increases to 36.7 ng/L in zone 3 (269-299 m), and finally drops dramatically to 0.5 ng/L in zone 4 (348-360 m).

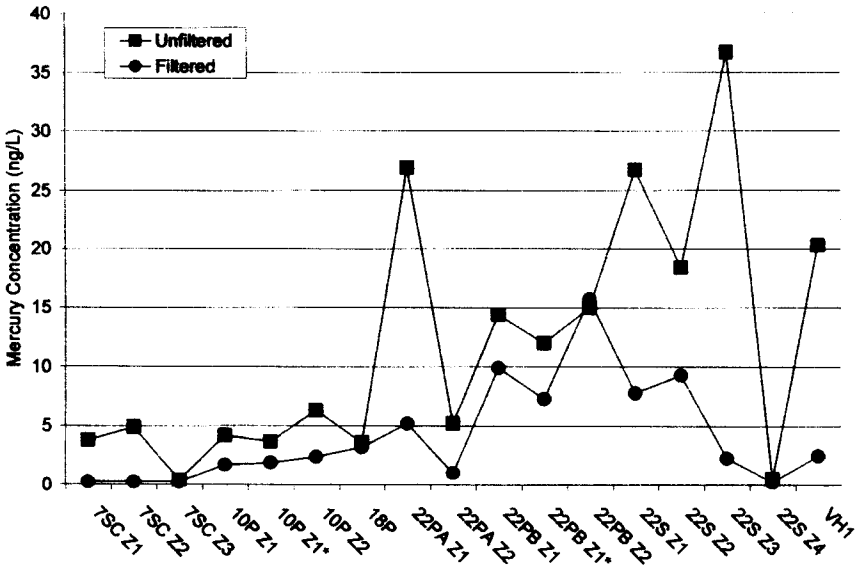

Figure 2. Mercury concentrations in groundwater from wells on and near the Nevada Test Site. Filters were 0.45 μm in diameter pore size. *denotes field duplicate.

For the filtered samples from this same well, there is a hint of a decrease in mercury concentration with depth but it is not convincing. From shallow to deep the mercury concentrations were 7.8 ng/L, 9.3 ng/L, 2.3 ng/L, and below detection limit. Gaseous atmospheric mercury, which has been shown to influence groundwater mercury concentrations (Krabbenhoft and Babiarz 1992) is probably not a factor at the depths used in this study. The shallowest depth of collection was still 24 m deep and most of the samples were obtained from over 150 m deep.

Overall, the concentration of mercury in the filtered samples ("dissolved" mercury) are quite uniform across the varied strata (mean 5.4 ± 4.3 ng/L), perhaps reflecting the removal of suspended particles and their attractive surface areas. Since there appears to be no correlation for mercury concentration with the differing lithology, it is likely that mercury, and/or the particles and colloids that mercury is attached to, are behaving conservatively in the system, particularly since the source of these waters have been reported to be from the same recharge areas (Farnham et al. 2000). Moreover, while there are some differences in lithology from which the samples were collected, the rock matrix is generally volcanic in origin. No samples were obtained from the deep underlying carbonate aquifer, which has much different groundwater chemistry. There was also no

obvious correlation for mercury concentration with pH, conductivity, temperature, and alkalinity, which varied little.

Like many other trace elements, the speciation of mercury in groundwater is dependent for the most part on redox conditions. In oxidizing groundwater, mercury is expected to be in the form of Hg^{+2}; whereas in more reducing conditions, it may be found as Hg^{+1} or Hg^{0}. The charged species can adsorb onto surfaces of particulate matter (i.e., the rock/soil matrix) in the aquifer, while elemental mercury can rise and possibly outgas from the groundwater, especially in thermal waters. Most of the groundwater in this study was found to be relatively oxidizing (dissolved oxygen content is typically around 2-8 mg/L). Interestingly, the sample with the lowest mercury concentration (7SC Zone 3) is believed to also have the lowest dissolved oxygen content and higher ratios of reduced species, such as As^{+3} versus As^{+5} (Don Shettel and Julie Bertoia, personal comm.). However, there is no significant correlation for mercury concentration and dissolved oxygen.

In summary, mercury concentrations in groundwater from the Amargosa Desert in southern Nevada were very low, generally <20 ng/L for unfiltered samples and <10 ng/L for filtered samples. These concentrations appear to be independent of the depth and volcanic lithology of the aquifer. The concentrations also indicate that mining activities in the region have not affected this groundwater as is the case in parts of northern Nevada. Data for mercury in area springs may be of greater interest than that in groundwater given the potential impact on wildlife.

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