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Bioventing results from a gasoline-ethanol-contaminated soil

Scientists from Brazil recently evaluated a biovented study of a gasoline-ethanol-contaminated soil. The purpose of the study was fourfold:

- to determine the influence of bioventing on gasoline and gasoline/ethanol in unsaturated soils
- to evaluate changes in microbiota as an indicator of soil toxicity
- to evaluate the effect of ethanol on gasoline degradation
- to determine whether GPR (ground penetrating radar) and culturable bacterial counts can be useful tools for monitoring distribution and degradation of PHC (petroleum hydrocarbons) in unsaturated residual soil

Gasoline with ethanol

In Brazil, gasoline has 26 percent (volume/volume) ethanol. More mobile than the usual gasoline components, ethanol is preferentially degraded over gasoline components. "BTEX compounds are degraded by inducible enzymes that can be repressed when easily degradable substrates are present at high concentrations. Also, ethanol degradation leads to a depletion of electron acceptors in soil for BTEX degradation. Poor oxygenation conditions may thus prevail in the aquifer, delaying BTEX degradation, supposedly leading to longer plumes. This situation is of special concern for benzene that degrades rather slowly in anaerobiosis" (Osterreicher-Cunha and others, 2004).

Soil blocks

For their study, researchers removed six soil blocks (undisturbed cubic soil blocks, 30 cm on a side) from a metropolitan area of Rio de Janeiro, Brazil. They

covered the blocks with aluminum foil, plastic film and paraffin to maintain a constant soil moisture content. The soil investigated, a young or saprolitic gneissic soil from the soil horizon C, was unsaturated and composed of two facies: a white facies, which was a silty sand with quartz and potassic feldspar, and a gray facies, made up mostly of a sandy silt with quartz and biotite as the main minerals. Of the six blocks:

- block 1 was a control, receiving neither contamination nor treatment
- block 2 was ventilated
- blocks 3 and 4 were contaminated with gasoline and gasoline-ethanol mixture and received no treatment
- blocks 5 and 6 were both ventilated after being contaminated with gasoline and gasoline-ethanol mixture

The treatment for the blocks consisted of bioventing, a common "technique to remediate PHC-contaminated soils, as it enhances the ability of soil microbiota to degrade natural and xenobiotic compounds. Air injected in the unsaturated zone provides microorganisms with adequate oxygen conditions so that degradation may continue efficiently for longer periods of time" (Osterreicher-Cunha and others, 2004).

Reviewer's comment: Bioventing in the literature is not well defined; most of the time, the term bioventing refers to the extraction of air from the unsaturated zone in a venting operation. As air is extracted, air from the atmosphere replaces it in the unsaturated zone, thereby increasing the oxygen loading in the subsurface. Bioventing has also been defined to include injection of air into the unsaturated zone; air moves through the subsurface and existing air is exhausted through the ground surface to the atmosphere.

Assessment techniques

Techniques to analyze the treated contaminated soil included

- traditional microbiological techniques, to evaluate culturable heterotrophic bacterial populations; its disadvantage is that only culturable microbial populations are represented
- enzymatic activity, which generally correlates with bacterial abundance
- gas chromatography to determine PHC amounts
- GPR; "GPR sends electromagnetic waves (EMW) into the subsurface aiming to detect differences in soil electric properties... During biodegradation, uncharacteristic high conductivities have been attributed to microbial activity in PHC-contaminated sediments because of acid and biosurfactant production by indigenous microorganisms"

Results

Subsurface physical and biological properties and distribution of microbiological properties are related to the environment's chemical and physical properties. Because of the great heterogeneity in these properties, a high microbial heterogeneity results. "Microbial activity correlates positively to clay content and negatively to sand content because of the protective effect of clays on enzymes. Soil fractionation studies also showed that microbial biomass is strongly associated with clays. Studies...show that bacteria are preferentially located in soil micropores, within micro-aggregates themselves, with only 4-10 percent of pore space in aggregates being colonized. These populations are not similarly exposed to contaminants or nutrients like those living in macropores; on the other hand, they are less subject to drastic changes in water availability leading to alternation of desiccation and wetting. Thus, their survival

and the intensity of their metabolic degradation activity depend less on their ability to adapt rapidly. However, microbial occupation of residual soils is still unknown."

Researchers found that both soils facies had

- a low cation exchange capacity
- a low colloidal activity
- a low organic matter content

Even when pure gasoline was added to the soil, changes in conductivity and dielectric permittivity were insufficient to allow for gasoline detection by GPR. Gasoline amended with 22 percent ethanol is visible on GPR because ethanol has a higher dielectric content than gasoline and most geological materials. Yet ethanol's kinetic behavior, high volatility and degradability may prevent detection by GPR.

Researchers found that "changes observed in GPR radargrams and dielectric constants of all blocks 30 and 100 days after contamination reflect variations in soil conductivity that may be the result of a water content increase and/or bacterial higher metabolic activity in soils... Bacteria probably present in contaminated soils, and greater culturable populations observed in non-contaminated soils, might be responsible for the formation of acid residues that increased soils conductivity."

The major factor in GPR attenuation seems to be water. In soils blocks that were biovented, drying has the effect of decreasing soil conductivity.

As for decreases in PHCs:

- the ventilated soils with gasoline and ethanol decreased by 98 percent
- the non-ventilated soils with gasoline and ethanol showed a 74 percent reduction
- ventilated soils with gasoline showed a 92.7 percent reduction

- non-ventilated soils with gasoline showed a reduction of 95.4 percent

Researchers concluded:

- bioventing had a greater impact on the ethanol-containing soils than on the gasoline-containing ones
- culturable bacterial populations decreased significantly when large amounts of gasoline with or without ethanol were added to the soil
- bacterial recovery occurred later in gasoline-ethanol- vs. gasoline-contaminated soils, suggesting toxicity lasts longer in gasoline-ethanol soils (ethanol tends to deplete electron acceptors in saturated soils, creating oxygen-limited conditions, thwarting BTEX degradation)
- once culturable bacteria growth resumed, populations of ventilated and non-ventilated gasoline-contaminated soils did not differ significantly
- microbiological data correlates with decreases in gasoline amounts but not with absolute numbers of contaminant residue in soil
- "if electron acceptor depletion caused by ethanol degradation occurs in unsaturated soil as it does in saturated ones, aeration may have allowed for BTEX degradation to persist"
- according to GC (gas chromatography) data, gasoline compounds in soil must drop below 1 percent before microbes recover; for gasoline-ethanol-contaminated soils, "recovery occurs only when contaminant amounts are no longer detected by the adopted methodology"
- GPR results showed decreased conductivity in ventilated soils, "even in gasoline-contaminated ones where no differences in culturable bacterial numbers were found"

- degrading activity from soil microbiota may alter GPR data, although increasing water content prevented detection of that activity in experimental conditions
- microorganisms, because of their small dimensions and morphological simplicity, are difficult to study; thus the vast majority of microorganisms, especially those of importance to the environmental industry, have not been studied; 90 to 99.9 percent of the total populations have not been studied
- "contaminant-induced selection probably prevented culturable bacterial populations from expanding while allowing the survival of highly specialized organisms, which would be very unlikely to grow on culture media"
- the bacterial populations most likely to grow in the laboratory are the less-specialized ones
- a delay in bacterial populations with gasoline-ethanol- vs. gasoline-contaminated soils indicated a possible preference for ethanol degradation
- bioventing appeared to accelerate soil detoxification and microbiota recovery

Researchers hope that "In the next steps of the present study, molecular tools combined with culture-dependent approaches may allow a better understanding of total bacterial population shifts due to contamination, bioventing, and contaminant degradation, and a better evaluation of microbiota's capacity to return to its original state and profile... Despite the fact that contaminant presence and degradation in soil were not detectable by GPR in the conditions of this study, its use in conjunction with other assessment techniques may still be of great value and should be further evaluated for this particular use in contaminated soil" (Osterreicher-Cunha and others, 2004).

Reference

Osterreicher-Cunha, P., Vargas, E.A., Guimaraes, J.R.D., Pereira de Campos, T.M., Nunes, C.M.F., Costa, A., dos Santos Antunes, F., Pais da Silva, M. and D.M. Mano, "Evaluation of Bioventing on a Gasoline-Ethanol-Contaminated Undisturbed Residual Soil," *Journal of Hazardous Materials*, Vol. 110, 2004; <http://www.sciencedirect.com/science/journal/03043894>



Spatial heterogeneity study

While investigating biodegradation rate data, scientists discovered that laboratory-measured biodegradation rates were higher than those from field data, an indication that "current techniques for measurement of intrinsic bioremediation are not adequate." To obtain better estimates of contaminant fate and transport, scientists "studied the distribution of microbial and geochemical parameters in contaminated and pristine regions of two gasoline-contaminated aquifers." The two aquifers studied were at the Pope Air Force Base and Rocky Point sites in North Carolina.

Kota and others (2004) examined microbial and geochemical vertical and horizontal spatial heterogeneity by obtaining samples from:

- 7.5 cm vertical intervals between 2.92 and 3.83 m (microbial population of contaminated sediments)
- pristine and contaminated samples collected at various distances from the source (examining geochemical and microbial populations obtained from the 3.35 to 3.96 m interval)

Researchers collected sediment samples under anaerobic and aseptic conditions and homogenized them prior to analysis. They then assayed the samples for

- solid phase Fe(II) and Fe(III)
- grain size

- total viable heterotrophs, or total bacteria
- iron reducers
- anaerobic and aerobic protozoa
- sulfate reducers

Groundwater samples, collected from the same locations as the sediment samples, were analyzed for

- Fe⁺²
- SO₄⁻²
- CH₄
- BTEX
- pseudocumene
- mesitylene

The analytical methods used to analyze the sediment and groundwater samples are described in the text.

Rocky Point site results

Sediments from the Rocky Point site were deposited in a shallow marine, open shelf environment in the Late Cretaceous. Site geology is characterized by "dark, gray and green micaceous fine sand overlain by 1.5 to 4.5 m of silts, clays and clayey sands." In 1987 a UST leak was discovered. Further research indicated that indigenous microorganisms were biodegrading BTEX, and iron reduction is a significant electron acceptor. Analyses indicated the following in the pristine and contaminated portions of the aquifer:

- aerobic and anaerobic protozoa
- Fe reducers (greater in the contaminated samples)
- methanogens not enumerated due to low concentration of dissolved methane
- total bacterial population, (AODC), of about 10⁶ cells/g
- protozoan population dominated by vegetative cells as opposed to cysts
- an absence of sulfate reducers

"In general, populations in the contaminated region... were higher than populations in the pristine region... which is consistent with microbial growth in response to increased carbon... Both aerobic and anaerobic protozoa decreased with depth..." (Kota and others, 2004).

For samples acquired at 0.3-m vertical intervals, to define vertical variability:

- the presence of Fe(II) suggests that iron reduction is an important electron sink, while the presence of sulfate indicates the potential for sulfate reduction
- methane concentrations never exceeded 0.1 mg/l, suggesting a minimal role for methanogenesis
- calculated biodegradation capacities suggest that Fe(III) reduction is the dominant terminal electron-accepting process
- at one interval, possibly elevated sulfate leads to increased sulfate reduction and precipitation of FeS
- hydrocarbon concentration varied considerably with depth, which could be explained by a sinking plume; however, depletion of m- and p-xylene relative to pseudocumene suggests varying biodegradation rates with depth; the depleted intervals also correlated with elevated iron-reducer populations
- variations in geochemical conditions govern Fe(II) dissolution and precipitation
- variations in Fe-reducing, anaerobic protozoan and hydrocarbon concentration data are consistent with biological activity with depth

For samples acquired to define horizontal variability:

- total heterotrophs were on the order of 10⁴ to 10⁵ cells/g of sediment
- the number of anaerobic protozoa ranged from 4 to 17 cells/g sediment and did not correlate with the reducing population
- vegetative cells always exceeded the number of encysted protozoa

- methane concentrations were low and this was consistent with low indigenous populations
- no sulfate reducers were detected
- there was little variability in Fe(II)_{aq}, sulfate and methane
- iron was the dominant electron acceptor although there was some potential for sulfate reduction

Thus, researchers agree that there exists substantial variation at Rocky Point, and that iron reducers are dominant relative to sulfate reducers and methanogens. "The failure to detect sulfate-reducing bacteria (SRB) was surprising given the reducing conditions and presence of sulfate in the aquifer... If SRB was present, then they appear to have rather narrow growth requirements." In addition, Fe was found to vary horizontally and vertically.

Pope Air Force Base

Geology here is mostly "naturally deposited alluvial sands, silts and clays...sediments that consist of brownish yellow to very pale brown, fine-to-coarse sand with thin, discontinuous silt and clay seams." Water-soluble constituents at the site (the site was used for training exercises) consist of BTEX; in the plume areas, "there is an increase in dissolved iron and methane and a decrease in sulfate, suggesting that iron and sulfate reduction and methanogenesis may be playing a role in contaminant biodegradation."

Analysis of the Pope Air Force Base samples indicated

- substantial spatial variability exists in microbial populations and aquifer geochemistry
- total heterotrophs, Fe-reducers, SO₄ reducers and methanogens were detected in most samples
- iron reduction, sulfate reduction and methanogenesis are ongoing processes

- total heterotrophs were higher on the horizontal as opposed to the vertical scale
- sediment texture did not influence microbial or geochemical parameters
- the Fe(II) aqueous phase is higher in this aquifer than in other aquifers

Horizontal comparison data indicated

- little variability in the iron- and sulfate-reducing populations, but consistent with vertical data
- elevated methane concentrations consistent with an elevated methanogen population
- total heterotrophs, iron reducers and sulfate reducers and methanogens detected in contaminated sediments
- no anaerobic protozoa detected at the 7.5-cm vertical intervals, thus researchers did not enumerate the protozoan populations
- total heterotrophs greater in the contaminated sediment, suggesting that increased numbers resulted from carbon substrate presence; detectable iron, sulfate reducers and methanogens were scarce in the pristine parts
- general decrease of dissolved hydrocarbons with distance, consistent with attenuation by biodegradation and dilution, but mostly biodegradation because benzene was still present
- no apparent correlation between sedimentary plus aqueous Fe and the iron reducer population in the contaminated sediment
- no apparent relationship between sulfate concentration and sulfate reducers

Vertical comparison data indicated

- hydrocarbon concentrations are fairly consistent with depth and exhibited no preferential depletion

- substantial variability existed in the distribution of the microbial populations
- methanogens were not detectable at the depths of the highest Fe-reducing population
- methanogens were lower than sulfate reducers and had no detectable pattern
- aerobic protozoa were detected, but not anaerobic protozoa
- variation in solid Fe fraction suggests that different chemical conditions characterize different depths; in addition, differences in bioavailability are associated with different mineral forms

From their analyses of closely spaced groundwater and sediment samples, Kota and others (2004) contend that "spatial variations in microbial and geochemical parameters exist at Rocky Point and Pope Air Force Base. Results of this study suggest that current techniques of utilizing blended sediment for measurement of in-situ biodegradation rates will provide misleading results. Also, the current practice of evaluating the importance of Fe(III) to the biodegradation capacity of the aquifer undergoing intrinsic bioremediation has to be reevaluated."

Reference

Kota, S., Barlaz, M.A. and R.C. Borden, "Spatial Heterogeneity of Microbial and Geochemical Parameters in Gasoline-Contaminated Aquifers," *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management*, April 2004; <http://www.pubs.asce.org/>



The electron acceptor Fe(III)

Probably the most important electron acceptor for hydrocarbon biodegradation in aquifers is Fe(III). Reduction of Fe(III) occurs as organic contaminants are oxidized and broken down. (Recall that reduction is a gain of one or more electrons by a substance, whereas oxidation is a loss. Fe(III) is also an electronic sink.) Fe(III) is abundant in soils, aquatic sediments and aquifers, and often the most abundant potential electron acceptor.

Fe(III) source and availability

Scientists have found that rates of "Fe(III) reductive dissolution of iron oxides appear to be inversely proportional to the degree of crystallinity" of the oxide minerals, e.g. hematite < goethite < ferric hydroxide. These minerals also vary in particle size, available surface area, reactivity, and oxidation state. The greater bioavailability of the less crystalline forms may be due to their greater surface area.

Attempts to estimate accurately the amount of bioavailable Fe, however, have not always been successful. Most attempts "were based on the use of selective extractions to determine the most chemically reactive fraction." Some techniques, such as a method that uses Fe(II) catalyzed dissolution of crystalline oxides by oxalate, results in an over-estimate of bioavailable Fe(III). Using accumulation of dissolved Fe(II) to estimate Fe(III) can underestimate Fe(III) availability.

Another factor that affects iron bioavailability could be mineral surfaces that are coated with sorbed or precipitated Fe(II). Iron coatings usually appear as a solid phase or in the reduced minerals: magnetite (Fe_3O_4), siderite (FeCO_3), and vivianite ($\text{Fe}_3\text{PO}_4 \times 8\text{H}_2\text{O}$). "However, the effects of sorption and/or precipitation of Fe(II) on Fe(III) bioavailability in sediments are not

well understood" (Kota and others, 2004). In one study that used an Fe(III)-reducing bacterium, sorption of Fe(II) to cell and oxide surfaces controlled Fe(III) oxide reduction."

Present study

Kota and others (2004) studied sediment from a petroleum-contaminated aquifer near Rocky Point, North Carolina. (See the previous UTTU article for additional information on this site.) The aquifer sediment here had "been exposed to anaerobic, organic-rich water for over 10 years" (Kota and others, 2004). Groundwater had the following characteristics:

- no measurable dissolved oxygen
- low sulfate concentration
- low methane concentration
- high dissolved Fe(II) concentration
- dissolved benzene, toluene, ethylene and xylene

In addition to the above, researchers also found ethanol and acetate in the sediment and groundwater.

The goals of this research were to:

- determine the amount of Fe(III) in the sediment available for microbial reduction
- relate Fe(III) depletion to shifts in microbial reduction processes
- evaluate the effect of Fe(II) on sorption and/or precipitation on Fe(III) availability
- identify suitable extraction methods that can indicate amounts of Fe(III) reduced

Macrocosms

Scientists created several macrocosms using the aquifer material and groundwater from the gasoline-contaminated site, and fed it a carbon source, benzaldehyde. Macrocosms created consisted of:

- three live macrocosms with added carbon

- one live control with no added carbon, to measure the effect of background organic carbon
 - one abiotic macrocosm with benzaldehyde
- Macrocosms were monitored/assayed for
- Fe(III) depletion
 - production of solid and aqueous phase Fe(II)
 - benzaldehyde degradation
 - accumulation of degradation intermediates
 - dissolved organics
 - CH_4 (headspace)

After about 16 days of macrocosm incubation, iron reduction slowed and fermentation products began to accumulate. Researchers attributed the changes to three possible hypotheses:

- Fe(III) availability was not limiting Fe(III) reduction, but some other factor was causing the shift (hypothesis 1)
- "mineral surfaces were being fouled by sorption and/or precipitation of Fe(II), reducing Fe(III) bioavailability" (hypothesis 2)
- "the mineral form of the remaining Fe(III) made it relatively unavailable for use by the sediment-associated microorganisms" (hypothesis 3)

For the test of hypotheses 1 and 3, "several different Fe(III) forms (amorphous-oxhydroxide, goethite and hematite) were added to separate microcosm incubations..." (All microcosms were incubated, and times of incubation varied.) The additions consisted of approximately 540 μmol Fe(III)/g. To evaluate hypothesis 2, researchers washed a portion of the sediment with either CaCl_2 or NaAc. In this scenario, the Fe(II) should undergo ion-exchange and precipitate. Treatments would also kill or remove most indigenous microbes... Both the mineral addition and sediment washing experiments were monitored for depletion of fermentation products

and reduction of Fe(III)" (Kota and others, 2004).

These macrocosms were assayed for

- dissolved organics
- Fe (solid and aqueous)
- CH₄ (headspace)
- CO₂

Researchers enumerated the macrocosms for

- Fe reducers
- methanogens (H₂ utilizers and acetate utilizers)

The Kota and others (2004) text gives details on these enumerations and analytical techniques used to determine the various iron concentrations. In addition, researchers analyzed aqueous samples for

- benzaldehyde
- benzoate
- benzyl alcohol
- hexanoic acid
- caproic acid
- butyrate
- propionate
- acetate
- ethanol

Researchers did not detect hexanoic acid, caproic acid, butyrate and propionate. They did periodically use a GC (gas chromatograph) to identify organic acids and biodegradation intermediates.

Results

Researchers found that "the total amount of Fe(III) present in the Rocky Point sediment was comparable to literature reports, suggesting that the Fe(III) present in the Rocky Point sediment was less reactive. Since the aquifer sediment (marine in origin, made up of

fine quartz sand in a clay matrix with minor pyrite and muscovite flakes) had been exposed to anaerobic, organic-rich water for more than 10 years, most of the readily extractable Fe(III) may have been reduced. Pristine sediment collected 50 m outside the contaminant plume contained a slightly higher percentage of Fe(III), indicating that previous exposure to the contaminant plume may have reduced the amount of bioavailable iron" (Kota and others, 2004).

In the microcosms, the benzaldehyde was transformed to benzoate and benzyl alcohol and was not further biodegraded. In the anaerobic biodegradation of some aromatic compounds, benzoate is a known intermediate, and this biodegradation can occur under Fe(III) reducing conditions. One study found that "*A. putrefaciens* was unable to couple the oxidation of benzoate to Fe(III) reduction even though it was able to oxidize a multitude of other electron donors. [Another study] concluded that the biogeochemical fate of specific organic acids observed in groundwater varied with the structure of the acid and the availability of electron acceptors... Therefore, the persistence of benzoate here can be attributed to the unavailability of a specific electron acceptor, nonmethanogenic conditions or the absence of required organisms" (Kota and others, 2004).

Researchers hypothesize that accumulation of hydrogen (produced during transformation of benzaldehyde to benzoate) led to an increase in production of benzyl alcohol. As H₂ was consumed during reduction of sedimentary Fe(III), and Fe(III) reduction stopped, hydrogen accumulated, causing a shift toward ethanol and benzyl alcohol production.

Acetate and Fe in the microcosms

Acetate accumulation in the benzaldehyde and live control microcosms suggested origin resulting from a low sediment pH, with a low initial number of methanogens, and/or benzoate activity. Acetate, a precursor

of methane in sediments, is "an important substrate for methanogenic and iron-reducing bacteria in anoxic environments." Followup incubations of sediment from the no-added carbon microcosms indicated acetate degradation and methane accumulation, whereas in the benzaldehyde macrocosms, methane was not produced, and acetate did not degrade.

In the no-added carbon microcosms, the primary terminal electron acceptor was thought to be Fe(III) because oxygen, nitrate and sulfate were below detection levels, and Fe(II) produced during the first 400-hour incubation was equivalent to 62 percent of the measured ethanol depletion.

Researchers also constructed microcosms using sediment and water from the benzaldehyde-amended microcosms. They amended the microcosms with "different iron mineral forms to determine if an added electron acceptor could shift the microbial activity away from fermentation and back to Fe reduction. Ethanol and benzyl alcohol degraded in the iron-treated microcosms, albeit at different rates, but did not degrade in microcosms without added iron. This indicates that the observed shift from iron reduction to fermentation was due to depletion of bioavailable iron" (Kota and others, 2004). In addition, acetate and benzoate did not degrade even in the presence of added iron minerals, indicating that their degradation is not limited by iron bioavailability.

These experiments also showed that "Fe(III) availability was limiting iron reduction, causing an accumulation of reduced fermentation products." After 1,500 hours of incubation, researchers added amorphous iron oxyhydroxide to a replicate from each treatment, and the iron stimulated iron reduction, resulting in ethanol and benzyl alcohol degradation. Also in these experiments, "the lag period prior to ethanol and benzyl alcohol biodegradation was significantly longer for the hematite treatment than for the oxyhydroxide and goethite treatments,

indicating that the iron mineral form may influence the lag period prior to resumption of Fe reduction" (Kota and others, 2004).

Results of microcosm studies

The results of these microcosm studies suggest the following:

- Fe(III) is probably one of the most important electron acceptors for contaminant biodegradation in most aquifers
- there are no reliable methods for assessing the amount of bioavailable Fe(III) and the extent of iron reduction
- "the most common approach used to estimate the extent of iron reduction in contaminated aquifers is to compare aqueous Fe(II) concentration in contaminated and uncontaminated portions of the aquifer"; using this approach at 25 natural attenuation sites, researchers found that "Fe(III) reduction was dominant at only two sites, while sulfate reduction and methanogenesis dominated at the 23 remaining sites"
- using only aqueous measurements of Fe(II) "may significantly underestimate the extent of iron reduction"
- the significance of the Fe(II) coating of iron oxide surfaces is poorly understood
- the present study (Kota and others, 2004) found that "ion-exchanged and precipitated Fe(II) on mineral surfaces reduced Fe(III) availability, resulting in an accumulation of reduced fermentation products"
- another study indicated "over 90 percent of the Fe(II) produced by a dissimilatory Fe(II) oxide-reducing bacterium was either incorporated as an

adsorption complex or as a precipitate on the Fe(III) oxide surface; iron reduction slowed after approximately 2.7 percent of the available Fe(III) was reduced"

- in still another study, "Fe(II) sorption on oxide and cell surfaces, together with Fe(II) complexation by or precipitation with medium components, all influenced the rate and extent of Fe(III) reduction"

Kota and others (2004) state that "It is not clear whether Fe(II) coating is an important limitation on iron bioavailability in contaminated aquifers since other factors including advective flushing may limit Fe(II) precipitation. Analysis of pristine and contaminated aquifer sediment at the Rocky Point site showed some depletion of Fe(III) in the contaminated zone but no detectable increase in Fe(II)."

Conclusions

From the macrocosm study, researchers concluded the following:

- ethanol accumulation suggests the absence of methanogenic conditions and can be considered a geochemical signature for bioavailable iron in this system (ethanol and benzyl alcohol began to accumulate when iron reduction slowed due to a decline in Fe(III)); shifts in microbial processes from iron reduction to methanogenesis have been reported to occur when H₂ concentrations are about in the range of 0.2 to 2 nM)
- high initial ethanol concentrations suggest that iron reduction in this aquifer is limited by Fe(III) bioavailability
- when macrocosms were constructed using the groundwater and the aquifer sediment, ethanol rapidly degraded via iron reduction, probably because of sediment mixing; in the aquifer, "soil agglomerates could reduce Fe(III) availability" but

when the macrocosms were constructed, the soil agglomerations were physically disturbed, exposing fresh surfaces and "enhancing microbial access to the Fe(III) surfaces"

- the presence of acetate here (acetate is known to be utilized under Fe(III) reducing conditions) suggests electron acceptor depletion and low pH, which inhibits methanogenesis

Reference

Kota, S., Barlaz, M.A. and R.C. Borden, "Influence of Solid Phase Fe(II) on Fe(III) Bioavailability in Aquifer Sediment," *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, April 2004; <http://www.pubs.asce.org/>

UTTU thanks Dr. Sreenivas Kota, Sreenivas_kota@urscorp.com, for his help on this article.



The City of Los Angeles Former Gas Station Sites Program, part II

Part II of this article on the City of Los Angeles brownfields program contains instructions on how to gather site information. This information is necessary to determine the appropriate remediation strategies and to identify funding sources for which the site may be eligible. This document assumes that the site is of interest because it appears to be abandoned, is vacant, or is causing blight. Although this series deals specifically with the City of Los Angeles brownfields, many of the strategies and issues described here can be applied to other brownfield areas.

Property identification

The first task of information gathering is to thoroughly identify the property. Street addresses are a useful but

an inexact method to track properties. In the City of Los Angeles, this address may or may not correspond to the address officially assigned by the City. A property may be composed of several parcels, each with a different address. A corner property may have a separate address for each street that it faces, and any of these addresses may be used by government agencies that have an interest in the property.

A more precise way to track properties is by the Assessor's Parcel Number (APN). The California State Board of Equalization publishes standards for county tax assessors to follow in mapping and numbering parcels. This standard recommends a three-part number consisting of the Map Book number, the page number in the book and the number assigned to that specific parcel on that page. In Los Angeles County, the APN is a ten-digit number in the following format: xxxx-xxx-xxx. Note, there may be more than one parcel per APN, or more than one APN per parcel. Be sure to identify all APNs that apply to the parcel.

Where to obtain addresses and other identification information

The City of Los Angeles provides property identification information to the public on properties located within the City through two GIS-based systems, iMapLA and Navigate LA. Enhanced versions are available to City employees through the City's intranet. A user can enter the address or cross streets and the system will map the parcels, and provide the APN numbers, assessed value, City Council district, special zones, assistance designations the property falls within, and other useful information. One can print the map showing the parcels surrounding the site to help identify the site in the field. Those with an interest in UST sites not in the City of Los Angeles can investigate sources of this information that are available in their own city. Often the Planning, Build-

ing and Safety or Public Works Departments tracks this information.

APNs and addresses can also be obtained through the Los Angeles County Tax Assessor's Web site, which has a Property Assessment Information Module. The viewer can enter either the cross streets, address or APN in order to access other data. This information as well as ownership information can also be obtained in person at the Los Angeles County Registrar-Recorder/County Clerk's office. If the property is located outside of Los Angeles County, and your city doesn't have this information, we recommend contacting your county clerk, tax collector and/or tax assessor.

Site reconnaissance

We cannot overestimate the importance of visiting the site as soon as possible in the investigation process. It is important to identify whether the site is truly a former gas station site and whether there are USTs still in the ground. The presence of gas pumps or gas station canopies provides clues, but USTs may or may not be present. A better indication that USTs are still present is a metal or concrete cover for the UST fill hole. When a UST is removed, the fill hole goes with it. There is normally one fill hole for each UST. Other features to note include level of blight, potential dangers to the community, surrounding uses, and redevelopment prospects.

Current and past owner's name and address

Los Angeles City staff can consult I-map or Navigate LA to find the current owner's name and address. Current and past owners are also available through the Los Angeles City Clerk's Land Records Division. Before going to that office, obtain the book and map numbers of the property from the Building and Safety Department Construction Services Center, (see Appendix A, <http://www.lacity.org/ead/labf>, for locations). Always verify

the location of any City office as these offices may have moved since this document was written.

For properties in Los Angeles County, current and past property owners are available through a manual search at the Los Angeles County Registrar-Recorder/County Clerk in Norwalk. There are also subscription-based, Internet access sources of property ownership information available such as LEXIS/NEXIS. An agency within your city, such as the city attorney, may already subscribe to such a service. If your city does not have this information, try the tax collector or tax assessor, or pay for a professional title search. A real estate professional can advise you on how this is done. If a Phase 1 Environmental Site Assessment is conducted, ask that it include historical ownership information.

Researching UST permits for the site

The type of environmental remediation that needs to be conducted at the site and what sources of funding may be available depend on whether or not the USTs are still in place, whether or not they were permitted, if so when and by whom, and other factors. Agency staff can gather this information themselves or pay for a Phase 1 Environmental Site Assessment to be conducted by an environmental engineering or similar firm. Chapter 4 of this document (<http://www.lacity.org/ead/labf>) provides a general description of Phase 1 and Phase 2 Environmental Site Assessments. A properly documented Phase 1 will have a photocopy of all relevant permits for the property. These permits can also provide information on who owned the property when the permit was obtained. The following describes how to gather some of this information yourself.

Permit records from the local agency that regulates USTs

In 1994, California passed a law authorizing local jurisdictions to unify the administration of six programs

related to hazardous materials under one local agency, now known as the Certified Unified Program Agency or CUPA. Regulation of USTs is one of these programs. The Fire Department (LAFD) became the CUPA in 1998 in the City of Los Angeles. LAFD has the most historical information on UST sites and UST permits. LAFD records are filed by street address, so bring all possible addresses for the site when visiting their office. It may also be helpful to talk to the inspector who oversees the geographic area where the site is located to determine if he/she has additional information or records on the site. Prior to 1998, the City Department of Finance collected the UST fees. If one asks at the Department of Finance office window, they will run a search on an address and then print a list of permits taken out on that property that are in their records.

Other cities may have a similar history whereby the UST program was moved from one agency to another, and records may be in two places. The fire department, building department or city engineer should be able to direct you to the correct departments.

The important information to gather includes the following:

- the date permits were obtained to install or remove any USTs
- owner at the time
- if the owner paid UST registration fees to the local agency
- years that fees were paid

It is possible to obtain a permit to remove a tank but then not actually remove it, so try to determine if the UST was actually removed. You may also want to photocopy the diagrams that indicate where USTs were installed.

The local agency that regulates USTs also ensures that all USTs have been either removed or upgraded as

required by federal law. (See Appendix B, <http://www.lacity.org/ead/labf>.) The regulating agency, however, may know of locations where old USTs are still in place. As explained in Part I, USTs may remain in place because the owner does not know they are required to be removed, or lacks the funds to remove them.

Older UST permits

Older UST permit records may be held by the local agency that grants building permits. Older City of Los Angeles UST installation permits may be available at the Building and Safety Department (B&S) records counter. Locations and hours are on the City's Web site under the Building and Safety Department. If this will be your first visit, you may wish to attend a brief training session offered by B&S on how to locate files. Call or consult the B&S Web site for training times and locations.

Tax delinquency

In Los Angeles County, the APN number can be used to determine whether a property is tax delinquent. This information is available on the Los Angeles County Tax Collector's Web site. Information on tax delinquent properties is also available through a Web site called Neighborhood Knowledge LA (<http://nkla.sppsr.ucla.edu/>). If the property owner has been delinquent for five years, the property may be subject to sale by the tax collector at an auction with a minimum bid for the amount owned on back taxes, plus penalties and fees. The significance of tax delinquency is covered in more detail in later sections.

Identify liens and bankruptcies

The best way to identify liens or bankruptcies against a property is through a professional title report. We recommend obtaining a historical title report, which gives names of past owners. If you hire a consultant to conduct a Phase 1 on the property, you can request

that it include a historical title report, although it is not normally part of a Phase 1.

Bankruptcies can impose liens on a property even after the bankruptcy is no longer active in the conventional use of the term. One must consult the original bankruptcy settlement to determine if there are creditors who have an ownership interest in the property that can be exercised. For example, the owner of a site we were investigating had defaulted on a mortgage many years before the City began looking at the site. The bank still had certain property rights that had to be addressed before the City could take ownership of the property.

Contact the owner

When you have gathered as much of the above information as possible, contact the site owner. Our first step is usually to send a letter offering to assist the owner in complying with the law and asking them to call us. Some owners think that because they have stopped paying taxes, they no longer own the property. In California, however, the ownership of tax delinquent properties does not change until the property is sold by the tax collector to a new owner. Question owners about the site history. Relevant information would include any bankruptcy, liens, or loans against the property, dates the property was last used as a gas station, and how it has been used since. Ask if the USTs were registered and if there are orders from government agencies imposed on the property. Our experience ranges from an owner who could not be located to owners who were anxious to work cooperatively with us.

Reference

"Guide to Resolving Environmental and Legal Issues at Abandoned and Underutilized Gas Station Sites," <http://www.lacity.org/ead/labf>.

UTTU thanks Maxine Leichter, maxineleichter@yahoo.com, for her help on this article.



Research notes

An improved method estimation of biodegradation rate with field data

Zhang, Y.K. and R.C. Heathcote, *Ground Water Monitoring & Remediation*, Vol. 23, No. 3, Summer 2003; <http://www.ngwa.org>

Zhang and Heathcote (2003) examined the Buscheck and Alcantar (1995) one-dimensional equations used to estimate plume biodegradation rate. The equations consist of regression methods and analytical solutions that "estimate the contribution of advection, dispersion, sorption and biodegradation to the overall attenuation of petroleum hydrocarbons." The equations "are valid for the concentration data observed in wells along the centerline and near a source of relatively large area as compared with the lateral dispersion of the plume. In cases where the source is finite and the lateral dispersion is significant, the method of Buscheck and Alcantar (1995) is likely to overestimate the biodegradation rate due to its usage of a solution to a one-dimensional advection-dispersion equation that does not consider lateral dispersion and finite source size." For instance, the method overestimated the biodegradation rate by 21 percent for a two-dimensional plume and by 65 percent for a three-dimensional plume.

Zhang and Heathcote (2003) point out that "The ratio of the longitudinal dispersivity to the transverse dispersivities in field-scale dispersion processes is usually much larger than those from pore-scale and column-scale dispersion experiments. Moreover, field tracer experiments have consistently shown a much larger longitudinal dispersion than transverse dispersion." Because a "contaminant source is usually finite and three-dimensional, lateral dispersion is significant."

The proposed and improved method for calculating biodegradation rate advocated by Zhang and Heathcote uses the multidimensional solutions of Domenico (1987) but requires the following of the plume under investigation:

- the plume must be at steady-state
- there must be a line of monitor wells approximately along the plume centerline extending downgradient from the source location
- the lateral and vertical dimensions of the contaminant source and the transverse dispersivities must be reasonably estimated

Application of health risk assessment to derive cleanup levels at a fuel-oil spill site

Chen, K.F., Wu, L.C., Kao, C.M. and C.C. Gordan Yang, *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management*, April 2004; <http://www.pubs.asce.org/>

Researchers evaluated and compared four different risk assessment approaches. They applied these techniques at a petroleum-hydrocarbon spill site and obtained the acceptable soil and groundwater remediation goals. They then evaluated the feasibility of using these risk assessment techniques at fuel-oil spill sites in Taiwan.

The four selected methods, and their characteristics are as follows:

- North Carolina Risk Analysis Framework: promotes consistent decision making, has a streamlined, tiered approach, uses look-up tables of non-site-specific target concentrations, and "allows the responsible party to calculate target concentrations using some site-specific data and specified models and equations" (Chen and others, 2004)
- Illinois Tiered Approach to Correction Objectives:

includes an option for pathway exclusion, uses area background concentrations as remediation objectives, involves three tiers for selecting applicable remediation objectives, includes use of site-specific information to calculate remediation objectives, and requires an understanding of human exposure routes

- Risk-Based Corrective Action Tool Kit for Chemical Releases: determines exposure concentrations, average daily intake, baseline risk levels and risk-based media cleanup levels; it uses a "system of analytical models linked to internal libraries of standard exposure factors and chemical/toxicological data for 150 compounds" (Chen and others, 2004)
- Exposure and Risk Assessment Decision Support System: consists of four coupled modules: development of risk scenario, receptor point concentrations, chemical intake and risk calculation and risk presentation

Using these four methods, scientists in Taiwan performed a risk assessment study on a tank farm facility that had leaked diesel fuel to both groundwater and soil. The range of soil remediation goals were as follows:

- benzene, .2 to 200 mg/kg
- toluene, 3.5 to 18×10^4 mg/kg
- ethylbenzene, 2 to 48×10^5 mg/kg
- xylenes, 2 to 310×10^5 mg/kg
- total petroleum hydrocarbons, 2.5 to $3,400 \times 10^5$ mg/kg

For groundwater:

- benzene, 0 to 1 mg/l
- toluene, 0 to 268 mg/l
- ethylbenzene, 0 to 29 mg/l
- xylenes, 0 to 120 mg/l
- total petroleum hydrocarbons, 0 risk

Among their conclusions, Chen and others (2004) stated: "In some cases, the obtained remediation goals were more stringent than the existing standards. Thus, application of RBCA procedures was recommended to obtain more site-specific remediation goals from the health-protective point of view... Risk-based corrective action is believed to be a more sound and defensible basis for site closure. It provides a clear, logical framework for making site remediation or closure decisions that can be easily revisited should the decision be questioned."

A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events

Eggleton J. and K.V. Thomas, *Environment International*, Vol. 30, 2004; <http://www.elsevier.com/locate/envint>

Eggleton and Thomas (2004) reviewed some factors that affect contaminant release and bioavailability. These include:

- changes in sediment chemistry
- exposure to a different chemical environment that could result in desorption and transformation of contaminants
- presence of clay minerals, Fe and Mn oxides/hydroxides, carbonates, organic substances and biological materials (algae and bacteria) onto which metals can partition
- presence in pore water of DOM (dissolved organic matter) that organic and organometallic contaminants preferentially partition; "the composition of pore water is a critical component in organic contaminant partitioning because of the variability in colloidal material, dissolved organic and inorganic chemicals, redox potential, pH and temperature... Contaminant concentrations in pore water are more closely related to the sediment toxicity than concen-

trations in bulk sediment"

- sediment disturbance that can lead to changes in sediment chemical properties; for instance, "an influx of dissolved oxygen (DO) results in a positive change in the redox potential (Eh); oxidation of anoxic sediment leads to increases in microbial (thiobacteria) activity and decreases in sediment pH (mainly due to the oxidation of sulphide); the extent of pH reduction depends on the amount of sulphide in the sediment and how much is oxidized"
- desorption rate, which can "substantially differ from those estimated by laboratory experiments"
- dynamics of the system and contaminant-particle association, which can determine contaminant transport; "High molecular weight PAHs (polyaromatic hydrocarbons) are thought to be associated with larger particle sizes and will therefore have different transport characteristics and fate compared to low molecular weight PAHs"
- reactivity of each contaminant
- presence of other chemicals that can antagonize or stimulate uptake
- partitioning behavior or binding strength of contaminants to the sediment

In their paper, the authors give more detailed descriptions of the fate of metals. They conclude that more work must be done for the following reasons:

- the fate of contaminants in undisturbed sediments is not well understood
- "the kinetic processes that regulate metal release during changes in redox potential are poorly understood"
- "the bioavailability of organic and organometallic compounds is not understood"

- "little or no data are available on the release of organometallic compounds from sediments during resuspension"

Environmental impact of unleaded gasolines in the Bay of Cadiz (Spain)

Ligero, R.A., Casas-Ruiz, M., Barrera, M., Lopez-Aguayo, F., Sales, D. and D. Garcia, *Environment International*, Vol. 30, <http://www.sciencedirect.com/science/journal/01604120>

Scientists used radioactive dating of sediments to study emitted lead from gasolines in the Bay of Cadiz. "Previous work has demonstrated the utility of radioactive measurements in sediments in order to establish a net of sampling stations for pollution control. It is possible to do a detailed study of the distribution of radionuclides in the zone, building a map of activity isolines based on the grid of stations used."

Scientists collected sediment samples and used gamma spectrometry to analyze the samples for radioactive species. (In addition, they also analyzed sediments for organic carbon content.) "The dating of the sediments is performed employing the profile of the radioelement ¹³⁷Cs originating from the radioactive fallout that originally fell after the nuclear tests and the accident of the Chernobyl nuclear power station. This dating specifically involves locating the layers of sediment presenting maximum activity of this radioelement, and that correspond to the events producing its maximum concentration in the natural environment generally. These events occurred in 1963 (massive testing of nuclear weapons carried out by the great powers) and in 1986 (the Chernobyl accident)" (Ligero and others, 2004).

Scientists found "From the 1940s up well into the 1980s, a significant and progressive increase of the lead concentration in the bay was produced, and not all of this can be imputed to motor traffic, since the use of the

automobile in Spain did not become popular until the 1960s, as a consequence of the relatively slow rate of economic development of the country. At the end of the 1980s, a sudden decrease is recorded in the concentration of lead in the submarine medium. Considering that the bridge over the bay was opened in 1969, and that unleaded gasolines were introduced from 1986, the decrease of lead contamination observed is likely, in principle, to be associated with the introduction of unleaded gasolines... Lead contamination in the Bay of Cadiz has been affected fundamentally by the use of gasolines that contained organic compounds of tetra methyl lead as an anti-knock agent. The introduction of unleaded gasolines has notably diminished the concentration of this metal in sediment, and its trend appears to be toward the total recovery of the previous levels of lead concentration, before the intensive motor traffic pollution in the bay" (Ligero and others, 2004).

Integrated chemical-biological remediation for polycyclic aromatic hydrocarbon-contaminated soil

Wang, J.Y., Stabnikova, O., Lee, S.S. and J.H. Tay, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, April 2004; <http://www.pubs.asce.org/>

Researchers endeavored to create an integrated remedial system that would have the following attributes:

- be technically efficient by using chemical treatment to degrade recalcitrant high-ring PAHs
- be cost effective by using bioremediation
- be environmentally friendly by minimizing chemical use

Thus, Wang and others created bioslurries of soil contaminated with naphthalene, phenanthrene and pyrene (in the laboratory) and treated them with Fenton's reagent to initiate the chemical treatment of PAHs (poly-

cyclic aromatic hydrocarbons).

Microorganisms for the bioremediation part were obtained from one of three sources:

- crude-oil-contaminated soils near a crude oil storage site
- activated sludge from a municipal wastewater treatment plant
- garden soil from a flower nursery

Researchers isolated and identified a bacterial strain from the garden soil identified as *Pseudomonas beteli* 16EC.

Analysis of the contaminated soils revealed that chemical treatment removed 76 percent of contaminants while later application of the microbial strain *Pseudomonas beteli* removed 96 to 97 percent of contaminants. "The proposed integrated chemical-biological remedial system was capable of treating PAH-contaminated soil efficiently in terms of high-ring PAH degradation, less-expensive process and short treatment time required" (Wang and others 2004).