TITLE: Preliminary Evaluation of Perchlorate Contamination of Ground Water In The Lower Colorado River Region

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CONGESSIONAL DISTRICT 9

DESCRIPTION INFORMATION

A. Problem and Research Objectives

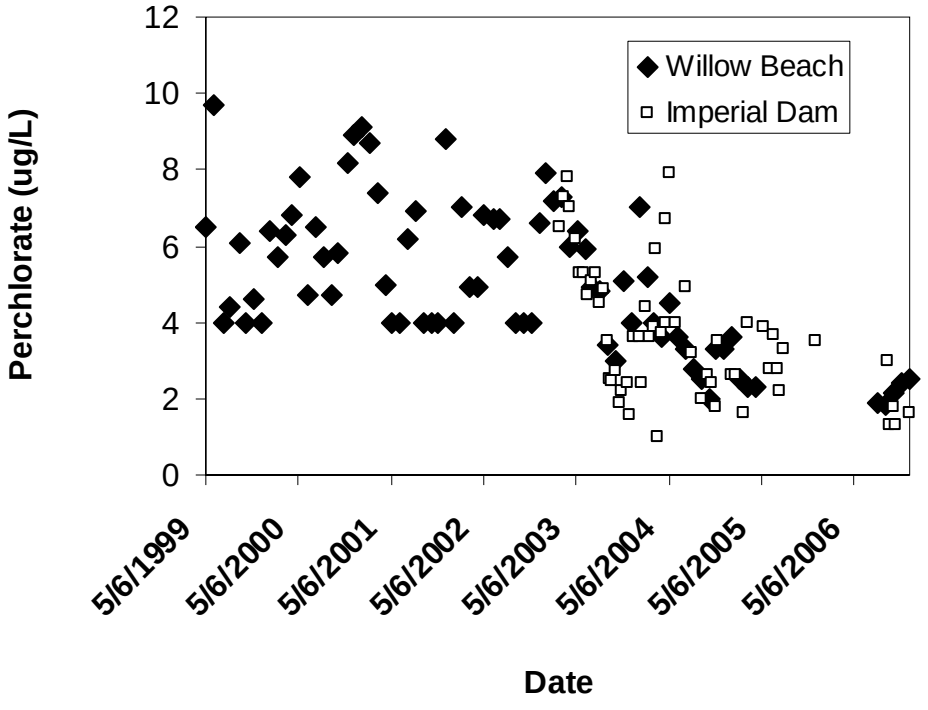
Perchlorate is a chemical linked with thyroid dysfunction. Perchlorate competitively inhibits uptake of iodine by the sodium-iodide symporter (NIS) of the thyroid (Greer et al., 2002). Particularly vulnerable to perchlorate exposure are pregnant women, fetuses, newborns, and individuals suffering from hyperthyroidism (Clark, 2000; NAS 2005). Perchlorate salts are used extensively by the ordinance and rocket propulsion industries as oxidants. It has been established that contamination from these industries have been contributing to the presence of perchlorate in the lower Colorado River (Hogue, 2003). Perchlorate concentrations in the Colorado River below Lake Mead have ranged from 5 to 9 μg/L (California Department of Health Services, 2000). It has been estimated that approximately 20 million people are exposed to perchlorate through drinking water drawn from the Colorado River (Hogue, 2003).

There is also a concern that years of irrigation with perchlorate contaminated water may have contaminated the groundwater of the region. In the lower Colorado River region, over 300,000 ha of land is irrigated using Colorado River water. In the greater Yuma

region of southwestern Arizona, Colorado River water is extensively used year round for irrigation.

Figure 1 shows perchlorate concentrations at Willow Beach from 1999 and concentrations at Imperial Diversion Dam since 2003. Perchlorate concentrations have ranged from 1 ug/L to 9 ug/L. More recently, they have declined due to remediation of the perchlorate plumes in the Las Vegas Wash near Henderson.

Figure 1. **Perchlorate concentrations in the Colorado River at Willow Beach and Imperial Diversion Dam. (The data collected at Willow Beach is from the Nevada Department of Environmental Protection and the data collected at Imperial Diversion Dam were determined in our laboratory).**



As stated earlier, years of irrigation with perchlorate contaminated Colorado River water may have contaminated the regional aquifer with perchlorate. Thus, rural communities around the greater Yuma region using groundwater as their source of potable water may be exposed to perchlorate by drinking contaminated groundwater. The objective of this survey was to determine the extent of the perchlorate contamination in ground water of lower Yuma Valley area of Arizona.

B. Methodology

Sampling program

The sampling program was initially sub divided into three stages. In the first stage, all the drainage wells associated with the irrigated fields of the Yuma region were sampled. The logic behind this was that the analysis of perchlorate in the water from the active drainage pump discharges would give a direct indication of the effect of irrigation using Colorado River water on the aquifer with respect to perchlorate contamination. After completion of the first stage of sampling, the sampling program was expanded to include the public water system (PWS) wells serving the greater Yuma region. Needless to say this was done to ascertain if the population served by the PWS of the greater Yuma region is being exposed to perchlorate. To improve the geographical distribution of well locations for the survey, the sampling program was expanded to cover rural households and commercial entities having individual wells to serve as the source of potable water. For this part of the survey, the greater Yuma region was sub divided into 6.0 km^2 block grids and at least one rural well was sampled per 6.0 km^2 block. Expanding the survey to

rural households also expanded the scope of the survey to ascertain if the rural households are being exposed to perchlorate via their potable water.

Based on the results of the first three stages of the sampling program, a fourth sampling stage was added, where shallow water depth observation wells (<20.0 ft in depth) of the US Bureau of Reclamation were sampled for perchlorate. All four stages of sampling were conducted between April 2005 and September 2005.

Sampling procedure

After a period of flushing to ensure well stabilization indicated by constant conductivity reading for a period of 15 minutes, representative grab water samples were collected in 250 mL containers filled to within an mL of full capacity at each well sampled. Conductivity, pH, and temperature was also reported at each well sampled. At each well sampled, GPS coordinates were also noted, and the well depth was also noted based on prior available data or simply by asking the owner of the well. For domestic wells, simultaneous to sampling, an impromptu survey was also conducted to determine if the water was being used for cooking, drinking, or only for other household uses such as washing, gardening, and other domestic usage. If the water was not being used for cooking and drinking, the participants of the survey were asked as to the reason they were not using the well water as their source of cooking and drinking water. The collected samples were stored at $4^{o}C$ for analysis.

Perchlorate analysis

These water samples were analyzed for perchlorate using a modification of EPA Method 314.0. Samples for perchlorate analysis were filtered through a 0.2-micron Gelman ion membrane syringe filter to remove particulate matter that may compromise the ion chromatograph column, followed by Dionix "On Guard II Ba", "On Guard II Ag", and "On Guard II H" syringe filters, to remove interfering anions such as chlorides, sulfates, and bicarbonates, and again through a 0.2-micron Gelman ion membrane syringe filter to remove particulate media carried over from the On Guard filters. Perchlorate analysis was performed using an ion chromatograph (Dionex 2500, Dionex Corporation, 527 Lakeside Drive, Building 5, Sunnyvale, California 94086). The Dionex 2500 contains an IP 25 isocratic pump an EG 50 eluent generator, a CD 25 conductivity detector, 2 mm AG16/AS16 guard and separation column pair, and an AMMS III suppressor. The column, suppressor, and detector were housed in a LC 30 chromatographic oven. The eluant was 50 mM KOH and the suppressant was 50 mM sulfuric acid. A 1000 μL injection loop was used and the elution time ranged from 9.5 to 10.9 minutes. An eleven-point multi-range internal calibration curve was constructed using duplicate injections over a concentration range from 0.5 to 500 μg/L (Ellington and Evans, 2000). We estimated a reporting level of 1.0 μg/L in water using the methods described above. For data analysis and data plots, any data point below 1.0 μg/L was reported as 0.0 μg/L.

C. Principal finding and significance

Occurrences and distribution of perchlorate in Yuma groundwater

In the first three stages of the survey, the sampling team was able to sample eighty wells consisting of drainage, irrigation, public water supply, and household wells. The range of depth of the wells surveyed varied from 20.0 to 810.0 ft; the average depth of the wells

surveyed was 193.0 ft, with the median depth being 220.5 ft. In reporting the depth of the drainage wells, an average value of 220.5 ft was reported for all drainage wells. This was done due to a lack of updating of official records reflecting the changes in the status of the drainage well. Many of the wells in the original database were redundant, retrofitted, or new-well drilled in the close vicinity of the original well, but the records were not updated and maintained accurately. Thus, it was thought prudent to take the original database regarding the depth of the drainage wells and report the average depth of 220.5 ft (max: 339.0 ft and min: 133.0 ft; n = 16) from the original database as the depth of all drainage wells in data presentation.

Results of the perchlorate analysis of the eighty well water samples collected showed that only 29.0 % of the wells surveyed had detectable levels (≥1.0 μg/L) of perchlorate. The perchlorate concentrations seen ranged from below detection to 12.3 μg/L. The concentrations seen do not exceed the state of Arizona advisory level of perchlorate in drinking water of 14.0 μg/L (Arizona Department of Environmental Quality, 2004). Only three percent of the wells surveyed exceeded perchlorate concentrations of 4.0 μg/L, and only one percent of the wells sampled had perchlorate concentrations greater then 10.0 μg/L. The perchlorate concentration for the first 80 wells surveyed in the Yuma regional aquifer is shown in Figure 2. The perchlorate distribution profile against well depth is shown in Figure 3. There is no correlation between perchlorate concentration and depth of the well for all the wells surveyed that were greater than 20.0 ft in depth.

Based on the results of the 80 wells sampled, the sampling program was further expanded to include shallow observation wells (<20.0 ft in depth) belonging to the US Bureau of Reclamation to ascertain the perchlorate concentration profile of the Yuma aquifer below 20.0 ft. The depth of the observation wells ranged from 3.2 to 19.0 ft, with a mean depth of 8.8 ft; the median depth of the observation wells sampled was 8.2 ft. The perchlorate distribution of the 20 US Bureau of Reclamation observation wells sampled is shown in Figure 4. Of the 20 observation well water samples collected, 55.7% of the wells surveyed had detectable levels (≥1.0 μg/L) of perchlorate. The perchlorate concentrations seen ranged from below detection to 19.6 μg/L. Approximately 16.5% of the wells surveyed exceeded perchlorate concentrations of 4.0 μg/L and 2.3% of the wells sampled exceeded the state of Arizona advisory level of perchlorate in drinking water of 14.0 μg/L. None of the observation well waters exceeded the DWEL of 24.5 μg/L calculated from the reference dose (USEAP 2005) of 0.7 μg/kg per day adopted by the USEPA on recommendation from the National Academy of Science (NAS, 2005). This reference dose is based on a no-observed effect level (NOEL) of 7 μg/kg from a human perchlorate dosing study to which a 10-fold uncertainty factor was applied to address potential sensitive subpopulations (Greer et al., 2002).

The perchlorate distribution profile against well depth for the observation wells are shown in Figure 5. There seems to be no significantly discernable correlation between perchlorate concentration and depth for the observation wells sampled.

It is important to note that even with years of irrigation with Colorado River water containing perchlorate, the Yuma aquifer water is safe with respect to perchlorate concentration. None of the well waters sampled exceeded the calculated EPA DWEL of 24.5 μg/L. All wells sampled with a depth greater than 20.0 ft had perchlorate concentrations less than the state of Arizona advisory level of perchlorate in drinking water of 14.0 μg/L. This implies that all PWS and domestic wells sampled in the Yuma region are safe with respect to perchlorate exposure and are not a public health concern.

Although within the calculated EPA DWEL of 24.5 μg/L, the presence of perchlorate in well water seems to be more prevalent in the observation wells (Note: the depth of the observation wells ranged from 3.2 to 19.0 ft, with 72.2 % of the wells surveyed having perchlorate concentrations ranging from below detection to 4.0 μg/L). The perchlorate concentration range seen in the observation wells is similar to the range of perchlorate concentrations reported for irrigation water (1.0 to 3.9 μg/L) for the year 2005 reported Figure 1. What this may imply is that the zone of influence of the irrigation events may be limited to the shallow depths of the aquifer. As the irrigation water enters deeper depths of the aquifer, the perchlorate concentration is possibly diluted by perchlorate-free water present in the aquifer, and, also, quite possibly, the perchlorate present is reduced by chemical and microbial action. Prior researchers have reported on the potential of chemical and microbial reduction of perchlorate (Coates et al., 1999; Coates et al., 2000; Chauduri et al., 2002). As efforts are underway in eliminating the source of contamination of perchlorate into the Colorado River (Hogue, 2003), the concentrations in the irrigation water should decrease further.

Quality of Yuma groundwater with respect to pH, conductivity, and taste

The field data comprised of measurements of pH, temperature, and conductivity. The pH of the well waters sampled ranged from 6.07 to 8.40, with the mean and median values of 7.41 and 7.45, respectively. The median temperature of the well waters sampled was 27.9 ^{o}C. The specific conductivity ranged from 398 to 1831 uS/cm; the mean and median specific conductivity was 874 and 820 uS/cm, respectively. While sampling domestic wells, a common complaint of the household users was that the water was salty in taste and, therefore, they were not using the well water for drinking. The primary use of the well water was for cleaning, gardening, and cooking. Rural households were more inclined to purchase reverse osmosis treated water from water stations

Summary

This report describes the preliminary investigation of perchlorate occurrence in the groundwater of the Yuma region of Arizona. There is a concern that years of irrigation with perchlorate contaminated Colorado River water may have contaminated the Yuma aquifer with perchlorate, and that communities around the greater Yuma region using groundwater as their source of potable water may be exposed to perchlorate by drinking perchlorate contaminated groundwater.

The results of the survey showed that well waters being used by PWS and rural households are well within regulatory limits of perchlorate. Detectable perchlorate concentrations are mostly limited to wells less than 20 ft in depth, and the concentration ranges seen reflect concentrations seen in the Colorado River water, which is within the calculated EPA DWEL of 24.5 μg/L.

PUBLICATION INFORMATION

The presentations and publications are pending, but we anticipate presenting the findings of the project at the National Groundwater Summit, 2007, and submitting a manuscript to the Journal of Hydrology of The Southwest Region.

STUDENT SUPPORT

The program "survey to determine the occurrence of perchlorate in the groundwater of Yuma Arizona" has served as a platform in the training of two students attending Arizona Western College, and a technician at the University of Arizona, Yuma Agricultural Center. Project personnel obtained valuable skills in procedures of water sampling, operation of wet chemistry equipment, and operation of Global Positioning System equipment. The participants were also exposed to the required procedural record keeping involved in conducting a regional water quality survey. The project personnel were trained by Dr. Nadim Khandaker, a highly experienced Environmental Engineer.

NOTABLE ACHEIVMENTS AND AWARDS

None to be reported.

References

Arizona Department of Environmental Quality. Perchlorate in Arizona: Occurrence study of 2004.

Chauduri, S. K., S. M. O'Connor, R. L. Gustavson, L. A. Achenbach, and J. D. Coates. 2002. Environmental factors that control microbial reduction of perchlorate. Appl. Environ. Micro. 68: 4425-4430.

Clark, J.J. Perchlorate toxicology (Chapter 3). In Perchlorate in the Environment, E.T. Urbansky, (ed.). Kluwer/Plenum. New York, NY. **2000**.

Coates, J.D., U. Michaelidiou, S. M. O'Connor, R. A. Bruce, L. A. Achenbach. 2000. The diverse microbiology of (Per)chlorate reduction (Chapter 24). In *Perchlorate in the Environment*, E.T. Urbansky, (ed.). Kluwer/Plenum: New York, NY.

Coates, J.D., U. Michaelidou, R. A. Bruce, S. M. O'Connor, J. N. Crespi, and L. A. Achenbach. 1999. The ubiquity and diversity of dissimilatory (per)chlorate-reducing bacteria. Appl. Environ. Microbiology 65: 5234-5241.

DHS. Standards for perchlorate in drinking water. Department of Health Services, Sacramento, California. **2000,** www.dhs.cahwnet.gov/org/ps/.

Ellington, J.J., and Evans, J.J. 2000. Determination of perchlorate at parts-per-billion levels in plants by ion chromatography. J. Chromatr. 898:193-199.

Greer, M. A.; Goodman, G.; Pleus, R. C.; Greer, S. E. 2002. Health effects for environmental contamination: the dose response for inhibition of radioiodide uptake in humans. *Environ. Health Perspect.* **2002,** *110*, 927-937.

Hogue, C. 2003. Rocket-Fueled River: Lower Colorado carries perchlorate to millions who drink its water, to those who eat lettuce irrigated with its water, and into a tribal well. Chemical and Engineering News. August 18. 37-46.

National Academy of Science. National Research Council of the National Academies Press (2005) Washington. DC.

U.S. EPA. U.S. EPA Method 314.0. U.S. Environmental Protection Agency. National Exposure Research Laboratory and Office of Research and Development, Cincinnati, OH 45268.

USEPA. Reference dose for chronic oral exposure. **2005**. http://www.epa.gov/iris/subst/1007.htm

Figure 2. **The perchlorate concentration distribution for the first 80 wells surveyed in the Yuma regional aquifer.**

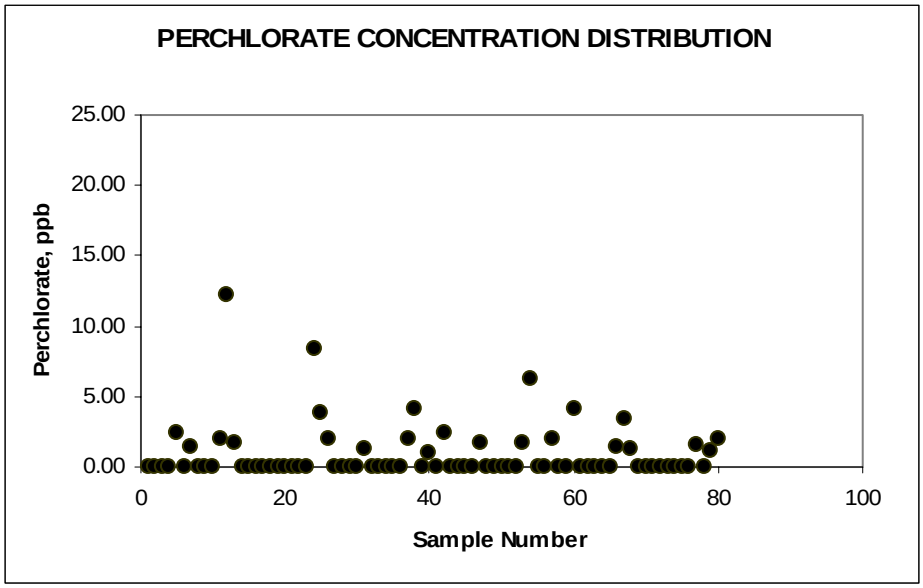


Figure 3. **The perchlorate distribution profile against well depth for the first 80 wells surveyed in the Yuma regional aquifer.**

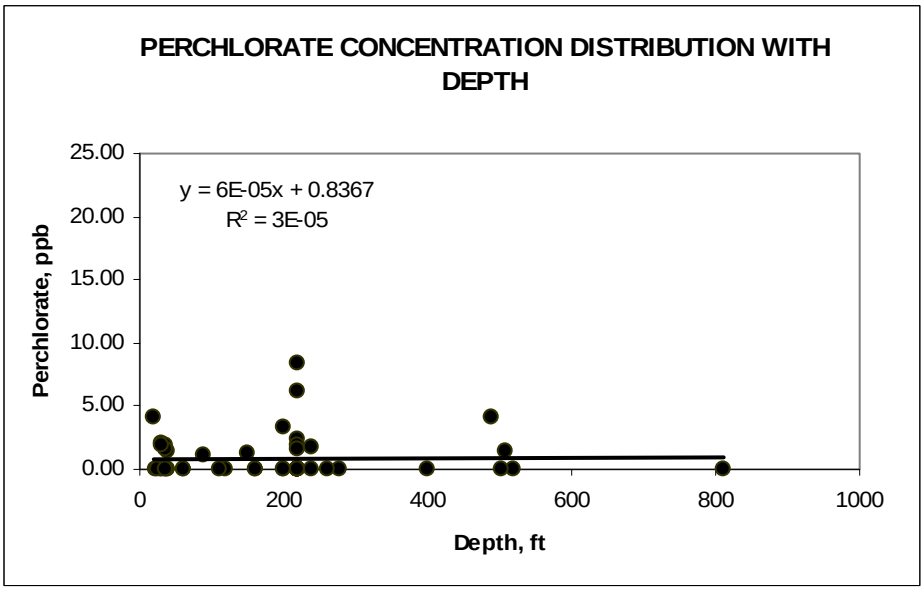


Figure 4. The perchlorate distribution of the 20 US Bureau of Reclamation observation wells sampled in the Yuma regional aquifer.

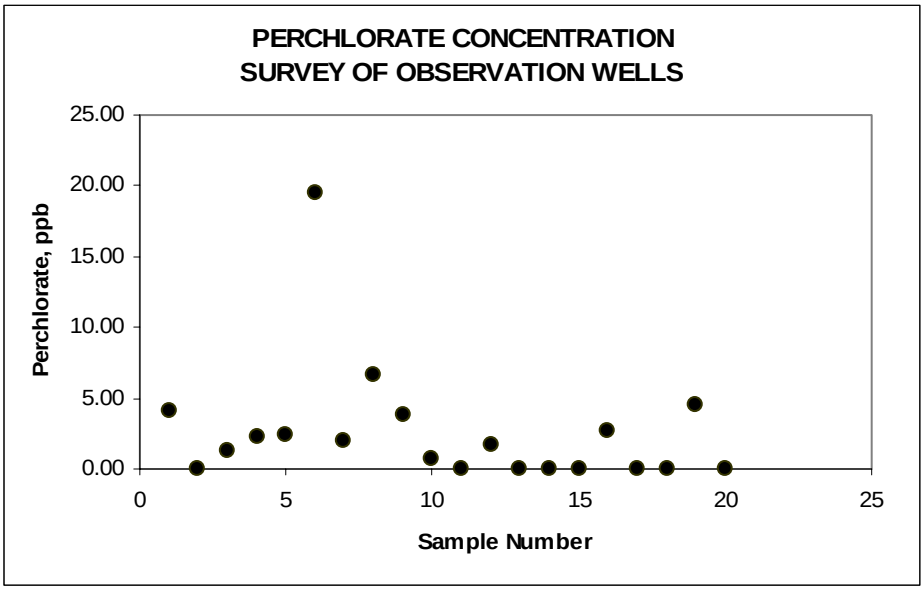


Figure 5. The perchlorate distribution profile against well depth of the 20 US Bureau of Reclamation observation wells sampled in the Yuma regional aquifer.