U.S. EPA TECHNICAL SUPPORT PROJECT
TECHNICAL SESSION SUMMARY

October 18-21, 2004
Hyatt Regency Hotel
Sacramento, CA

COMMUNICATION • TRAINING • TECHNICAL SUPPORT •
TSP
Technical Support Project

U.S. EPA TECHNICAL SUPPORT PROJECT CO-CHAIRS

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Monday, October 18

Statistical Analysis (Kriging) of Water Level Data and Optimization of a Pump and Treat System and Analysis of Capture Zones for Pumping Wells
Matthew Tonkin, S.S. Papadopulos and Associates

Capture zones are typically delineated using numerical/analytical models, or through interpolation (mapping) of measured water levels. Numerical models offer great flexibility and predictive power, but the level of effort required to confidently assess capture zones is often prohibitive. Maps of water level data are intuitively appealing; however, contours of water level data are typically unsuitable for delineating capture zones. Inspection of most water level maps indicates large departures from the mean in areas of localized discharge or recharge, or other boundaries, and inference is actually limited to broad features such as principle directions of flow. Combining the kriging interpolation method with analytical trend or drift models (termed "universal kriging"). can account for many aspects of the physics of ground-water flow. Data requirements are limited to knowledge of the location and rates or elevations of significant boundaries. A primary benefit of this approach is an improved estimate of the hydraulic gradient and velocities suitable for particle tracking to delineate capture zones.

To view Matthew Tonkin's presentation for more details, click here.

Results of an Extensive Passive Diffusion Bag Sampler Demonstration
John Tunks, Parsons Engineering (now with Mitreteck Systems

John Tunks presented preliminary results of a recent DOD demonstration that compared the use of passive diffusion bag samplers (PDBSs) with conventional methods for collecting ground-water samples for chemical analysis. The demonstration, conducted at 20 DOD installations across the country, evaluated and compared analytical results and costs associated with the two methods. The ground-water samples were analyzed for 48 VOCs, including contaminants now emerging at federal facilities.

The demonstration encompassed 1,494 PDBSs deployed in 480 ground-water wells over a period of two years. Multiple PDBS were deployed at 3-foot intervals in wells at least 2-inches in diameter to derive vertical profiles of the potential contaminants at each test site. Conventional sampling in each well was typically performed by the base environmental contractor.

Comparison of the laboratory results obtained from PDBSs and conventional sampling was accomplished using a simple regression and the calculation of correlation ratios. The slope of an x-y scatter plot for all compounds tested had a slope of 0.93 and r^2 of 0.77, showing a good correlation of the data and a tendency of the PDBSs to yield slightly higher concentrations of contaminants. The slope for TCE alone was 1.06 (r^2= 0.83) showing slightly lower concentrations of TCE using PDBS.

Correlations ratios—the ratio of the number of correlations to the number of comparisons made—were calculated. The PDBS data were considered to correlate with the corresponding conventional sampling data if at least one of five different correlation criteria were met:

- the PDBS result was greater or equal to the result obtained by conventional sampling;
- the relative percent difference was less than or equal to 50%;
- the difference between the results was equal to the reporting limit, if both results were less than or equal to three times the reporting limit;
- the difference between the PDBS and conventional results was less than or equal to 5 : g/L; and

- the compound compared was appropriate (nine were judged inappropriate to compare for various reasons).

The overall results of statistical analysis indicate that 44 of the 48 VOCs met correlation criteria in at least 70% of the sampled wells. In addition, 87% of the 445 wells met correlation criteria for at least 70% of the compounds detected. Potential use of PDBSs was deemed appropriate in the 334 wells that met the correlation criteria for all detected compounds. Non-correlation may have several explanations, including the deployment duration, stratification of the contaminants, characteristics of the sampled aquifer, etc. However, inherent differences between the sampling methods were deemed most important.

The cost savings of using PDBS during the demonstration were determined to be $241 per well per sampling event, which can mean significant savings in long-term monitoring. The demonstration concluded that a PDBS strategy can effectively monitor VOC concentrations in ground water. Validation of PDBS technology prior to full-scale application is recommended to ensure site- and well-specific conditions are met.

Questions and Answers

Question: The presentation indicates that low-flow samples collected from a single screen interval were compared to samples collected at multiple levels. How can a comparison of non-comparable data such as these be valid?
Answer: Ideally, comparable samples are collected from the same interval and at the same position within each interval. Comparisons may be limited, however, by device deployment variations and accessibility limitations within the interval and well.

To view John Tunks' presentation for more details, click here.

Demonstration of Alternative Ground-Water Sampling Technologies at McClellan AFB
John Tunks, Parsons Engineering (now with Mitretek Systems)

Parsons Corporation and the Air Force partnered with other federal agencies, contractors, and sampler manufacturers to evaluate several no-purge ground-water sampling devices capable of monitoring all compounds. They compared the results with those of conventional methods of sampling (i.e., low-flow purge and 3-volume purge sampling) on the basis of analytical results, ease of use, and cost. The evaluation and comparison involved four diffusion-based devices (passive diffusion bag sampler, polysulfone membrane sampler, rigid porous polyethylene sampler, and the regenerated cellulose sampler) and two grab-based devices (HydraSleeve® and the Snap Sampler™).

Mr. Tunks summarized the construction and use of each type of sampler and some of their advantages and disadvantages. In order to adequately compare this number of samplers, some of which had limited sample volume and analyte capabilities, the team had to identify a site with enough wells containing the target analytes and sufficient screened depths for vertical profiling. Larger well diameters were also required in order to deploy several samplers simultaneously at the multiple depth intervals. Several issues were considered when developing a sampling plan including concurrent deployment of multiple samplers in a well at multiple depths, equilibration time required for deployed samplers, and minimum sample volume analysis requirements. Due to the equilibration periods required for the no-purge samplers, sampling had to be phased and sequenced to deploy, retrieve, and purge the wells while minimizing well disturbance.

McClellan AFB was selected for the demonstration due to the large number of large-diameter wells and target analytes. A three-phased approach to sampling the wells was taken: I) deploy the diffusion samplers (May 17-21, 2004); II) retrieve the diffusion samplers and deploy the grab samplers (June 6-11, 2004); and III) retrieve the grab samplers and collect the conventional samples (June 13-19, 2004).

The analytical results of each sampling technique were compared to the corresponding results from the other sampling techniques using three statistical methods: x-y scatter plots, median relative percent difference (RPD), and the Wilcoxon Matched-Pairs Signed Rank method. Each method was performed on six different data sets: all results for every compound, 1,4-dioxane, anions, hexavalent chromium, metals, and VOCs. If all three approaches yielded the same conclusion, then that conclusion was considered "validated." If only two of the three results corresponded, then no definitive conclusion was made. The results of the statistical comparisons showed that conventional sampling methods did not always sample the highest concentrations in a well. No one sampling method was found to produce the most conservative result. The initial results of this demonstration suggest that depending on a site's DQOs, sampling techniques other than conventional ones may be appropriate.

Tuesday, October 19

Welcome and Introduction

Kathleen Johnson, U.S. EPA, Region 9, Branch Chief of Federal Facilities and Site Cleanup Branch and Rick Brausch, California DTSC, Assistant Secretary for External Affairs

Kathleen Johnson (Region 9) welcomed participants to Sacramento and gave a general overview of the Federal Facility and Site Cleanup Branch's responsibilities in the Region. Although new to her current position, Kathleen has been with EPA in the Superfund Division for 17 years. She has worked extensively with lawyers, engineers, and scientists throughout her career and understands the importance of communication among groups with different training and experience. Kathleen applauded the TSP for furthering technology transfer and the dissemination of critical scientific knowledge across divisions, programs, branches, and regions. In order to adequately protect human health and the environment, EPA must rely on good science and sound decision-making. OSWER and ORD deserve tremendous credit for supporting the work of the three TSP forums. Emerging contaminants present great challenges, and the topic of this meeting is timely considering some of the contaminant issues that Region 9 must address. In the past five years, EPA has seen numerous contaminants without MCLs emerge as true threats to human health and the environment. The TSP will help the Agency disseminate pertinent technical information relating to these emerging contaminants in an effective and efficient manner.

Rick Brausch (CA DTSC) helps coordinate cleanup programs within the State of California. He regularly works with the Regional Water Quality Control Boards and other state organizations to ensure that environmental issues are dealt with in a consistent fashion across the state. The growing threat posed by perchlorate and other emerging contaminants has alarmed state regulators in recent years, and his office considers the characterization and cleanup of these contaminants to be a priority. The state's public heath goal for perchlorate, which is currently 6 ppb, is not as low as DTSC would like. The California Department of Health Services (DHS) is developing a drinking water standard that should be effected in the near future.

California has a long history of water supply issues, and perchlorate contamination has recently been added to the list of concerns. Perchlorate has been detected in over 350 public water supply systems throughout the state, eclipsing the incidence of MTBE. The state is focusing on identifying the sources of this contamination. DTSC has been working with U.S. EPA, DoD, DHS, and the California Department of Fish and Game to get a handle on the situation and cement partnerships that will lead to the assessment, monitoring, characterization, and cleanup of areas contaminated with perchlorate. Some areas of the state, such as Los Angeles County, are farther along in addressing perchlorate contamination than others. Because of limited budgets, funds must be allocated and spent wisely. Private industries also are being asked to partner with the state to address perchlorate concerns at or near factories, storage centers, and manufacturing facilities. Perchlorate contamination is of critical importance in California because water is a precious commodity. Rick thanked the TSP and EPA for their contributions toward understanding the nature and extent of perchlorate contamination and for disseminating important information to critical stakeholders.

Perchlorate Introduction

Kevin Mayer, U.S. EPA, Region 9 Superfund Division

Perchlorate is both a man-made and naturally occurring salt that has recently been discovered as a threat to drinking water supplies. Manufactured perchlorate is a component of solid rocket fuel and is used for explosives, fireworks, and other applications. This chemical is of concern because it can adversely affect the thyroid in adults and can pose a greater health risk to infants and children. Perchlorate can be taken up and accumulated in some plants and can adversely affect the thyroid of animals.

Prior to April 1997, perchlorate could not be detected in low concentrations. Little was known about its toxicity, how to remove it from water, or the extent perchlorate had contaminated drinking water supplies. In 1997, the California DHS developed a new analytical method to detect very low levels of perchlorate in water. Since then, this chemical has been found in the water supplies of more than 16 million people in California, Nevada and, Arizona. It has also been found in surface and ground water throughout the United States—in 35 states plus Puerto Rico.

Currently, there is no Federal Maximum Contaminant Level for perchlorate. In March 2004, California established Public Health Goal of 6 ppb in drinking water and is considering a formal drinking water standard based on this level. Seven other states (AZ, MA, MD, NV, NM, NY, and TX) have advisory levels ranging from 1 to 18 ppb. In January 2002, EPA published a draft toxicity assessment which suggested that perchlorate may pose a risk, particularly to newborns and children, at levels near 1 ppb. EPA's scientific analysis has been challenged by some of the affected parties who participated in funding the recent studies. The National Academy of Sciences will be evaluating EPA's draft toxicity assessment.

EPA Region 9's Superfund Program is actively involved in addressing perchlorate issues due to the chemical's presence at 12 Superfund NPL sites and more than 30 other locations within the Region. At Superfund sites in California, pioneering efforts have led to successful implementation of full-scale perchlorate treatment systems using physical/chemical and biological methods. These systems remove perchlorate from tens-of-millions of gallons of contaminated water per day. They are treating water with as much as 5,000 ppb of perchlorate and attaining levels well below the 6 ppb California Action Level. Significant strides also have been made to improve methods to detect lower levels of perchlorate with increasing certainty.

EPA Perchlorate websites:
http://www.epa.gov/fedfac/documents/perchlorate.htm
http://www.epa.gov/safewater/ccl/perchlorate/perchlorate.html
http://www.clu-in.org/perchlorate

To view Kevin Mayer's presentation for more details, click here.

ITRC-Perchlorate Action Team
Mark Malinowski, CA DTSC

Mark Malinowski (CA DTSC) gave an overview of Interstate Technology Regulatory Council's (ITRC) most recent activities relating to perchlorate. ITRC is a state-led, national coalition of regulators working to improve state permitting processes and speed the implementation of new environmental technologies. Their goals are to achieve better environmental protection through use of innovative technologies, reduce technical and regulatory barriers associated with the use of these technologies, and build confidence about using new technologies. In addition to state regulators, representatives from academia, industry, federal and state agencies, and the public often contribute to ITRC deliverables and participate in workgroups. ITRC appoints teams of individuals to work on issues important to the regulatory community. The co-leaders of ITRC's Perchlorate Team are Mark and Sara Piper (Nevada Division of Environmental Protection). There are 47 active members of the perchlorate team, 13 of whom represent 10 states. Representatives from EPA, DoD (Air Force, Army, and Navy), and other stakeholders and tribal entities also are members of the team. In addition, there are 24 interested parties that support the efforts of the 47 team members.

The Perchlorate Team's mission is to identify existing and emerging perchlorate treatment technologies and streamline the review, assessment, and approval process for these technologies. The team is primarily involved with publishing an overview document, compiling state standards survey results, identifying stakeholder issues, and establishing a basis for the development of a technical/regulatory document.

Early in 2004, the team divided into sub teams and completed a first draft of the overview document in August. A second draft is in progress and will go out for review early in 2005. A final overview document is expected later in 2005. The overview document covers risk and the status of the current toxicological evaluation, existing state standards and guidance, current management practices, analytical methods and issues, and remediation technologies. The state standards survey was distributed in August 2004. Results will be incorporated into the overview document and will be posted to ITRC's website (www.itrcweb.org) when available.

In the near future, ITRC's Perchlorate Team hopes to publish the overview document (early 2005), a technical and regulatory guidance document (2006), and conduct outreach and training (2005-07).

Questions and Answers

Question: What does the technical/regulatory document contain?
Answer: The document discusses potential uses of new technologies, how to implement them, and the regulatory barriers to their use. It also will include information on costs and will present several case studies.

Question: Will the results of the state surveys be available to anyone?
Answer: Yes, they will be accessible on the ITRC website.

Question: Do you know the number of people who have been exposed to perchlorate in California?
Answer: In California, 357 wells have concentrations at or above 4 : g/L. Between populations served by water originating from the Colorado River or Lake Mead, total exposure is likely between 10 and 20 million.

To view Mark Malinowski's presentation for more details, click here

Assessing Perchlorate Exposure: Occurrence in Large Geographical Areas and Uptake in Mammals

Todd Anderson, Texas Tech University

Texas Tech University (TTU) conducted two studies on perchlorate occurrence in west Texas. Discoveries of high levels of perchlorate in ground water during the late 1990s led to the initial study, which focused on identifying the distribution and sources of perchlorate in the High Plains Aquifer System, which includes the saturated portions of the Ogallala Formation, Cretaceous strata of the Trinity and Edwards Groups, and Cenozoic strata. Hundreds of wells were sampled within a 54-county area. Researchers postulated that the distribution of perchlorate observed may correspond to areas of human activities. Although perchlorate is a naturally occurring substance, particularly in arid region, it also is commonly associated with industrial, DOD, DOE, and agricultural activities.

The project team collected ground-water samples from 560 public well supplies and 76 private wells covering an area roughly one-third the size of California. The data set was augmented by sample data from 100 locations periodically tested by the High Plains Underground Water Conservation District (HPUWCD), 29 existing USGS sampling locations, and 16 nested wells installed by TTU and USGS. Additional samples were collected from 10 private wells in a two-county area of eastern New Mexico.

Ground-water samples were analyzed for perchlorate in accordance with EPA's Method 314.0. Perchlorate concentrations exceeded 4 ppb in 18% of the public wells, 30% of the HPUWCD wells, 41% of the USGS wells, 30% of the private wells in Texas, and 60% of the private wells in New Mexico. Perchlorate was detected in all four of the area's major aquifers. Perchlorate concentrations were found to inversely correspond with depth to the water table and thickness of the saturated zone. Ground-water samples from nested wells also showed that perchlorate levels tend to be higher in samples with tritium levels indicative of post-atomic bomb age (>0.5 tritium units) indicating newer water.

The extent of perchlorate in the region can be attributed to historical and current irrigation activities, which typically result in highly mixed aquifer systems. The estimated total perchlorate mass in the unsaturated zone ranges by two orders of magnitude across the 54 counties, but peaks at 490,000 kg in Gaines County. Based on the estimated mass of perchlorate that could be present due to potential human sources (including seismic explosions, highway flares, and tainted nitrate fertilizers) TTU researchers concluded that human sources could not have produced all of the perchlorate present in the environment. Thus, naturally occurring perchlorate from oxidative weathering and the atmosphere, must contribute to the total mass. They noted that samples containing elevated iodate levels—suggesting an atmospheric source—also tended to have higher perchlorate levels.

TTU conducted a second study to better understand the potential for perchlorate uptake in large mammals, and the subsequent potential for perchlorate uptake in humans via milk consumption. The study was conducted on: (1) two reference calves and two calves with 14-week exposure to perchlorate-contaminated ground-water springs in McLennan County, TX (near the Naval Weapons Industrial Reserve Plant); and (2) adult cows with long-term perchlorate exposure via water consumption from contaminated ponds in Morris County and Cherokee County, KS (near slurry explosives plants).

In the Texas study, blood samples were collected and analyzed every two weeks for perchlorate and thyroid hormones. Urine samples were collected when possible and analyzed for perchlorate, and tissue samples were analyzed at the study's conclusion. The drinking water was analyzed every two weeks. Although perchlorate was detected in all of the water samples (concentrations ranging from around 18-33 ng/mL), perchlorate was detected in only two of eight blood samples, slightly above and below the MDL of 13 ng/mL. Perchlorate was not detected in the tissue samples, and there was no significant differences in thyroid hormones between the exposed calves and reference calves.

In the Kansas study, blood from the adult cows was sampled once for both perchlorate and thyroid hormones. The drinking water supply and vegetation were also sampled once for perchlorate. Urine samples were collected when possible. Perchlorate concentrations in the drinking water ranged from non-detect to 200 ppb, and ranged from non-detect to greater than 6 ppm in the vegetation samples. Although the exposure scenario was more variable in this study, detections of perchlorate were also infrequent and thyroid hormones appeared normal.

QUESTIONS AND ANSWERS

Question: In the initial study regarding perchlorate occurrence, did differing amounts of rainfall across the study area impact the findings?
Answer: The amount of rainfall was generally the same throughout the study area.

Question: How did the study account for reports showing that 60% of the rain samples collected in west Texas show extremely elevated concentrations of perchlorate?
Answer: Recent analytical results for rain samples collected in many regions of the U.S. show similar results, although the cause is unknown. As such, TTU's study did not attempt to address the problem of perchlorate elevation in rain water.

Question: Which of the two natural causes—oxidative weathering or atmospheric influence—is more likely to create the inconsistent perchlorate distributions exemplified in west Texas?
Answer: We suspect that atmospheric influence may be the most significant factor.

Question: Would it be reasonable to sample the milk from dairy cows to assess uptake of perchlorate if cattle are exposed to high concentrations of perchlorate?
Answer: It is possible to observe perchlorate in dairy milk, but most perchlorate is excreted from large mammals through urine. Therefore, development of a urine method offers the best chance for determining the animals' uptake.

Question: Would the presence of ammonium ion in urine affect perchlorate analyses?
Answer: Cations usually do not pose a problem with the analysis, but we haven't examined this possibility.

Question: Is it possible that the cattle take up perchlorate by eating alfalfa grown in areas irrigated with perchlorate-contaminated water?
Answer: The cattle in the Kansas study area are generally pasture fed with supplements of hay; therefore, contaminated alfalfa is not an issue. Generally, perchlorate uptake in vegetables with high water intake (such as lettuce and cucumbers) is known to pose problems.

Question: What is meant by the 8-hour half-life of perchlorate in cattle?
Answer: This refers to the half life in the cattle's body. Although the urine samples were collected daily at 9 am, if an animal had just urinated prior to sampling, perchlorate would not be observed.

Question: Dr. Andrew Jackson (TTU) indicated that 60% of the rainwater samples contained perchlorate. Were these samples collected in the Texas Panhandle?
Answer: Those samples were collected all over the U.S., not just Texas.

Question: Given that commercial milk samples tested at TTU contained perchlorate, even though perchlorate supposedly is excreted, are you confident in the urine screening method used in the cattle study?
Answer: The milk data have been used out of context, so we cannot be confident in the data. It is inappropriate to report ion chromatography data less than 1ppb. A lot of work must be done to develop a sensitive method for milk analysis that we can have confidence in.

To view Todd Anderson's presentation for more details, click here

Perchlorate in Selected Natural Materials and Perchlorate Occurrence in Ambient Waters

Stephen Kalkhoff, U.S. Geological Survey

Stephen Kalkhoff presented some preliminary data from research led by Greta Orris (USGS) on the presence of perchlorate in selected natural materials and their derivative products, as well as his own research of perchlorate occurrence in the waters of the central and southwestern United States. Potash ores, playa crusts, hanksite crystal, kelp, and various fertilizers were tested for their perchlorate content. Very little perchlorate was found in the fertilizers and other derivative products. The potash ores, playa crusts, hanksite, and kelp samples did contain measurable levels of perchlorate demonstrating that perchlorate can be found in naturally occurring materials.

Manufacturers and users of perchlorate are present in virtually every state, and releases from these sources have been identified in at least 25 states. Potential sources of perchlorate, other than perchlorate manufacturers and users, include wastewater discharges from related industries, mineral fertilizers, and precipitation. The USGS study concentrated on a possible correlation between the occurrence and distribution of perchlorate in rivers, streams, and ground water in the central and southwestern U.S., and the use of mineral fertilizers and the amount of precipitation.

In the Midwest, fertilizer application rates were used to determine sampling frequency with the hypothesis being that application rates and perchlorate concentrations could be correlated. In addition to farmland, the sampling was also conducted in some urban discharge areas and some relatively undeveloped basins that might represent background levels.

To shed some light on what affects precipitation (percolation and runoff) has on perchlorate concentrations in surface and ground waters, sampling also was conducted across a precipitation gradient with sampling areas ranging from very high levels of precipitation (Louisiana) to very low levels (Arizona and Nevada).

Along with measuring perchlorate concentrations in the water samples, general water chemistry parameters were measured and biological community information was collected for surface water samples. A number of land use and physiographic parameters also were noted at each sampling point. Using a method developed by Texas Tech University, researchers expect to achieve a detection limit for perchlorate of less than 1 ppb. The sampling was done during the summer of 2004, and there are no analytical results available yet.

Questions and Answers

Question: Have you done any reverse particle tracking to the recharge areas to determine if they are sources?
Answer: No.

Question: Are you analyzing perchlorate concentrations in precipitation to see if there is a correlation to concentrations in ground water?
Answer: Only indirectly. The research is focusing on at the amount of precipitation versus concentrations in ground water.

Question: What is the schedule for releasing the study reports?
Answer: The analytical data will be compiled by the end of the 2004. The first draft of the report is expected by the end of FY05. The data report should be completed by the end of next summer.

Question: If you should find surprising results, such as a high concentration in a given area, how would you deal with that?
Answer: We would resample the area and collect duplicate samples to ensure the numbers are real.

Question: What data do you have on the fertilizers being used in the states in which you are sampling?
Answer: We have not analyzed samples of the fertilizers being applied in the research areas but are relying on the work of others, such as Greta Orris. If we do not find perchlorate in the water samples, it does not necessarily mean it is not present in the fertilizer.

To view Stephen Kalkhoff's presentation for more details, click here

Perchlorate Treatment at the Goodyear Wastewater Treatment Plant
Laurie LaPat-Polasko, Geomatrix Consultants

Ground water at the Phoenix Goodyear Airport North Facility (PGA-N) is pumped from five extraction wells and treated for VOCs using an air stripper. Air stripping does not treat perchlorate; however, this compound has been recently detected in the ground water at the site. As an alternative to the current approach of reinjecting the ground water, Dr. LaPat-Polasko proposed discharging the VOC-treated ground water to the local sewer system for biological treatment at the Goodyear Wastewater Treatment Plant (GWWTP). At the GWWTP, wastewater discharges to an anoxic zone, followed by a tapered aeration zone, which is then followed by an anoxic basin, where denitrification and perchlorate biodegradation occur. The effluent then passes through a clarifier prior to discharge.

Biodegradation of perchlorate was shown to occur even though samples were maintained on ice or in the refrigerator. These analytical results prompted the development of a new preservation technique. Samples were first filtered through a 1-:m filter to remove microorganisms, and then amended with a final concentration of 10 mg/L hypochlorite This procedure sufficiently inhibited further biodegradation of the collected sample.

Perchlorate has been found to biodegrade under denitrifying conditions Bench-scale tests were conducted at PGA-N to demonstrate biodegradability of perchlorate at the site. Samples containing perchlorate at the levels found at the site as well as samples spiked with higher levels were tested. The results showed that after 13 days, the percent reduction in perchlorate by biodegradation was >99.3%, whereas sterile samples without microorganisms yielded <9.1% reduction. Both sterile and non-sterile samples yielded similar decreases in nitrate concentrations.

Flow measurements made before and after discharging ground water from PGA-N were used to evaluate the potential for leaks in the pipeline between PGA-N and the GWWTP. Two weeks before ground water was discharged to the GWWTP, the flow rate was approximately 0.7 MGD to the plant. Following discharge from PGA-N, the flow increased to approximately 1 MGD. The average increase in flow rate was similar to the average discharge rate from PGA-N (0.3 MGD), so the flow balance identified no substantial loss of water. The sewer was also tested to estimate biodegradation losses of perchlorate within the sewer line. The measured concentration at the end of the sewer line was 5.6 :g/L versus the projected 12.8 :g/L concentration if no biodegradation occurred. These results indicate a significant decrease in perchlorate, which is likely due to biodegradation in the sewer line.

To assess whether treatment would work at full-scale, a bromide tracer test was conducted at the GWWTP. Bromide and perchlorate were injected into the GWWTP at known concentrations. If the perchlorate disappeared faster than the bromide, then biodegradation was confirmed. The measured perchlorate levels were much lower than expected based on the measured bromide levels, indicating that biodegradation was indeed occurring.

The subsequent pilot-scale testing was done in three phases: I) with an approximate 100 gpm groundwater discharge and a blended (with industrial/municipal wastewater) influent perchlorate level of approximately 5 : g/L; II) with an approximate 200 gpm discharge and a blended influent perchlorate level of about 8 : g/L; and III) with an approximate 300 gpm discharge (full flow) and a blended influent perchlorate level of about 9 : g/L. Each phase yielded effluent concentrations within acceptable levels (less than EPA's perchlorate treatment goal of 4 : g/L).

Phase IV testing involved monitoring water quality parameters (ORP, COD, NH_4^+ as N, NO_3^- as N, and TKN) as well as perchlorate concentrations during full-scale treatment. As ORP increased, so did nitrate levels in the effluent. Increases in ORP levels in the effluent were controlled with the addition of methanol. Although the COD of the influent increased with time due to a higher raw wastewater flow rate, COD in the effluent remained consistent. Perchlorate levels in the effluent remained consistent at <2 : g/L throughout Phase IV testing.

Questions and Answers

Question: Did you look at the effect of BOD on the concentrations of perchlorate?
Answer: Yes, but BOD did not significantly change at the plant because methanol was added to maintain appropriate biological conditions, which allowed for affective perchlorate biodegradation.

Question: Were you concerned about using methanol to control ORP?
Answer: No.

Question: Which analytical method was used for perchlorate?
Answer: We sent the samples to a laboratory in Richmond, CA, for analysis by Method 314.1.

Question: What was the co-eluding peak observed in the fourth chromatogram you presented?
Answer: The peak may represent bacteria cells, but this was not confirmed.

Question: What level of nitrate was found to affect the degradation of perchlorate?
Answer: At the GWWTP, in general nitrate concentrations were usually less than 1-2 mg/L. However, when concentrations were as high as 4-6 mg/L nitrate, perchlorate effluent levels still remained below 2 : g/L.

Question: What was the mean retention time of wastewater in the plant?
Answer: Approximately 24 hours.

To view Laurie LaPat-Polasko's presentation for more details, click here.

Perchlorate Impacts to Private and Municipal Wells in Santa Clara County, CA
Tom Mohr, Santa Clara Valley Water District

Summary to be posted at a later date.

1,4-Dioxane and Other Solvent Stabilizer Compounds: A ROD Re-Opener?
Tom Mohr, Santa Clara Valley Water District

Summary to be posted at a later date.

To view Tom Mohr's presentation for more details, click here.

Regulation of Perchlorate Impacts to Surface Water at a Rocket Motor Plant in Santa Clara County, CA

Keith Roberson, California Regional Water Quality Control Board (RWQCB), San Francisco Bay Region

Perchlorate is a completely soluble, highly mobile, inorganic anion that is used as an oxidizer in explosives. Perchlorate affects the thyroid by interfering with iodide uptake. It affects fetus development, but has not been shown to be a carcinogen. Although perchlorate is currently unregulated, the California Office of Environmental Health Hazzard Assessment has set a public health goal of 6 ppb. Currently, the California DHS is working to establish an MCL for perchlorate, but a national U.S. EPA MCL is likely years away.

United Technologies Corporation (UTC) is a 5,000-acre site located south of San Jose near the Anderson Reservoir. UTC has manufactured solid rocket motors since 1959, and ground-water contamination was confirmed in the 1980s. Remedial activities began in the late 1980s, with site cleanup requirements (SCRs) issued in the 1990s to address solvent contamination. Current efforts are focusing on perchlorate contamination. Millions of pounds of ammonium perchlorate, the main ingredient in solid rocket motors, have been used at the site. Much of the waste propellant was burned in open pits. The majority of the perchorlate has been detected in two alluvial valleys that cut through the site. UTC is one of the largest ground-water remediation sites in the region, with 730 monitoring wells and five ground-water treatment systems in place. To date, perchlorate has not been detected in Anderson Reservoir, although this area is monitored monthly using a detection limit of 4 ppb.

The onsite ground-water treatment systems were modified in 2002 to remove perchlorate using ion exchange. Ground-water migration into area creeks is controlled by extraction, and soil composting has been successful for treating perchlorate in shallow soils. The primary challenge at UTC is to halt the discharge of perchlorate into creeks, which is prohibited. The approach has been to remediate source areas, reduce ground-water concentrations, control discharge, and intercept and treat storm runoff.

Perchlorate is regulated by the State under legally binding orders. At UTC, the RWQCB has established an order that sets ground-water and surface water cleanup standards for perchlorate at 6 ppb onsite and non-detectable concentrations offsite; it sets the cleanup standard for soil at 20 ppb. These cleanup goals were derived from the risk assessment submitted by UTC in November 2003. This order requires refined site characterization, enhanced remedial actions, enhanced stormwater sampling, and quantification of perchlorate mass discharge. It also prohibits the discharge of perchlorate to creeks and offsite migration.

This order took about a year to complete. The Water District and discharger's staff were actively involved throughout process. The discharger's risk assessment was used to set cleanup goals, resulting in an uncontested order. Ultimately, this order will improve water quality and protect resources and public health.

Questions and Answers

Question: Was there an explosion at UTC last year?

Answer: Yes, there was a large explosion. Following the incident, the samples that were collected did not show any significant release of perchlorate.

Question: How deep is the contamination within fault zones?
Answer: The contamination is limited to the alluvium, which does not extend deeper than 50 feet below ground surface.

Question: What is the electron donor used in composting? What are the bugs being fed?
Answer: Manure and mushroom compost and methyl soyate.

Analysis of Human Exposure to Perchlorate Through Coupled Modeling of Ground Water and a Surface Water Distribution System

Graham Fogg and Eric LaBolle, University of California, Davis

For many years, the Aerojet facility in Rancho Cordova pumped ground water from the underlying aquifer to treat TCE contamination. The treated water was re-injected into the aquifer, and the water was subsequently captured by municipal wells, located to the west and north of the injection wells, that distribute water to the local population. Aerojet later discovered that the re-injected water contained perchlorate; therefore, ground-water treatment was expanded to address perchlorate as well. Since the municipal distribution system contains multiple extraction wells located throughout the city, the challenge was to determine which residents had the highest probability of exposure over time.

A team from University of California, Davis, was asked to develop a ground-water model that would reflect the capture of the contaminated water by supply wells as well as contaminant concentrations at the tap. This necessitated modeling both the ground-water system and the municipal distribution system. The distribution system model needed to estimate the amount of clean and contaminated water being placed in the water pipes and its ultimate destination and use (e.g., residences or businesses). EPANET was used to model the distribution system, and a numerical model based on geostatistical (stochastic) simulations of the subsurface heterogeneity with small block sizes (100 x 200 x 4-ft) was used to model ground-water flow and transport of the perchlorate. A regional model previously prepared for Aerojet by others was used to constrain the boundaries of this more detailed model.

The Aerojet site is underlain by typically heterogeneous alluvium that includes gravel, sand, silt, and clay beds. The surface and near-surface comprise fluvial sediments and dredge tailings from hydraulic mining. In the stochastic modeling approach used, 400 different scenarios (realizations) were run to account for uncertainties in spatial patterns of hydraulic properties between data points. Comparisons between measured and simulated head values showed that the model was reasonable and consistent with data on the basic flow system.

In complexly heterogeneous subsurface environments like the one at Rancho Cordova and most alluvial settings elsewhere, borehole flow can be a very important factor when the pumping wells have moderate to long screened intervals. It is no secret that in many such instances, contaminants can migrate vertically along the borehole from contaminated intervals having higher head to previously uncontaminated intervals having lower head. Interestingly, we showed this to be possible, if not likely, for certain wells, even during pumping of those wells. This mechanism appears to explain the occurrence of perchlorate contamination at wells that one might normally assume would be protected form contamination by upstream, pumping wells.

Results of the 400 simulations as well as the field data show that that contaminant concentrations vary tremendously in time and space. Furthermore, this variability is large enough to confound interpretation of data collected from sparse well networks or, say, from quarterly or even monthly sampling campaigns. The team chose three municipal wells that were most likely to have received the most contamination and compared the actual concentration data with those produced by the 400 scenarios. Based on these comparisons, they chose 30 scenarios that best fit the actual data for use in simulating the exposure.

The distribution model includes information on daily demand, pipe diameter, pipe roughness, etc. It is used to predict where water from any given pumping well is likely to end up. By using multiple runs and sensitivity analysis the team was able to produce a map that shows the most likely areas of exposure within the distribution system over time and the concentration ranges. This data will be combined with health data being collected by the State of California for exposure evaluation.

Questions and Answers

Question: Why do you consider the model solution to be non-unique?
Answer: A non-unique solution means that when a small change to the input is made, the results change. We were concerned that the uncertainty of the distribution system model would be greater than the ground- water model. However, the distribution system spread the water from each well out, and in so doing washed out small errors coming from the wells. [Added later by author: I think the question may have been referring to the multiple scenarios (realizations) of heterogeneity used in the analysis. This was done not to deal with a particular model's non-uniqueness, but to deal with the uncertainty that is inherent in subsurface characterization.]

Question: Are the residents and commercial users on septic tanks or sewer lines?
Answer: Most are on city sewer, but some may have septic systems.

Question: How representative is the Rancho Cordova water system in terms of its distribution of production wells? In Southern California, many cities use well fields rather than scattering the wells in the neighborhoods.
Answer: The distribution system (and the geology of Rancho Cordova) is rather typical in the Sacramento area, Modesto, Fresno, and Davis.

Question: What percentage of the water budget is contributed by borehole flow phenomena versus movement through the soil matrix?
Answer: I have not done the calculations, but the percentage could be significant, especially for confined aquifers.

Question: Are you looking to restore the aquifer and use the model to estimate a time frame for recovery?
Answer: This has not been done yet, but is planned.

Question: How well-characterized is the distribution of perchlorate other than at the injection wells? Are there overlapping plumes?
Answer: We simulated recharge from the spray fields, but because of the layering in the system, the contamination does not move very fast. As a result, the injection wells provide a reasonable input for human exposure. There may be other perchlorate sources because Aerojet has been operating from the 1950s. However, these sources have apparently not been associated with well contamination.

Wednesday, October 20

Aerojet Corp. and McClellan AFB each made presentations to the TSP forums regarding cleanup operations at the facilities. The presentations were followed by guided tours of the facilities to view first-hand cleanup efforts addressing perchlorate, radon, and unexploded ordnance.

Overview of Aerojet Cleanup, Rancho Cordova, California

Rodney Fricke, Chris Fegan, and Chris Fennessy, Aerojet Corp.

Rodney Fricke, Craig Fegan, and Chris Fennessy described contamination problems at the Aerojet facility near Rancho Cordova, California and provided an overview of the site's history and current cleanup status. Since 1953, Aerojet has manufactured and tested liquid rocket engines and solid rocket motors at this facility for military and commercial applications. Extensive ground-water contamination at the 8,500 square-acre site resulted from former practices and equipment leaks at the Aerojet facility and adjacent property, previously owned by the McDonnell Douglas Corporation.

In 1979, VOCs were found in offsite private wells in eastern areas of the Sacramento Valley. The site was added to the NPL in 1983. Multiple ground-water extraction and treatment systems (GETs) have been constructed since then to address VOC contamination and have been subsequently enhanced to address recently discovered perchlorate in ground water.

Ground water is extracted by municipal, domestic, industrial, and irrigation wells throughout Rancho Cordova, and the nearby American River supplies public water for much of Sacramento County. The ground water contains VOCs, primarily such as TCE, with lesser amounts of DCA, Freon-113, and other VOCs, as well as other rocket propulsion components such as perchlorate and NDMA. In addition to VOCs and perchlorate, soil contains elevated concentrations of metals in relatively small, localized areas.

Contaminants have migrated through dredge tailings and are present at depths between 100 and 400 feet in sedimentary rocks. The seven treatment facilities employ nine well fields that extract ground water from the Laguna and Mehrten Formations. The latter formation consists of water-bearing volcaniclastic rock ranging in thickness from less than 400 feet beneath the Aerojet Site to approximately 1,200 feet to the west along the axis of the Sacramento Valley. The formation contains highly permeable fluvial sand layers with intervals of confining tuff-breccia layers.

Ground-water extraction wells are in place to control migration of contaminated ground water, and several ex-situ treatment technologies remediate ground water, including ion exchange, UV/oxidation, air stripping, and biological fluidized bed reactors (FBRs). In addition, Aerojet has conducted pilot tests on the use of in-situ biodegradation for source control and reduction of the TCE and perchlorate plumes (using manure at the surface and corn syrup, citric acid, oleate, ethanol, acetate, and lactate in the subsurface).

In 2003, Aerojet treated ground water at a rate approaching 9,000 gpm. Depending upon the location and the treatment technology employed, treated water is discharged into an unlined ditch for filtration through dredge tailings, discharged onsite into recharge wells, or discharged into local surface water.

Welcome and Overview of McClellan Air Force Base

Paul Brunner, Air Force Real Property Agency (AFRPA)

Paul Brunner (AFRPA) welcomed participants to McClellan AFB. AFRPA's mission is to execute the environmental programs and real and personal property disposal for major Air Force bases in the United States that are being closed or realigned under the authorities of the Base Closure and Realignment Act of 1988 and the Defense Base Closure and Realignment Act of 1990. McClellan AFB, located outside Sacramento, was a depot repair and system management base for aircraft and communications, electronics, and space equipment. Groundbreaking took place in 1936, and the base was officially closed in 2001. At McClellan, approximately 369 acres of the 3,452-acre site have been transferred to the local redevelopment authority, and total transfer is not anticipated until FY 2017. AFRPA signed an Economic Development Conveyance in August 1998 with Sacramento County. AFRPA's goal is to transfer the land by deed as opposed to long-term lease.

In 1979, soil and ground-water contamination from past disposal practices and leaking facilities and pipes was discovered. Off-base residences bordering the ground-water plume were placed on residential water supplies in the 1980s. The site is currently on the NPL with the prime contaminants of concern being organics, although other contaminants (e.g., hexavalent chromium, plutonium, radium 226, PCBs. PAHs, and industrial waste sludges) are present. As of July 2004, soil and ground-water cleanup systems had removed 1,259,692 pounds of solvents. Ground-water treatment for hexavalent chromium, low-level radiation surveys, soil removal, and capping of disposal facilities are other cleanup activities being conducted. The cleanup budget at the base is between $30 and $40 million per year. To date, the Air Force has spent approximately $437 million on site cleanup activities, and anticipates a total projected cleanup cost of $1.76 billion.

Questions and Answers

Question: Does the base turn over all water and mineral rights when land is transferred?
Answer: Yes, but we do not turn over contaminated soil or ground water. We will not transfer land that isn't clean.

Question: Does the Air Force have any control over future uses of the property?
Answer: The Air Force will establish cleanup goals from the ROD. If in the future, the owner wants to change the land use zoning or challenge restrictions, they will be responsible for cleaning up the property to meet new standards.

To view the McClellan AFB presentations for more details, click here.

Introduction to the Soil Vapor Extraction (SVE) Radiation Control Effort at the Former McClellan Air Force Base

Jeremy Scott, URS

Jeremy Scott (URS) summarized the radiological hazard at the SVE vapor-phase granular activated carbon (VGAC) systems at McClellan AFB. In 1995, SVE systems were installed to treat the contaminated vadose zone at the base. There are currently 13 systems in operation using both oxidizers and VGAC treatment.

In April 2002, the operating SVE systems were surveyed for radiation, and although the oxidizers did not contain elevated levels of gamma radiation, the VGAC vessels were found to be trapping radon and its progeny. Regulatory agencies initially suspected radiation hazards at SVE systems situated near known radioactive spill and disposal sites. However, radon concentrations were very high in soil vapors at all sites surveyed.

Because SVE is not a licensed activity, there were no Nuclear Regulatory Commission nor EPA regulations regarding the radiation levels produced. Therefore, the Air Force applied 10 CFR 20, Standards for Protection Against Radiation. This stipulated that the system may increase the dose rate no more than 6 mR/hr above background levels at the system fenceline (assuming continuous occupancy, 24 hours per day, 365 days per year). Since background was 8 mR/hr, the fenceline threshold was set at 14 mR/hr. The SVE systems were shut down for approximately 30 days, then restarted after the fence lines were extended. In addition, shielding walls were constructed around the VGAC vessels. The changeout procedure for the carbon filter was modified to include a 24-hour ambient air purge. An Environmental Radiation Monitoring Plan was prepared that included real-time monitoring as well as the use of passive environmental dosimeters for workers and passive radon gas detectors.

The shielding walls are performing as designed, with radiation exposure attenuated by a factor of ten in most cases. Both the public and site workers are protected because of the actions taken. The dosimeters show no dose, and the workers are exposed far more than the public. A modified action level of 500 mR/yr, was deemed more appropriate for occupational exposure than the 50 mR/yr originally set for the public. Signs have been posted indicating the presence of a radioactive material near the SVE systems. Radiological considerations will be included in future health and safety plans and in the Basewide Remedial Action Work Plan.

Questions and Answers

Question: Does the radon get trapped inside the charcoal within the VGAC vessels?
Answer: We collected samples from the charcoal beds and tested them with gamma spectrometry. We found that the carbon contained deposits of lead 214 and 210. Daughter products of radon were found in the vessel.

Question: Is this a general concern at any site with radon in the substrate?
Answer: The vadose zone at McClellan AFB extends approximately 100 feet below ground surface. If the substrate at a different site is high in radon, then you will likely have similar concerns.

Question: What are the vessels made of?
Answer: Steel.

Question: Is there an indoor radon problem in site buildings?
Answer: Not that we've found.

To view the McClellan AFB presentations for more details, click here.

Potential Unexploded Ordinance (UXO) at McClellan Air Force Base
David Green, U.S. Air Force

Recently, a former contracting officer that worked at McClellan AFB from 1970 until 1998 told base officials that he suspected that unexploded ordnance (UXO) might be buried at McClellan. Years ago, a civil engineer told the contracting officer that bombs from World War II were buried at an unmarked disposal site situated to the west of CS-007. AFRPA immediately notified all appropriate agencies, including regulators, the fire department, LRA, McClellan Business Park, the sheriff's department, contractors, and Air Force explosive ordnance offices. Access to the site was controlled by locking gates and fencing the site on three sides (the fourth side is bordered by Don Julio Creek). In addition, the site was placed under daily surveillance.

A contract was awarded to Blackhawk Geophysical & UXO Services to conduct a visual inspection of the site and perform a geophysical survey. The visual inspection and geophysical survey were completed in September 2004. A final report is expected from Blackhawk in November 2004. If no anomalies are detected, AFRPA will confer with the Air Force Range Support Unit. If they agree with the findings, then no further actions will be taken. If the survey indicates a potential for UXO, the Air Force will hire a UXO contractor to develop a work plan and health and safety plan for UXO removal and submit them to the Air Force Safety Center (AFSC) at Kirtland AFB. Following AFSC concurrence, the plans will be forwarded to the DoD Explosive Safety Board for approval. The contractor will then implement the removal plan.

Questions and Answers

Question: How much money have you spent investigating this site so far?
Answer: We have spent about $30,000.

Question: Did you consider conducting an electromagnetic induction survey?
Answer: None of the bids we received included electromagnetic induction.

Question: Has the creek been checked for the presence of dissolved propellants?
Answer: No.

Question: If no anomalies are detected, is there any chance that you investigated the wrong area?
Answer: Our decision to investigate in this area is based on second-hand information, but it is the best information we have. We take information like this very seriously.

To view the McClellan AFB presentations for more details, click here.

Thursday, October 21

Incorporating Evolving Science in Program Practice

David Cooper, U.S. EPA OSRTI

David Cooper described strategies used by OSRTI's Policy Branch to ensure the use of risk-based science in site cleanup decisions regarding chemical toxicity. OSWER currently uses a three-tired hierarchy for determining toxicity based on: (1) IRIS values, (2) provisional peer-reviewed toxicity values, and (3) toxicity values issued by agencies such as the California EPA and ATSDR. Unfortunately, many of the issues involving emerging contaminants and evolving science are not addressed by this hierarchy. This has led OSWER to consider developing other guidance. OSWER is considering both generic guidance to address evolving science and will consider developing chemical-specific guidance, as necessary to provide direction on specific issues.

Preliminary remediation goals (PRGs) based on toxicity values (primarily IRIS) are used to determine potential remedial activities and may serve as the basis for final cleanup levels. Existing cleanup levels will be affected by changes in the chemical-specific toxicity values listed in IRIS. The IRIS program has received new resources so that in can increase the number of new chemicals with toxicity information and increase the speed at which they are developed. This is good news for risk assessment, because it allows more quantitative risk assessment, but it may create uncertainty concerning remedy decisions, because these additional chemicals may not have been evaluated quantitatively in the risk assessment or remedy selection.

The challenge for OSWER is balancing the need to use the best available science, ensuring that our remedies are protective, while achieving finality with our cleanup actions. Both RCRA and CERLCA have provisions to incorporating evolving science into their programs. The difficulty incorporating these changes will depend on the magnitude of the change and where a specific project is in the investigation/cleanup process.

Some kind of screening process is advisable to provide a better understanding of how disruptive changes resulting from evolving science will be to the program and to individual projects. Consideration of how original cleanup levels were established, data quality, site conditions and history, weathering of contaminant all could play a role in determining how big an impact any scientific change will have a at site. The Agency recognizes a continued need to integrate evolving science into site-specific decisions that support long-term protection of human health and the environment. Five-year reviews offer opportunities to integrate new science.

OSWER is evaluating emerging contaminants, including PCBs, 1,4-dioxane, dioxins, hexavalent chromium, and TCE as vapor intrusion, as well as other compounds already targeted by Cal EPA.

Questions and Answers

Question: Which other chemicals may be tracked by the Agency for potential regulatory changes?
Answer: Asbestos-related toxicity issues will be followed due to the ongoing problems associated with this mineral. In addition, arsenic will be tracked due to the potential differences in toxicity between its inorganic and inorganic states. Although inorganic arsenic has a higher toxicity level in humans, it is excreted as organic arsenic.

Question: Is the Agency developing additional techniques for contaminant detection?
Answer: The Agency's Analytical Operations Branch is responsible for evaluating and addressing the need for additional techniques.

Question: Have efforts been made with DOD management to discuss various ways for integrating evolving science in national policy and site-specific decisions?
Answer: Yes, preliminary discussions have been held.

Question: What is the hierarchy for updates to the list of contaminants listed under RCRA Appendix 9?
Answer: Although the hierarchy is unclear, the Agency's RCRA program office is responsible for updating any RCRA listings. OSWER has formed an interoffice science team to coordinate cross-program questions and issues such as these.

To view Dave Cooper's presentation for more details, click here.

Perchlorate Biodegradation: ARA Experience
Ed Coppola, Applied Research Associates, Inc. (ARA)

As a chemical engineer and former officer in the U.S. Air Force, Ed Coppola has worked with the government and private industry on perchlorate-related issues since 1984. In addition to rocket propellant research and development, for the past nine years he has focused on the development of perchlorate treatment technologies and full-scale implementation of processes that destroy or remove perchlorate in wastewater and ground water.

ARA, under sponsorship of the Air Force Research Laboratory at Tyndall Air Force Base, FL, developed a perchlorate biodegradation process in the early and mid-1990s. A pilot system was constructed and tested at Tyndall AFB. ARA has further developed and patented this technology and has evaluated other perchlorate treatment approaches including membrane bioreactors (MBR), ion exchange, and thermal destruction.

In the ARA ex-situ biodegradation process, wastewater or extracted ground water is pumped into reactor vessels for direct contact with microorganisms in a suspended-growth, anoxic process. Perchlorate is reduced to chloride by microbial anaerobic degradation. The process is normally configured as two continuous-stirred-tank-reactors (CSTRs) in series. The first-stage reactor reduces nitrate, other easily reducible oxi-anions, and most of the perchlorate present. The second-stage reactor further reduces perchlorate to below the EPA 314 method detection limit. Nutrient is added to the first-stage reactor. Typical operating parameters for the biodegradation process are hydraulic retention time of 8-24 hours, temperature of 15-40ºC, and pH of 6.5-8.5. Mr. Coppola discussed the commercial application of this process at two sites. The system at ATK-Thiokol, Promontory, Utah has been in operation since December 1997 and treats wastewater from rocket propellant production and demilitarization operations that contains up to 5000 mg/L of perchlorate. Another system in Herington, Kansas, treats effluent from a gunpowder manufacturer.

Biodegradation of perchlorate is inhibited by high levels of total dissolved solids (TDS) or high levels of perchlorate (>5000 to 10,000 mg/L). Regenerable ion exchange processes typically generate perchlorate-containing, sodium chloride brine. The ability to treat and reuse the brine would greatly reduce regeneration cost. ARA adapted their patented biodegradation technology to create a membrane bioreactor (MBR) system for treating ion exchange treat brines. The MBR system uses an ultrafiltration membrane to retain biomass in the reactors.

Mr. Coppola discussed the use of MBR in pilot-scale demonstrations on actual spent ion exchange brine that was greater than 6-7% salt. Complete nitrate and perchlorate reduction was obtained for nutrients that included molasses, corn syrup, and acetic acid. The MBR system was also tested on simulated ground water with perchlorate concentrations of 100 ppb and 1000 ppb. During this demonstration the carbon source was successfully transitioned from de-sugared molasses to acetate. In addition to complete perchlorate reduction, the ability to proportionately reduce nutrient concentration resulted in a treated permeate that would meet typical NPDES permit standards.

Questions and Answers

Question: Is bioreactor technology capable of treating munitions-related contamination?
Answer: Bioreactors have successfully treated nitroglycerin and Explosive-D (ammonium picrate) and could be successful treating waste streams containing other munitions constituents, including TNT and RDX.

Question: Does the presence of sodium-based plasticizers in waste streams present problems?
Answer: No. Neither sodium-based plasticizers nor ammonium should disrupt the biodegradation process.

Question: Which types of halophilic microbes are effective in bioreactors?
Answer: HAP cultures containing a consortium of bacteria have effectively degraded perchlorate at salt concentrations up to 6-7%.

Question: Are the military sectors of countries other than the U.S. using perchlorate extensively?
Answer: Israel and the former Soviet Union nations are known to use different formulations for propellants that also pose potential, but largely unaddressed, problems.

Emerging Concerns Over NDMA in Groundwater: An Overview of NDMA—Sources, Formation, Transport, and Treatment
Rula Deeb, Malcolm Pirnie

Summary to be posted at a later date.

To view Rula Deeb's presentation for more details, click here.

Remedial Strategy for Perchlorate-Bearing Commingled Plumes at an Explosives Test Facility
Vic Madrid, Lawrence Livermore National Laboratory

Vic Madrid discussed the remedial strategies for addressing perchlorate-bearing, commingled plumes at Lawrence Livermore National Laboratory's high explosives test facility (Site 300). Site 300 occupies 11 square miles to the east of Livermore, California, and includes a high explosives processing facility, an open-air firing table, and a facility for testing explosives under different temperature and pressure conditions. Waste liquids from the processing facility were treated only with a clarifier and cloth filter to remove solids prior to discharge to an unlined lagoon, dry well, or septic system. Solid wastes were sent to an open burn facility, and gravel and shot debris from the firing table were disposed in unlined landfills.

Materials processing, explosives testing, and waste disposal practices contaminated the site with high explosives (including perchlorate), radionuclides, solvents, and heat exchange fluids. Since 1990 when Site 300 was added to the NPL, hundreds of borings and monitoring wells have been installed and sampled in the course of CERCLA investigations at the site, and a broad range of chemical data, including data on isotopes, have been collected. Perchlorate sampling began in 1998 at the request of the RWQCB. To date, there have been 730 detections of perchlorate in 122 wells, with a maximum detection of 65 µg/L.

In the northern part of Site 300, in the area of open-air detonation experiments and several disposal pits, perchlorate is commingled with tritium, depleted uranium, and elevated nitrate. The primary sources of the tritium are the firing table and unlined landfills. Both anthropogenic and natural uranium are present at the site, but treatment methods do not distinguish between the two. In addition to the nitrate present from explosives testing, natural levels of nitrate were found to be elevated. One option being considered to treat this commingled plume is an in-situ permeable reactive barrier containing bone char or apatite, and ion exchange resin. Another is a funnel and gate system to channel the plume toward an extraction system where ground water would be pumped to an ex-situ reactor vessel containing bone char or apatite, and an ion exchange unit. Each option would involve construction of a hydraulic diversion system to prevent the accumulation of water in the pits, thus decreasing the mobility of site contaminants.

The most widespread perchlorate contamination at Site 300 is located beneath the high explosives processing area, where the plume is commingled with VOCs, RDX, and elevated nitrate. A conceptual model of the Neroly upper blue sandstone formation ($Tnbs_2$) shows that the aquifer is a synclinal structure that plunges southeast. Ground water flows to the southeast from an unconfined portion of the aquifer that underlies potential contaminant sources, toward a confined portion of the aquifer. Contaminant concentrations in $Tnbs_2$ are highest near the sources and decrease downgradient to the southeast. TCE is the only contaminant plume to extend past the unconfined/confined aquifer boundary. There is a steep nitrate concentration gradient toward the southeast that matches the dissolved oxygen concentration gradient. Thus, conditions appear to favor anaerobic denitrification, which is also supported by trends observed in nitrogen / oxygen isotopes along the ground water flow path and the presence of excess dissolved nitrogen (N_2) in the oxygen-depleted, confined groundwater. Monitored natural attenuation is an option being considered for nitrate commingled with other contaminants.

Currently, there are 13 ground-water treatment facilities at Site 300, seven of which include perchlorate treatment. Because no POTW is available, discharges from these facilities are regulated by NPDES. Given the large-scale, dilute, multiple-constituent plumes present in low-yield aquifers, the challenge at Site 300 is to develop cost-effective strategies for ground-water extraction and treatment.

One treatment being implemented is a low-cost, solar-powered, treatment train with a containerized wetland that utilizes local indigenous plants. Influent containing 10-15 µg/L perchlorate is pumped at a rate of 1 gpm through granulated activated carbon (GAC) for treatment of VOCs and RDX before passing through the containerized wetland for perchlorate and nitrate treatment. A containerized wetland avoids creation of a wetlands habitat. A final ion exchange polishing step ensures compliance with effluent discharge standards. Effluent concentrations of perchlorate and nitrate are less than 4 µg/L and 10 µg/L, respectively.

A second treatment option that has been implemented involves pumping water through GAC to remove VOCs and RDX and then through a fixed-film bioreactor and an ion exchange unit for perchlorate and nitrate removal. The bioreactor is designed to treat nitrate using denitrifying bacteria to minimize the nitrate load on the ion exchange reactor. The Sybron SR-7 nitrogen-specific ion exchange resin used in the reactor selectively removes perchlorate from nitrate-bearing water. The perchlorate-laden resin is difficult to regenerate, so it must be disposed as a hazardous waste.

A key element in managing for the extraction well fields at Site 300 is to balance site boundary pumping with upgradient pumping to maintain hydraulic control of source areas. Treated effluent is strategically injected to (1) reverse the natural gradient at the site boundary, (2) flush contaminant source areas, and (3) preserve the ground water resource. Nitrate loading on the ion exchange resin must be minimized to reduce waste disposal costs, and studies involving the collection of isotopic and dissolved gas data are ongoing in support of MNA of nitrate.

To view Vic Madrid's presentation for more details, click here.

Use of Novel Analytical Techniques for Detecting Perchlorate and RDX Degradation Products in Water

Harry Beller, Lawrence Livermore National Laboratory

This presentation highlights how electrospray ionization/tandem mass spectrometry is proving to be a powerful and rapid method for analyzing a diverse range of environmentally relevant compounds. Here we focus on two chemically disparate compounds that occur in ground water at Lawrence Livermore National Laboratory (LLNL) Site 300, perchlorate and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), both of which were found to be very amenable to low-level analysis by tandem mass spectrometry. In the case of RDX, we are interested not in the contaminant itself but in its "signature" metabolites, which, by their mere presence in ground water, definitively demonstrate the in-situ transformation of RDX.

Perchlorate Analysis: An electrospray ionization/tandem mass spectrometry (ESI/MS/MS) method was developed at LLNL to measure part-per-billion (µg/L) concentrations of perchlorate in ground water. Selective and sensitive perchlorate detection was achieved by operating the mass spectrometer in the negative ionization mode and by using MS/MS to monitor the ClO_4^- to ClO_3^- transition. The method of standard additions was used to address the considerable signal suppression caused by anions that are typically present in ground water, such as bicarbonate and sulfate. ESI/MS/MS analysis was rapid, accurate, reproducible, and provided a detection limit of 0.5 ug/L perchlorate in ground water. Accuracy and precision of the ESI/MS/MS method were assessed by analyzing performance evaluation samples in a ground-water matrix (4.5 to 75 µg/L perchlorate) and by comparing ion chromatography (IC) and ESI/MS/MS results for local ground-water samples (<0.5 to 35 µg/L perchlorate). Results for the performance evaluation samples differed from the certified values by 4 to 13% and precision ranged from 3 to 10% (relative standard deviation). The IC and ESI/MS/MS results were statistically indistinguishable ($P > 0.05$) for perchlorate concentrations above the detection limits of both methods.

Use of Signature Metabolites in Monitored Natural Attenuation (MNA) of RDX: An important element of monitored natural attenuation is the detection in ground water of distinctive products of degradation or transformation. In this study, three distinctive products of the explosive RDX were detected in contaminated ground water from the Iowa Army Ammunition Plant; the products were MNX (hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine), DNX (hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine), and TNX (hexahydro-1,3,5-trinitroso-1,3,5-triazine). These compounds are powerful indicators of RDX transformation for several reasons: (a) they have unique chemical features that reveal their origin as RDX daughter products, (b) they have no known commercial, industrial, or natural sources, and (c) they are well documented as anaerobic RDX metabolites in laboratory studies. The products were analyzed by LC/MS/MS (liquid chromatography/mass spectrometry/mass spectrometry) with selected reaction monitoring and internal standard quantification using [*ring*-U-^{15}N] RDX. Validation tests showed the novel LC/MS/MS method to be of favorable sensitivity (detection limits ca. 0.1 µg/L), accuracy, and precision. The products, which were detected in all ground-water samples with RDX concentrations of > ca. 1 µg/L (25 out of 55 samples analyzed), were present at concentrations ranging from near the detection limit to 430 µg/L. MNX was the typically the most abundant of the three nitroso-substituted products; concentrations of the products seldom exceeded 4 mol% of the RDX concentration, although they ranged as high as 26 mol% (TNX). Geographic and temporal distributions of RDX, MNX, DNX, and TNX were assessed. This extensive field characterization of MNX, DNX, and TNX distributions in ground water by a highly selective analytical method is significant because very little is known about the occurrence of intrinsic RDX transformation in contaminated aquifers.

Questions and Answers

Question: Is DOE investigating the toxicity of the nitroso- metabolites of RDX?
Answer: We (LLNL) have performed some unpublished mutagenicity studies. The studies indicate that DNX poses the most concern (relative to RDX, MNX, and TNX).

Question: Do you treat the samples before injecting them into the liquid chromatograph?
Answer: The samples are treated minimally. We remove particulates, preserve with 20% methanol, and spike with an isotopically labeled internal standard.

Question: Are commercial laboratories interested in this method for RDX metabolites?
Answer: Right now, there is no regulatory driver to analyze for these compounds, so the expense of buying a tandem mass spectrometer is not justified for commercial laboratories. Also, the metabolite standards are not commercially available (again, because these compounds are not regulated). However, in the future, as a wider range of compounds that are not amenable to GC/MS analysis become of more regulatory interest, commercial labs will probably begin to buy this kind of equipment.

To view Harry Beller's presentation for more details, click here.

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