

PROCEEDINGS

DESERT REMEDIAL ACTION TECHNOLOGIES WORKSHOP



October 2-4, 2007
Phoenix, AZ

Workshop Sponsors:



Desert Remedial Action Technologies (D-RAT) Workshop Day 1: October 2, 2007

This publication contains the proceedings for the Desert Remedial Action Technologies Workshop, which was held from October 2-4, 2007 in Phoenix, AZ. Desert environments in the southwestern United States and similar areas present a number of unique challenges to subsurface cleanup. Groundwater can be extremely deep and the presence of clays and fractured rock can reduce the effectiveness of some standard cleanup technologies. The goal of the workshop was to gather practitioners and others with remediation expertise in these desert environments and to present both lecture and poster presentations on their ideas for remediating soils and groundwater. The scope of the workshop was limited to sites with VOCs, perchlorate and chromium, as these contaminants present some of the greatest challenges for cleanup.

All information from the workshop, including abstracts, bios, presentations, and these proceedings, will be posted at the following EPA webpage:

<http://www.epa.gov/osp/stlworkshops.htm> .

9:00 Opening Remarks – Mike Gill, U.S. EPA and Alan Dulaney, Arizona Hydrological Society/Arizona Department of Water Resources

Mr. Gill opened the first day's sessions, welcomed attendees, and thanked the conference organizers and speakers. He noted that there are numerous challenges to remediating desert subsurface environments; the goal of this workshop was to gather experts to present their ideas on improving remediation of these sites, particularly as it pertains to volatile organic compounds (VOCs), perchlorate, and chromium. He added that this was intended to be a "green" workshop; pre-conference information and materials were posted online at the meeting website (<http://www.epa.gov/osp/stlworkshops.htm>), and the presentations and final proceedings would also be available online after the conference. He then reviewed the workshop agenda and introduced the next speaker, Mr. Alan Dulaney (president of the Arizona Hydrological Society).

Mr. Dulaney thanked EPA Region 9 and the Arizona Department of Environmental Quality (ADEQ) for their work in organizing the workshop. He invited attendees to join the Arizona Hydrological Society (AHS), which was founded to promote responsible use and management of water resources in the Southwest. Historically water has not been reliable for residents of Arizona, and although technology developed in the last century (*e.g.*, deep wells and powerful pumps) solved the problem of reliability, it also created problems with contamination of the water reserves. With continued growth, water quality will become increasingly important as the resident population demands reliable water quality as well as quantity. Mr. Dulaney concluded by inviting participants to attend the AHS-sponsored Sixth Annual International Symposium on Managed Aquifer Recharge taking place later this month in Arizona. The conference website is www.ismar2007.org.

Session 1 – Biological Technologies
Chairperson: Leanne Austrins (CH2MHill)

Ms. Austrins opened the first session, reviewed logistics for the conference, and introduced the first session speaker, David Abranovic.

9:15 Pilot Test of Deep Aquifer Permanganate Treatment
David Abranovic, PE (ERM-West, Inc.)

Mr. Abranovic presented a method for trichloroethene (TCE) oxidation by permanganate, a compound which is very efficient at oxidizing TCE. A site map was presented for the Peoria Avenue site in Phoenix, AZ, along with VOC concentrations, which have historically been moderate. A pump and discharge (hydraulic control) remedy had previously been used for decontamination, and the investigators used this existing system in their pilot study. The pilot study was designed to apply the maximum mass of permanganate into the subsurface, identify site specific difficulties associated with the application of permanganate to site groundwater, measure the persistence of permanganate in the aquifer, and monitor the reduction in VOC concentrations in the aquifer near the application well. The application and mixing methods were described and illustrated by images of the equipment used. Results were presented for three monitoring wells and two extraction wells, at various distances downgradient from the treated area, showing both VOC and chromium concentrations. Results for one monitoring well showed an increase in VOCs, but the other two monitoring wells showed decreases in VOC concentrations of 98% and 93%. Extraction well results showed that permanganate did migrate downgradient at varying rates, and that it persisted for over three years in one of the wells. Transient (outlier) chromium concentrations were also observed, however these did not result in a long-term chromium problem. The method was overall deemed effective, primarily because of the low organic carbon, which allowed the permanganate to persist for three years; permanganate can also be transported across long subsurface distances for a wide distribution, making this method viable for deep and expansive VOC plumes.

Questions and Discussion

A question was raised on whether TCA was plotted with the results, since it could be used as a marker to study absorption and desorption effects. The speaker replied that there was a spike in the magnitude for TCA, and that desorption effects were seen, but he could not comment on their magnitude.

In response to whether the permanganate solution was tested for chromium, Mr. Abranovic explained that they used high grade permanganate which did not contain chromium.

In response to a question about the performance measures used, Mr. Abranovic responded that water quality measurements for two quarters to up to a year from treatment were used to measure performance.

Regarding the injection technology and timing, Mr. Abranovic noted that injections were continuous for a 2.5 day period, and both wells were injected simultaneously, and then flushed. There were no problems encountered with injection, however, cleaning the mixing tanks was difficult, and was eventually accomplished by using sugar to react with the permanganate.

Another audience member asked whether the permanganate found at the extraction wells signified a problem with the technique. Mr. Abranovic noted that there was treatment going on at the site; the permanganate was not problematic other than the fact that they did not want to pump out all the permanganate; to avoid that, the treatment system was shut down while this study was being conducted.

The cost of the permanganate was about \$1.50 per pail, with total costs of \$50,000 for the entire project.

A question was raised about the cause of the spike in perchlorate, TCE, and contaminants concentrations seen in the data presented. Mr. Abranovic agreed that, had the treatment been successful, these increases in concentration should not have been there. He explained that some of the wells may not have been in the right place, and that in the lower well a vertical gradient was created by the process of sampling.

In response to a follow up question, he replied that these concentrations have since decreased, and the contaminants having been oxidized over time.

Lastly, he confirmed that the state was not concerned about the longevity of permanganate in the soil.

**10:00 *In-Situ* Bioremediation for Treatment of Chlorinated Solvents and Perchlorate
Impacted Groundwater in Desert Environments
Sam Williams, PG, CHg (Geosyntec Consultants)**

Mr. Williams' presentation focused on the techniques and challenges of remediation of VOCs and perchlorate. *In-situ* bioremediation can be accomplished through monitored natural attenuation, biostimulation, or bioaugmentation. Delivery of biostimulant or bioaugmentation material is of foremost importance, and is contingent on good site characterization. Other important factors for *in-situ* bioremediation are aquifer and microbial conditions. The Borehole Imaging Processing System (BIPS) can be used to characterize a site, and is especially effective for fractured rock settings. The system takes oriented photographs of the borehole, and shows fractures intercepting the borehole as sinusoidal patterns on a graph. Examples of the results and photographs using this system were presented. Delivery can be accomplished using active or passive systems; advantages and disadvantages for both systems were summarized. One type of bioremediation involves reductive dechlorination of VOCs using bacteria of the genus *Dehalococcoides*. Bioaugmentation (*i.e.*, adding these microbes to the soil) is appropriate in some situations and can accelerate remediation, particularly the rates of dechlorination. Data were presented showing the long term impact of bioremediation compared to other technologies, since the bacteria keep working long after the delivery system has been shut down. Case studies

were summarized where bioremediation was used at an aerospace manufacturing facility (passive injection); a Superfund site containing perchlorate and TCE (bioaugmentation with an active bio-barrier); a NASA/Air Force site containing dense, non-aqueous phase liquids (DNAPL); and a road flare manufacturing site contaminated with perchlorate. Conclusions from the studies confirmed the importance of an accurate conceptual site model, and of using an appropriate electron donor, having an active microbial culture, and population.

Questions and Discussion

A member of the audience asked how the transport of microbial populations was encouraged. Mr. Williams replied that increasing the flow would work for an active system (closed loop). The donut approach, used in one of the case studies, also showed promising results; and recirculation may help, depending on the delivery technique used.

Further questions addressed whether the microbes could be used in combination with a thermal treatment, *i.e.*, if they could tolerate high temperatures. Mr. Williams said he has not tried that approach, and did not know the upper temperature limit; he did note that the microbes would not work well at temperatures below 55 F.

Mr. Williams confirmed, in response to another question, that reductions in perchlorate were seen when using an electron donor dosing system; however, those results were not conclusive.

Another attendee asked about problems with biofouling; Mr. Williams confirmed that they had seen such problems, and they were addressed using aggressive clean up and treatment of the wells. There was no difference in the frequency/amount of biofouling between the bioaugmentation and biostimulation phase.

A question was posed on whether the investigators were concerned about chlorine and dissolved oxygen. Mr. Williams explained that the water was mixed with 1% emulsified vegetable oil, unlike the "cushion" injection, which was anaerobic water. Chlorine was tested nevertheless, and only low levels were found.

A participant asked why bioaugmentation (rather than biostimulation) was used in the Aerojet case study. Mr. Williams replied that bioaugmentation was chosen because it would work more rapidly.

Questions were also raised on whether sulfate concentrations were tracked, and about the power requirements and costs of the treatment. Mr. Williams said that sulfate was one of the limiting factors; there was a reduction in sulfate (at the Florida site), and no hydrogen sulfide was observed.

Treatment costs for the passive study (with a plume area of about 2 acres) were less than \$0.5 million. An attendee commented that in a study conducted by ARCADIS, treatment costs were in fact higher when bioaugmentation was included; the cost of the recirculation system also has to be taken into account.

Regarding the power requirements of recirculation, Mr. Williams said that it requires a lot of power, and would not be feasible to run on power from solar panels alone.

11:00 Evaluation of a Hydrogen Release Compound (HRC) and HRC-Primer Injection at a TCE-Impacted Site after the Operation of a Dual Phase Vacuum Extraction System

Gustavo Valdivia, PE (Bureau Veritas North America, Inc.)

Mr. Valdivia began by presenting background information on the Joint forces Training Base site at Bldg. 35 in Los Alamitos, CA, including soil type and TCE source, current plume area and TCE concentrations. The pilot test was conducted on an area with TCE levels that represented the typical concentration within the plume. A plot of the pilot test area with well locations was also presented. A primer was used prior to injecting the HRC in order to produce faster results; although HRC is a slow-release, viscous fluid, the primer is more biodegradable, leading to a faster release of hydrogen. Direct push injection rigs were used and were operated two at a time for greater efficiency. Results were presented for several wells, located at the center of the injection area and at various distances downgradient of the injection perimeter. Concentrations at the injection site decreased following the injections except for total organic carbon (TOC), which increased, indicating that HRC was present in the well. A decrease in TCE concentration was also seen in a well approximately 28 feet down-gradient, where no effect was expected. Another downgradient well also showed an increase in TOC after injection. Overall, TCE concentrations decreased in an area of about 6000 square feet following the pilot test injection. The test results indicated that HRC injection was successful in enhancing bioremediation. A full scale application following the pilot study is still ongoing, but preliminary results show its effects to be similar to those seen during the pilot test.

Questions and Discussion

A member of the audience asked whether there had been a cost analysis conducted of using different concentrations. Mr. Valdivia responded that higher concentrations of HRC are generally more effective at degrading TCE; however, lower concentrations need to be used at low permeability sites. He confirmed that the project has been running for nine years, using different configurations for different phases.

Another attendee asked why injecting with a geoprobe was selected in favor of using a reinjectable system. Mr. Valdivia explained that HRC is long-lasting, and as a result there was no need for the ongoing cost of continuously pumping or recirculation systems.

A comment was made regarding redox conditions in the aquifer: specifically, some of the sulfate should have been reduced as a result of the treatment. The commenter asked whether methane and ethane were being monitored. Mr. Valdivia stated that sulfate, methane, and ethane were all being analyzed; although only baseline values are currently available, the expectation is that they will indicate anaerobic activity in the soil.

A participant asked why that particular area of the site was selected for the pilot study, and specifically why the injection well locations were chosen. Mr. Valdivia responded that the locations were chosen so that investigators could be sure that any impact they observed was not due to contamination from other wells.

In response to a comment that the shape of the plume seemed contrary to the groundwater gradient, he explained that the major influence was the pumping gradient, not the natural gradient.

Session 2 – Mechanical Technologies **Chairperson: Kevin Murdock (CH2MHill)**

Mr. Murdock opened Session 2, reminded participants of logistics details, and announced evening activities and the next day's "Desert RAT" run.

1:30 Perchlorate, TCE, and 1,4-Dioxane Investigation and Remediation at a Rocket Propellant Facility in a Semiarid Environment *Edward (Ted) Tyler and Dave Jenkins (Kleinfelder West, Inc.)*

The presentation was divided in two parts: a discussion of perchlorate, TCE and dioxane remediation at a rocket propellant site in California, and summaries of other case studies. Mr. Tyler presented maps of the first site and summarized the chemical properties of the contaminants (perchlorate, TCE, and dioxane). U.S. EPA Method 314.0 was used for analyzing perchlorate in drinking water, and Method 6850 for groundwater; data were presented that showed the two methods yield comparable results. Several views of the conceptual model for the site were then presented, including sampling points and concentrations of perchlorate and TCE in soil and groundwater. The site conceptual models were used to determine the best remediation approach, using the scenario that remediation would be needed for all three contaminants (dioxane being the most restrictive). A flow diagram of the planned remediation process for dioxane was presented, using extraction and *ex-situ* treatment. Additional treatment needs may still exist for TCE and dissolved perchlorate, even after extraction and *ex-situ* treatment (*e.g.*, resin incineration for perchlorate, air strippers, a HiPOx system for TCE). However, due to the high cost of extraction for TCE, alternative treatments may be more cost-effective. Given these factors, soil remediation at this site is expected to include *in-situ* donor injection, excavation, and/or capping. Groundwater remediation will include some combination of *ex-situ* dioxane/TCE treatment utilizing advanced oxidation processes (AOP), and *in-situ* donor sparging for perchlorate and/or TCE. Two case studies on bioremediation of perchlorate in soil were then presented by the second speaker (Dave Jenkins). At an explosives manufacturing/testing site in Nevada, compost blending and addition of molasses, followed by a nitrogen purge, was used to reduce soil perchlorate concentrations. At the Stringfellow Superfund Site, perchlorate bioremediation in groundwater was accomplished using nitrogen gas delivered *in-situ* through a sparge well. In both cases, the costs of the study were comparable to other remediation methods available.

Questions and Discussion

The speakers were asked whether there had any concerns about the migration potential of [nitrogen] gas after it has passed through the plume. Mr. Tyler responded that it would depend on how the site responds; since gas is being pulled from above, that pull can be adjusted if needed.

Another participant asked what depth was used to estimate the costs [in the last case study]. One of the speakers responded that the cost depends on the substance, adding that it averages \$30-\$100 per foot of depth. Well angle must also be taken into account, since a vertical well may decrease the area of influence.

In response to a question regarding results [from the last case study], the speakers confirmed that only bench scale work had been completed, so results were not yet available.

2:15 Systematic Remedial Methodology for Chlorinated VOC Contamination of Soils and Groundwater Underlying Desert Landfills *Harold Bentley and Stewart Smith (Hydro Geo Chem, Inc.)*

Mr. Bentley discussed a quantitative, *in-situ* remediation methodology that relies on site-specific evaluation and numerical simulation to develop a conceptual model of the contamination problem, and a remedial engineering design that meets corrective action goals at maximum efficiency and minimum expense. The site in question had soil and water beneath a landfill contaminated with volatile chlorinated organic compounds (VCOCs), specifically PCE. Characteristics of the distribution of the VCOC contamination led investigators to believe that there was a contamination source in addition to the landfill itself; a numerical model was used to simulate contamination up to 20 years after landfill closure, and confirmed that the vadose-zone VCOCs beneath the landfill were the source of past and continuing groundwater contamination. Given those results, soil vapor extraction (SVE) was selected as the most cost effective option for remediation. Technical issues related to this technique were summarized; a particularly important goal was minimizing the number of SVE wells (extraction wells), as each can cost more than \$50,000. Performance criteria included early removal of deep vadose zone VCOC sources to groundwater; minimal drawing of VCOCs from shallower to deeper soils; minimal air intrusion into the overlying landfill to maintain the landfill's anaerobic character; and removal of low-volatility organics from any leachate present beneath the landfill by aerobic biodegradation. Numerical modeling taking into account relevant data from the site (soil air permeabilities, VCOC distributions, soil characteristics, and gas generation rates) was again used to determine the optimal number of wells necessary. Model results indicated that remediation could be accomplished with three perimeter extraction wells and one central air injection well. A simulation using this setup showed depleting PCE over time at the water table, with residual concentrations left at the vadose zone (where they should have no impact); running the simulation longer shows that vadose zone concentrations will also decrease. A comparison of this optimized SVE approach to a conventional radius of influence (ROI) layout revealed significant cost savings using the SVE method, primarily because of the small number of wells

needed. In addition, pneumatic data collection followed by optimized SVE resulted in higher collection system efficiency and more rapid remediation.

Questions and Discussion

A participant asked about the total mass balance of the VCOCs present. Mr. Bentley replied that, although a total mass balance was attempted, the results varied: the number obtained after pumping with SVE was always higher than that obtained from monitoring probes.

Another attendee commented that he had considered supplemental SVE systems in sites that already have extraction systems in place. Mr. Bentley noted that, for passive systems, one has to make sure that they operate efficiently in terms of flow rates (as compared to active systems); in general, passive systems are not effective.

In response to a question regarding landfill gases, he replied that this could be done at different rates: carbon dioxide takes longer than methane, and VCOCs take even longer.

3:15 Combined Groundwater Remediation Strategies Using Electrical Resistance Heating (ERH)

David Fleming (Thermal Remediation Services, Inc.)

Electrical resistance heating (ERH) is a method of remediation using high voltage electricity to heat the soil to the boiling point of water and contaminants, forcing a phase change from liquid to gas. Vapors and steam are recovered at the surface for treatment, and *in-situ* degradation also takes place via increased biotic and abiotic reaction rates. ERH is a fundamentally simple and cost effective technology with costs for most commercial, full-scale sites ranging from \$200K + \$40-\$70 per yd³. Once the source area has been determined, standard drilling techniques are used to drill wells 10-12 inches in diameter and about 15-20 feet apart. Electrodes are placed inside the drilled holes, and each hole back-filled with steel shot, to increase the effective diameter of each electrode. Once the system has been set up and tested for safety, the boiling process is started: *in-situ* steam stripping forces contaminants to the surface of the water table and a vacuum pulls the free product to the surface. The soil then takes about two years to return to ambient temperature. The system is designed with multiple levels of safety and has had a perfect safety record in the ten years it has been in use. It does require moisture in the subsurface, but it can be as low as 4%. Very little water needs to be disposed at the end of the process, and it can be disposed of without any further treatment. ERH also increases dissolved organic carbon (converting TOC to water soluble forms) and microbe (*Dehalococcoides*) counts, and reduces contamination to below toxic levels by increasing hydrolysis rates. Heavy compounds (e.g., heavy oils, grease, creosote) can also be recovered using this technology. The technology can be applied in crowded public areas, and can be used in the presence of other utilities. Examples were shown using the system at a dry cleaning facility next to a public street, and an operating Air Force facility, where it was demonstrated using air sampling that the steam and vaporized contaminants could be controlled. A case study was presented of a site in Ft. Lewis, WA, where ERH was used to remove TCE from soil (2-30 feet bgs) and groundwater; 99.99% reduction of TCE in soil and 99% in groundwater was achieved, and the concentrations

continued to decline after the system was shut down. It was estimated that about 30% of these reductions were due to enhanced *in-situ* destruction. The total cost was about \$164 per yd³. A second case study involved 1,1,2,2-Tetrachloroethane (TeCA) remediation at a site in Annapolis, MD. TeCA undergoes hydrolysis and degrades to TCE, so that about 50% of the vapor steam was recovered as TCE. Final data from that site based on about 14 samples showed a 99.9% average reduction. The total cost of the remediation was \$72/yd³.

Questions and Discussion

Questions were raised on whether the costs quoted included the cost of electricity, and whether there was a difference in the amount of power used in briny versus fresh groundwater. Mr. Fleming responded that the costs of electricity were included in the totals reported; they represent about 15-20% of total cost in most areas. In areas with briny groundwater, the challenge is sizing cables to carry sufficient current to overcome the salinity, but the amount of energy used is similar.

A member of the audience asked whether sampling techniques were modified to account for high temperature samples. Mr. Fleming confirmed that a technique was developed for high temperature sampling; once collected, samples were allowed to cool before analysis.

In response to a question on whether ERH had been used in arid soils, Mr. Fleming replied that it had not been, however, it only requires 4% soil moisture, which exists in most vadose zones.

He also clarified, in response to questions, that electrodes are generally left in place once a project is complete; and that the amount of heat needed is determined by the boiling point of the contaminant(s).

4:00 Soil Vapor Extraction Pilot Test Study, Sierra Army Depot, Building 210 Area, Herlong, California *Jackie Saling, P.E. (ARCADIS, Inc.)*

The Building 210 Area site is near Reno, NV and currently stores war reserves and munitions, but has been used to store explosives, missiles, and fuels in the past. It is surrounded by mountains, a wildlife preserve, and a lake. Local agricultural activity also contributes to the flow into the groundwater; the site is a closed basin, with no water flowing out of the basin. Potential contaminant source areas were illustrated on a map of the area immediately surrounding Building 210. Site investigation for contaminants (soil and groundwater) was first conducted in 1983, and continued between 1992 and 2002. No volatiles were detected in any of the soil samples, however, significant TCE was found in soil gas. TCE was also detected in groundwater, with the highest concentrations nearest to Building 210. A pump and treat technique was used as an interim remedial activity, however, the efficiency of groundwater recovery decreased steadily over time due to significant fouling issues, which were not successfully resolved by acid or mechanical cleaning. Pilot tests were then conducted of other remediation techniques: HRC, zero valent iron (ZVI) injection, enhanced reductive dechlorination (ERD), and soil vapor extraction (SVE). Based on results from the pilots, the site

conceptual model (originally constructed in 2004 from available data) was revisited. Groundwater was found to be flowing Southeast at 0.5ft/day (rather than no movement); both vapor migration and groundwater are involved in TCE transport (rather than groundwater alone); and the plume is not as thin as initially thought due to diffusion of TCE in the groundwater over time. Some aspects of the model remained the same: there was no connection observed between possible source areas and groundwater impact; no vertical transport of contaminants from sources to the groundwater; and there was significant mass in the vadose zone. Of the technologies tested in pilot studies, SVE and ERD were both found to be viable for this site. Full scale SVE implementation was proposed for moving forward as it is a proven technology for the best mass removal at low cost. However, options to overcome the diffusion limitations associated with SVE will need to be considered and evaluated.

Questions and Discussion

A member of the audience asked whether air sparging had been considered. Ms. Saling responded that it was not considered due to the low permeability zone.

Another attendee commented that, in modeling efforts, air flow over groundwater should be included.

The same commenter noted that permanganate may also work in an oxidative system, and could be more cost effective even at depths of 95 feet.

Closing Remarks

Mr. Murdock thanked the presenters and attendees and adjourned the day's sessions.

**Desert Remedial Action Technologies (D-RAT) Workshop
Day 2: October 3, 2007**

9:00 Opening Remarks – Mary Aycock, U.S. EPA

Ms. Aycock opened the second day's sessions and thanked the speakers and audience for their participation. She briefly reviewed conference etiquette and logistics, and reminded those interested in attending the site visit the next day of their transportation options. Lastly, she thanked the conference sponsors, ARCADIS and TRC, for providing refreshments.

**Session 3 – Nanotechnologies
Chairperson: Mike Gill (U.S. EPA)**

**9:15 Nanoscale Zero Valent Iron Bench Scale Kinetic and Phase II Injection Testing,
Phoenix-Goodyear Airport North Superfund Site, Goodyear, Arizona
*Robert J. Ellis, LG (ARCADIS, Inc.)***

Mr. Ellis reviewed the use of nanoscale zero valent iron (ZVI) at the PGA North Superfund site in Goodyear, AZ. ZVI reacts with chlorinated organic compound molecules in several ways, the most important of which is direct reduction on the metal surface. Using nanoscale ZVI increases reaction times about three-fold compared to milli- or micro-ZVI. A graph was presented showing size ranges of nZVI, broken down by particle behavior. There is a limit to how small a particle can be injected into the ground: colloid suspensions become unstable with particles below 100nm, and solutions with particle sizes greater than 10 microns are subject to sedimentation. Controls on nZVI reactivity and delivery were also listed; these are not trivial with this technology, but are becoming better understood. A map and description was presented of the PGA North Site, which was previously used by the aerospace/defense industry and is contaminated primarily by perchlorate and TCE in the groundwater. ARCADIS conducted a two-phase evaluation of nZVI technology at PGA North. The first phase included reactivity and kinetics testing, column studies, groundwater geochemical analyses, an injection tracer test, and a field injection test. Some significant challenges were identified as a result of this phase of testing, including the lithology and aqueous geochemistry of the site; the poor predictive value of column studies for the success of field injections; agglomeration of aged nZVI particles that resulted in clogging; and limited distribution of nZVI in the aquifer. The second phase of testing was intended to understand and overcome some of these challenges, and is still ongoing. It includes additional groundwater testing; shelf life/longevity of nZVI in terms of reactivity; and kinetics studies to better understand TCE reduction once nZVI is introduced into the ground. It was observed that a dispersing agent (SHMP) could be used to overcome the agglomeration issues and aid in dispersal in the subsurface, and that nZVI remained reactive for thirty days after production. TCE degradation was slower in groundwater than in de-ionized water (in the pending results of the bench and field tests), however, nZVI was still highly reactive in the presence of groundwater. Work is ongoing on testing and enhancing nZVI technology, which remains a viable option for remediation of TCE in the source area at the site.

Questions and Discussion

Questions were raised about using permanent wells for injections, and on performance measures to ensure there were no "dead zones". Mr. Ellis noted the technology could be used either as direct push, or using existing monitoring wells; both options are being evaluated. Regarding performance measures, a bromide tracer was used to observe nZVI transport.

In response to a question about the type of water used, Mr. Ellis replied the water was from the main treatment site effluent, and was similar in chloride content to the site groundwater.

Another participant commented that injecting that much iron could change the resistance of groundwater, and suggested leaving probes in the ground to check for that.

A member of the audience asked whether nZVI remains continuously reactive once injected. Mr. Ellis explained that it remains reactive only until the iron surface is corroded.

A question was raised whether intact or disturbed columns were used for the bench-scale studies. An audience member stated that only disturbed materials were used, as it is impossible to get intact materials from these depths. Mr. Ellis added that some conditions (such as the pressure at 110-120 feet bgs) could not be reproduced at the bench scale.

A participant asked whether injection pressures would influence nZVI reactivity. Mr. Ellis responded that he was not aware of any such influence; pressure was monitored, but only to make sure there was no excessive stress to the well.

Another question concerned the water used for injection, and whether dissolved oxygen (DO) was a concern. Mr. Ellis replied that there is enough iron to offset the DO; in Phase II, the treatment will include sparging with nitrogen to make sure DO is stripped.

In response to questions about the cost of iron, Mr. Ellis explained that it has decreased significantly in recent years.

A member of the audience added that, for nZVI, much less iron is needed than the amounts used with iron probes.

Another comment was made noting that the diffusion coefficient of iron is very small. Mr. Ellis noted that this was true of any injection technology.

10:00 Bench-Scale and Field-Scale Evaluation of Nanoscale Iron Transport and Reactivity *Laurie LaPat-Polasko, PhD (Geomatrix Consultants, Inc.)*

Metallic nanoparticles have been discussed in the literature for about ten years. Their use in groundwater remediation is promising because their small size and surface area allow for faster reaction times and effective delivery to natural systems. A bench scale study was conducted to

test the transport times of nanoscale iron from four sources (two universities and two commercial vendors). Iron supplied from Auburn University had the best transport rate, and was then tested for reactivity (by measuring degradation of TCE), but results were poor. Further testing at Auburn involved manipulating the iron particles to increase their reactivity by adding a starch stabilizer. These findings were then used to conduct a pilot test at an aerospace facility contaminated with PCE (primarily), TCE and Freon, in order to test the logistics of using this material in the field – specifically in terms of transport and reactivity. Carboxyl methyl cellulose (CMC) was added to provide stability to the iron. nZVI particles were also coated with palladium for greater reactivity, and sodium bromide was added as a tracer. The *in situ* transport and reactivity of nZVI particles was then tested by a series of push-pull tests, where the solution was injected into the groundwater and pulled back to the surface to measure how much was recovered. Four series of these tests were run with different lag times before measuring for bromine and iron, and different concentrations of iron solution. Although the bromide tracer was recovered in all the tests, iron recovery was very low: the highest recovery was 31%, using no lag time and 340mg/L of iron. Conclusions drawn from these tests were that iron mobility decreases over time, and may be due to the starch stabilizer being consumed by soil microorganisms; and that addition of palladium does provide some benefit. The rate of dechlorination of CVOCs increased initially, but decreased sharply beginning about 100 minutes after injection. Nevertheless, this is a feasible technology for field application, and did achieve complete dechlorination of CVOCs at a rapid rate.

Questions and Discussion

A participant asked why the transport column studies did not use the observed field concentrations. Ms. LaPat-Polasko responded that several concentrations were tested, in accordance with each vendor's protocols.

Another question was raised about how changing the viscosity of the solution changed its transport through the substrate. The speaker explained that the nanoscale iron is delivered in a viscous form, and must be diluted before it can be injected, usually to a concentration of 1mg/L.

A member of the audience commented that the more the iron can be stabilized, the better the transport rates will be.

The same person asked whether this method would leave too much iron in the groundwater. Ms. LaPat-Polasko agreed that larger concentrations of iron might result in water quality issues, though 1mg/L should not. It also does not move far enough from the injection site, and would not be likely to, e.g., migrate to a drinking well.

Another attendee noted that if nanoparticle use becomes mainstream, they may have some impact, and added that there is no technology available to detect them.

A member of the audience asked whether remediation could have been achieved simply by adding the methyl cellulose. Ms. LaPat-Polasko agreed that it would have stimulated bioremediation, and may in fact be the best option for this site, despite the objectives of the original study.

Questions were asked about the transport distance of iron (from the injection point), and whether remediation continued after treatment. Ms. LaPat-Polasko responded that the estimated distance the iron traveled was less than ten feet; regarding remediation after injection, there has not been any significant change since the treatment ended.

Session 4 – Above Ground Treatment Alternatives
Chairperson: Cathy O'Connell (ADEQ)

**11:00 Catalytic Destruction of Gas-Phase TCE and PCE in Ground Water and Soils –
Laboratory Study and Field Investigation**
Song Gao, PhD (University of Arizona, Department of Atmospheric Sciences)

Dr. Gao discussed a catalysis method that includes both reducing and oxidizing components for remediation of chlorinated solvents in groundwater in an aboveground system. Each component of catalytic destruction has shortcomings that must be overcome. Oxidation requires high heat, results in catalyst poisoning by blocking active sites, and in cases of incomplete oxidation, produces furans and dioxins. Reduction requires hydrogen gas (at high cost) and can produce rapid deactivation through coking. The hypothesis for this study was that using oxidation and reduction simultaneously may negate some of these problems. This was tested at the lab scale, and later applied to a field pilot study. A catalytic converter (obtained from an automobile converter) was enclosed in a glass tube reactor and placed in a tube furnace to form the reactor system. Analytical measurements were taken of chlorinated and dechlorinated hydrocarbons, carbon dioxide, hydrogen, and oxygen. Furnace temperature during the experiments began at 75°C and increased at 2°C increments per minute to the desired temperature. At the end of the experiment, gas streams (except oxygen) were turned off and the temperature held at 450°C in order to clean the catalyst surface. Multiple reactions are involved in this redox system. Results of the PCE conversion rates were presented under redox and oxygen only conditions; at the optimum conditions (redox, at a ratio of 2.2 hydrogen to oxygen and 400°C), PCE conversion rates were higher than 90%. In addition, high conversion rates were also seen at much lower temperatures. The simultaneous presence of hydrogen and oxygen minimized catalyst poisoning and resulted in catalyst "self cleaning" as higher temperatures were reached. Homologous alkanes were also tested for their potential to replace hydrogen as a reductant, and it was determined that bond energy plays a deciding role in reaction rate and conversion efficiency. Propane was then used as a reductant in an extended field test at the Park Euclid site, where near 100% removal was achieved after 240 days. The cost of this technology is slightly higher than granular activated carbon (\$10 vs. \$7), however, this cost decreases with higher concentrations of contaminants. Redox catalysis holds potential for a low-cost, large-scale field alternative to current remediation technologies.

Questions and Discussion

A participant asked whether modeling was used to predict daughter product formation. Dr. Gao said that the effluent was measured [in the field study] and no intermediates were observed.

Questions were raised about whether the cost of energy used was included, and whether treatment costs were compared to bioremediation. Dr. Gao replied that all costs were included in his estimate, but noted that the other costs were insignificant compared to the cost of propane, which represented 80-90% of the total; propane costs can be offset somewhat by using higher temperatures. He added that no cost comparison was conducted between this technique and bioremediation, but it may be done in the future.

Another participant asked why the temperature was increased so gradually. Dr. Gao responded that the purpose was to carry out the reaction every minute, *i.e.*, make sure a reaction is occurring at all the incremental temperatures.

Session 5 – Chromium Technologies **Chairperson: Mary Aycock (U.S. EPA)**

1:30 Remediation of Mixed Chromium and TCE Releases *Paula Chang (ERM-West, Inc.)*

Ms. Chang summarized remediation techniques for chromium and TCE releases. In desert environments, chromium VI is more likely than TCE to be retained in vadose zone soils. Different factors control the distribution and persistence of chromium VI vs. TCE. For chromium, most discharges occur as chromic acid (Cr III in its acid form – *e.g.*, from acid baths used in metal plating), which likely converts to chromium VI upon encountering vadose zone soils. In the subsurface, dichromate reacts with calcium as well as with ferric iron and the ratio between calcium and iron (through mineralogy) often determines transport (*i.e.*, plume length). Ion exchange of minerals (especially with sulfate) is also a significant cause of rebound. Various remediation options exist for Cr VI, including flushing, and biological and chemical reduction. Coincidental reduction also takes place in the process of reduction of iron. However, biological reduction often fails when chromium is not serving as an electron donor in the indirect processes; requisite bacteria are not present; low pH or inability to maintain reducing conditions exist; and chemical reduction is limited by reaction time (which is dependent on kinetics, rather than reactivity). Screening was conducted of various reductants in a treatability study, which determined calcium polysulfide to be the most effective reductant in terms of both reaction time and cost. Biological and chemical reduction treatments were compared in terms of reaction rates, and chemical reduction was determined to be cheaper, faster, and more reliable. Several options are also available for TCE remediation, including SVE, recirculation wells, chemical reduction (using ZVI) or oxidation, and others. Recirculation wells can be paired with oxidizing or reducing technologies, or with a sparging system. A number of oxidants are potentially usable: ozone, peroxide, and permanganate are the most widely used and are generally commercially available. Technologies available for TCE remediation were then examined for their impact on Cr VI, and vice versa, indicating that some technologies could achieve remediation of mixed spills (*e.g.*, pump and treat, chemical reduction or oxidation). However, the difficulty of reductive dechlorination in the vadose zone may mean that different technologies are required for remediation of the vadose and saturated zones.

Questions and Discussion

In response to a question, Ms. Chang clarified that the Cr VI form was more toxic to microbes than Cr III.

A participant commented that the bacteria needed for chromium reduction through bioremediation are prevalent even in desert environments (unlike those needed for TCE remediation).

The same commenter added that attention must be paid to the mobilization of arsenic and manganese when reducing chromium. Ms. Chang agreed on both counts, and added that some aged plumes include petroleum products, in which case biological metabolism will use up oxygen and result in anaerobic conditions.

Another comment was made to the effect that arid soils generally contain less iron, so might retain less hexavalent chromium compared to a temperate environment.

A member of the audience asked whether transport of chromium occurs in a completely liquid form. Ms. Chang confirmed that most likely it would be added as chromic acid, and would be dissolved in a carrier.

She also confirmed, in response to an observation, that any issues with organic acids would be more complex in temperate environments than arid soils.

Another question was asked on what would happen if a reducing agent were used in a chromium complex. A member of the audience responded that the reaction time should be faster.

2:15 *In-Situ* Geochemical Fixation of Chromium in Groundwater in Arid Climates: A Comparison of Chemical Reductant Technologies *Peter Storch (URS Phoenix)*

Mr. Storch's presentation focused on identifying key parameters for evaluating and selecting chemical reductant technologies for chromium. Selection criteria most frequently used include effectiveness; subsurface distribution; safety and handling; regulatory acceptance; and cost. Effectiveness is defined as Cr VI reduction per mass reductant as demonstrated in the field, and persistence. Nanoscale ZVI had the highest reactivity, however, no field data were available; calcium polysulfide (CPS) and HRC were the most reactive based on field data. Data on technologies in use in the field reveal CPS and bioreduction to be the most common; however, nanoscale iron will likely be used with more frequency as the technique is developed. Persistence is also used in selecting a treatment, since higher persistence results in fewer injections. Dithionite, CPS, and nZVI were the most persistent; however, dithionite's persistence is dependent on naturally occurring iron. Distribution is affected by transport parameters, reaction kinetics, and migration through the groundwater. Comparing distribution factors reveals that dithionite, ferrous sulfate, and CPS would work well; CPS's persistence is due to a slow

decomposition step, which allows for distribution throughout the aquifer. Nanoscale iron can also have a high distribution rate if injected using a nitrogen gas carrier. Distribution is higher the closer the viscosity of the injection is to that of water. Safety is not generally a concern with reductants, although there are some risks to both human health and groundwater. Regulatory concerns vary by treatment, but typically include dilution; degradation of groundwater quality from byproducts; pore space plugging; displacement; and preferential pathways. Costs are lower (per unit) for CPS and dithionite, but total cost should also be considered, as the cost of the chemical rarely drives the total cost of the project. Examples were presented of the best treatments for various soil types and site characteristics. The attributes of each treatment were also summarized, and ZVI, CPS, and bioreductants were identified as good choices for arid environments.

Questions and Discussion

In response to a question regarding arsenic mobilization, Mr. Storch replied that he had not encountered that, although it is always a concern.

A member of the audience asked about disulfide, which was listed initially but not discussed further. Mr. Storch responded that it was considered, but it is an old technique, which resulted in changes in the soil color and temperature. Another commenter said that the cost for disulfide was relatively low, but noted that he had not used it in over two decades.

A question was asked about the most common delivery mechanisms for calcium polysulfide. Mr. Storch replied that direct push or direct injection through wells are commonly used; it has good reducing power, so it is possible to get good results with a mixture of less than 1% polysulfide mixed with corn syrup.

A follow-up question was raised on whether polysulfide stimulated *in-situ* bioremediation when co-injected with an electron donor. In laboratory situations, microcosms are often killed by the reducing power of CPS. Mr. Storch said that he has observed this, because of either high pH or high CPS concentrations. However, bioactivity can return after the sulfide concentrations decline.

3:00 Army Corps of Engineers Chromium Presentation

Waleed (Wally) Shaheen, PE (US Army Corps of Engineers) and Paul Lear (Shaw Environmental)

This presentation summarized a case study of *in-situ* biological treatment (ISB) of hexavalent chromium at the Selma pressure treating Superfund site. Contamination sources included phenol from drip-drying treated wood and spillage from tanks. Several remediation strategies were used prior to 2003, when ISB was proposed as remedial enhancement. The project was divided into phases (corresponding to sections of the plume), beginning at the area of highest concentration. Phase 1 became a pilot study, while the other phases involved actual remediation. Bench tests were first conducted by collecting microcosms from the site and amending with EHC (a trademarked product that contains carbon and reduces the Eh), lactate and molasses. The

samples were also evaluated for arsenic mobilization and degradation rates of Cr VI. Bench test results indicated that Cr VI reduction was faster using molasses (compared to lactate), and biodegradation was observed even at high concentrations. Cr VI reduction occurs before nitrate reduction, and can occur in the presence of oxygen. Neither arsenic mobilization nor conversion of Cr III to Cr VI were observed. The pilot test portion of the study used injection points (direct push) 30 feet apart and high concentrations of molasses. Reducing conditions were achieved quickly, and Cr VI and total chromium reductions were also rapid. Nitrate, manganese, ferrous iron, and sulfate showed an increase, followed by a decrease; these will continue to be monitored until they return to ambient levels. These findings likely indicate that too much molasses was used, creating excessive reducing conditions. This treatment is also limited to depths of 110 feet bgs. For Phase 2B of the project, groundwater recirculation with metered substrate addition was selected. This system was powered by the pumps in the extraction wells. The high concentration of molasses in this case resulted in biofouling, and limited distribution from the injection well. Lactate was added, and led to improved progress in reduction. Results showed the soil was in the reducing range, with hexavalent chromium decreasing significantly over 300 days. Further phases will include a biocide system to eliminate biofouling. Overall, *in-situ* remediation was found to be effective for the treatment of Cr VI; however, field testing is necessary to confirm feasibility of the system design, and delivery methods and chemical/biological processes must be optimized for the site conditions.

Questions and Discussion

A participant asked whether horizontal drilling was considered, particularly for the portion of the site that is under the highway. The speaker responded that this was discussed, but will not be necessary, as the contaminated ground [near the highway] will be treated with injections on either side of the highway to allow for sufficient coverage under the road.

Clarification was requested on the biocide used; the speaker explained that it was a commercial product named "Bio-Cide".

A comment was made on the biofouling, and it was suggested that the amendment be injected downgradient of the injection well if possible.

In response to a follow up question, the speaker responded that only low traces of methane had been observed in areas where there was biofouling.

Another attendee asked what quality molasses was used, and whether it resulted in any secondary water quality issues. The speaker responded that food grade molasses was used.

Regarding water quality, manganese was an issue in the direct push injection area, and will be allowed to return to ambient levels through diffusion.

Closing Remarks

Ms. Aycock thanked the speakers and audience, and reminded participants of the planned evening activities and site visit. Mr. Gill asked the audience for any further comments on

anything that had been discussed, particularly suggestions for remedial opportunities that were not covered. No comments were made, and Mr. Gill adjourned the conference, noting that conference materials would be available on the workshop website by December 1, 2007.

Poster Session Presentations

HOW'D THAT GET IN THERE? A Practical Approach to Determining Sources of Unexpected Contaminants or Why Geochemical Characterization is Key to Remedial Investigations
(Tiffany Downey, PhD – GeoTrans, Inc.)

In Situ and Ex Situ Perchlorate Bioremediation in Vadose Zone Contaminated Soil
(Laurie LaPat-Polasko, PhD – Geomatrix Consultants)

In-Situ Bioremediation for Treatment of Chlorinated Solvents and Perchlorate Impacted Groundwater in Desert Environments
(Ronald Johnson – Geosyntec Consultants)

Thermally Enhanced Soil Vapor Extraction to Remediate Volatile Organic Compounds
(Jay Dablow – ERM-West, Inc.)

Injectable Micro-Scale Iron for Source Treatment of Chlorinated Solvents in Deep Groundwater
(Paula Chang – ERM-West, Inc.)

Field Scale Investigation of Mass Flux Reduction as a Function of Source Zone Mass Removal for Immiscible Liquid
(Erica L. DiFilippo – University of Arizona, Department of Hydrology and Water Resources)

Desert Remedial Action Technologies (D-RAT) Workshop
Day 3: October 4, 2007
Field Trip

About 30 attendees participated in a morning field trip to the Phoenix-Goodyear Airport – North (PGA-North) Superfund site. They toured outside the former Unidynamics facility area, where VOCs and perchlorate contamination are in the subsurface. The group was given a tour of the SVE treatment system, the Main Treatment System, a “dry wells” area (the original source), and extraction well 33A, where the discharge point is into the Roosevelt Irrigation District canal. ARCADIS engineers Rob Ellis and Chase McLaughlin provided the background at each stop of the tour. Rob Ellis also discussed the nanoscale zero valent iron pilot test for remediating VOCs at the dry wells (source) area.



Arizona Soil: Why remediation is such a challenge!



This is the Main Treatment System located at the PGA-North (Unidynamics) site. The system treats contaminated groundwater for TCE and perchlorate at the main site, and then the water is reinjected into the aquifer through a network of injection wells in Subunit A.



This is the extraction well 33A treatment system for TCE treatment. The system is designed to extract contaminated groundwater from Subunit A at the northwest portion of the plume and treat it for TCE prior to discharge to the Roosevelt Irrigation District (RID) Canal. The system located in the front of the picture is actually part of a sand trap pre-filter that filters the water before it goes to the carbon vessels.



Extraction well 33A system discharge into the Roosevelt Irrigation Canal (RID)

ACKNOWLEDGEMENTS

It was due to the efforts of many people that this workshop was a success. Thanks go to US EPA's Mary Aycock and Glenn Bruck for developing the workshop idea, Cathy O'Connell and her colleagues at the Arizona Department of Environmental Quality (ADEQ) for their support, EPA's Office of Science Policy within the Office of Research and Development for their financial support (Mike Gill's office), Leanne Austrins, Kevin Murdock, and colleagues of CH2MHill's Phoenix office for planning and on-the-ground assistance, our field trip sponsors (Mike Hansen of ARCADIS and Al Bilzi, working under contract to the Crane Company), our snack sponsors (again Mike Hansen from ARCADIS and Terry Maize from TRC), our EPA support contractor, Nathalie Panayiotakis from CSS, Inc., and the planning committee (pictured below). Of course, the speakers and poster presenters get the most credit, as they took the time to share their knowledge and experience with all of us. They really made the workshop a success!



D-RAT Workshop Planning Committee: Kevin Murdock (CH2MHill), Cathy O'Connell (ADEQ), Nathalie Panayiotakis (CSS, Inc.), Mike Gill (US EPA), Glenn Bruck (US EPA), Leanne Austrins (CH2MHill), Mary Aycock (US EPA)

Summary of Desert – RAT Workshop Evaluation Form

The talks and presenters are listed below in order of their feedback score (the number before the talk title). The feedback scores shown represent averages of all feedback received from attendees, which ranged from 1 (best score) to 5 (worst score). Pertinent comments are listed following the scores.

(1.8) Nanoscale Zero Valent Iron Bench Scale Kinetic and Phase II Injection Testing, Phoenix-Goodyear Airport North Superfund Site, Goodyear, Arizona - Robert J. Ellis, LG – ARCADIS

(1.9) In-Situ Bioremediation for Treatment of Chlorinated Solvents and Perchlorate Impacted Groundwater in Desert Environments - Sam Williams – Geosyntec Consultants

(2.0) Combined Groundwater Remediation Strategies Using Electrical Resistance Heating - David Fleming - Thermal Remediation Services

(2.0) In-Situ Geochemical Fixation of Chromium in Groundwater in Arid Climates: A Comparison of Chemical Reductant Technologies - Peter Storch – URS Phoenix

(2.0) Corps of Engineers Chromium Presentation - Wally Shaheen & Paul Lear

(2.1) Catalytic Destruction of Gas-Phase TCE and PCE in Ground Water and Soils – Laboratory Study and Field Investigation - Song Gao, PhD – University of Arizona, Department of Atmospheric Sciences

(2.1) Remediation of Mixed Chromium and TCE Releases - Paula Chang – ERM-West, Inc.

(2.1) Systematic Remedial Methodology for Chlorinated VOC Contamination of Soils and Groundwater Underlying Desert Landfills - Harold Bentley and Stewart Smith – Hydro Geo Chem, Inc.

(2.3) Pilot Test of Deep Aquifer Permanganate Treatment - David Abranovic, PE – ERM-West, Inc.

(2.3) Bench-Scale and Field-Scale Evaluation of Nanoscale Iron Transport and Reactivity - Laurie LaPat-Polasko, PhD – Geomatrix Consultants

(2.4) Perchlorate, TCE, and 1,4-Dioxane Investigation and Remediation at a Rocket Propellant Facility in a Semiarid Environment - Edward (Ted) Tyler & Dave Jenkins – Kleinfelder West, Inc.

(3.1) Soil Vapor Extraction Pilot Test Study, Sierra Army Depot, Building 210 Area, Herlong, California - Jackie Saling – ARCADIS

(3.2) Evaluation of an HRC and HRC-Primer Injection at a TCE-Impacted Site after the Operation of a Dual Phase Vacuum Extraction System - Gustavo Valdivia, PE – Bureau Veritas North America, Inc.

Pertinent Comment Summary

- Sites where closure was achieved were well received
- Attendance would have been better with more advertising earlier
- Great chances for communication with attendees and presenters
- More emphasis on desert field environments would be preferred
- Too much propaganda not enough ground truthing of methods, weak data
- Would like additional academic presentations from local universities and presentations from ADEQ/EPA
- Would like to have repeat of this workshop
- Liked that most presentations had lessons learned segments
- Suggest one day of topics be pertinent to state superfund sites and technologies that would benefit them
- Good exposure to different technologies
- Good venue size, good website
- Good questions
- Enjoyed the run
- Podium closer to audience
- Liked the snacks
- Appreciated conference adherence to schedule
- Indicate to attendees that they are responsible to bring their own printed materials if desired