

Measurement & Monitoring: 21M² 13th Literature Update

Adaptive Sampling and Analysis Programs (ASAPs), Innovative Technology Summary Report
U.S. DOE, Office of Environmental Management.
DOE/EM-0592, 29 pp, Aug 2001

An alternative to traditional sampling programs is Adaptive Sampling and Analysis Programs (ASAPs). ASAPs rely on field analytical methods to generate sample results quickly enough to have an impact on the course of the sampling program. Rather than a static work plan, ASAPs are based on dynamic work plans that specify the logic for how sampling numbers, locations, and analyses will be determined as the program proceeds. To ensure that the sampling stays on track, ASAPs also rely on rapid, field-level decision making. ASAPs require (1) field analytical methods that are appropriate for the types of expected contaminants and media present at the site, and (2) a way of supporting decision making in the field that is appropriate for the goals of the program. ASAPs utilize a dual approach to the sampling strategy problem. First, they use a Geographical Information System (GIS) specifically designed for site assessment work to integrate, manage, and display site characterization data as it is being generated, such as SitePlanner™. Developed by ConSolve, Inc., SitePlanner™ is a graphical, object-oriented database designed to provide qualitative support of environmental site assessments. Coupled with the GIS is Plume™, an interactive software package developed at Argonne National Laboratory. The ASAP approach, supported with SitePlanner™ and Plume™ software, is designed specifically for characterization of the presence and extent of contamination in ground water, surface soils, and subsurface soils.

<http://apps.em.doe.gov/OST/pubs/itsrs/itsr2946.pdf>

Application of an Integrated Environmental Monitoring System to an Incineration Plant
Morselli, L. (Univ. of Bologna, Italy); M. Bartoli; B. Brusori; F. Passarini.
Science of the Total Environment, Vol 289 No 1-3, p 177-188, 22 Apr 2002

This paper reports results from environmental monitoring near a typical Italian incinerator plant. Mathematical dispersion models helped determine zones of maximum pollutant depositions to establish a defined monitoring network. Heavy metals, chosen as environmental indicators, showed a wide flux range in gas emissions from the incinerator over different sampling years. Principal component analysis allowed better visualization, showing an interesting correlation between heavy metals observed both in gas emissions and in soil samples. Soil distant from the incinerator was less affected by heavy metal contamination. Atmospheric wet and dry depositions indicated a significant dependence on distance from incinerator, though extremely variable metal fluxes registered during different months. Vegetation samples, seasonal or evergreen, provided no evidence of significant heavy metal enrichment, apart from an apparent dependence on contamination source distance.

Application of Gas Microstrip Detectors for X-Ray Absorption Spectroscopy in Common Process Gases

Vollmer, A. (Univ. of Cambridge, UK); J.D. Lipp; J.R. Lee; G.E. Derbyshire; T. Rayment. Analytical Chemistry, Vol 75 No 23, p 6571-6575, 1 Dec 2003

A new gas microstrip detector (GMSD) for use in X-ray absorption spectroscopy can be applied to the study of catalysis and material science. GMSDs can operate not only with the gas mixtures normally used in proportional counters but also with the majority of gas mixtures used in common catalytic reactions. The detector functions well in the presence of water vapor. EXAFS investigations of a test system of NiO on Ni metal have demonstrated that depth profiling using electron yield X-ray absorption spectroscopy is possible in a wide variety of gaseous environments. Electron detection of XAS using GMSDs is applicable to metals, semiconductors, and insulators presented in films, pellets, powders, crystals, and liquids.

Application of SF₆, Bromide and 3H/3He for Tracing Groundwater Transport Beneath a Landfill
Stute, M. (Columbia Univ., New York, NY), H.J. Simpson, S.N. Chillrud; E. Law-wai, N. Santella, J. Ross, D.T. Ho, P. Schlosser, Y Zheng, and GM Dobbs.
Eos. Trans. AGU, Vol 82 No 47, Fall Meet. Suppl., Abstract H22C-0371, 2001

At a landfill in Maine, redox manipulation of the reducing arsenic-contaminated ground water is being evaluated in pilot experiments. Engineers analyzed ground water for 3H and He isotopes and conducted two SF₆ forced gradient tracer experiments. 3H/3He ages range from 0 to >40years, and the age distribution confirms the extreme heterogeneity of the site and the influence of reinjection from the treatment system. Few studies have involved purposeful injection of SF₆ as a tracer in ground water studies, though SF₆ has the advantage of relatively easy detection by GC-ECD with a dynamic range of at least five orders of magnitude, and a low environmental background level (<2fmol L⁻¹). During the first experiment, SF₆ was injected primarily into high permeability zones via a single well. After 50 days, 90% of the tracer was recovered in the pumping well. The center of the plume moved at a velocity of ~1m/day. During the second tracer experiment, SF₆, bromide, and an oxidizer were mixed and then injected uniformly at a series of points along a line over the entire thickness of the aquifer and monitored in a series of multilevel wells installed downstream of the injection line. SF₆ and Br breakthrough curves were very similar, indicating that both tracers behaved conservatively. After seven months, about half of the tracer mass had been recovered. SF₆ concentrations were translated into flow patterns that were instrumental in the interpretation of the redox manipulation experiments.

Application of Strontium Isotopes for Tracing Landfill Leachate Plumes in Groundwater
Vilomet, J.D. (CEREGE, UMR, Aix en Provence, France); B. Angeletti; S. Moustier; J.P. Ambrosi; M. Wiesner; J.Y. Bottero; L. Chatelet-Snidaro.
Environmental Science & Technology, Vol 35 No 3, p 4675-4679, 1 Dec 2001

A municipal landfill located in southeastern France has no bottom liner, and wastes are placed directly on the ground. A study based on the evaluation of chloride concentration identified a plume extending a maximum of 4,600 m. Strontium isotopic composition characterized natural ground water and landfill leachate contamination. The evolution of mixing ratios obtained with strontium also revealed that fertilizers provided a second source of ground-water contamination. These results suggest that isotopic

signatures can be used to provide useful information on sources of ground-water contamination where conventional water quality parameters yield ambiguous results.

Application of the Thermal Wave Resonator Cavity Sensor to the Measurement of the Thermal Diffusivity in Air Contaminated with Vapours of Different Liquid Hydrocarbons

Marín, E. (Univ. de La Habana, Ciudad de La Habana, Cuba); J.A.P. Lima, M.G. da Silva, M.S. Sthel, S.L. Cardoso, and H. Vargas (Univ. Estadual do Norte Fluminense, Campos dos Goytacazes, RJ, Brazil).

Analytical Sciences, Vol 17, p s475-s478, Apr 2001 [Special Issue]

This paper describes a measuring device based in thermal wave interference in a cavity. It was tested measuring air thermal diffusivity with good accuracy. The device also was applied to the measurement of the thermal diffusivity of air mixed with the vapors of liquid hydrocarbons of the paraffin family (n-pentane, n-hexane, and n-heptane). The results illustrate how the diffusion of the vapors in air can be monitored by a simple method and how the thermal properties (i.e., the thermal diffusivity) of the gas mixture change as a result of this mechanism. Based on these results, the researchers predict the development of a device suitable for in field measurements.

<http://wwwsoc.nii.ac.jp/jsac/analsci/special/076.pdf>

Assembled Chemical Weapons Assessment (ACWA) Program, Immobilized Cell Bioreactor Toxicity Monitoring

Haley, Mark V.; C.W. Kurnas; M.A. Guelta, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD. Report No: ECBC-TR-263, DTIC: ADA417394, 21 pp, June 2003

Until recently, incineration was the only proven technology, adopted by the U.S. Army, that successfully destroyed chemical agents. However, public opposition to incineration redirected research to evaluate alternative technologies. Through the Alternative Technology Program, the U.S. Army adopted biodegradation as a proven method for destroying the mustard stockpile at Aberdeen Proving Ground. However, research did not address the destruction of mustard when mixed with explosives generated from the destruction of Assembled Chemical Weapons. The Assembled Chemical Weapons Assessment (ACWA) Program was tasked to find alternatives to the incineration/destruction of assembled chemical weapons. The ACWA Program has been evaluating biodegradation to determine if tetrytol (explosive) will disrupt the biodegradation process. Microtox (MTX) assays were used to monitor changes in toxicity due to changes in feed composite. The MTX assay uses a luminescent marine bacteria (*Vibrio fischeri*) that can survive high salt concentrations. When subjected to toxic substances, cellular respiration decreases, resulting in a corresponding decrease in luminescence. Feed and effluent samples were monitored for toxicity using the MTX assays over a 42-day period.

<http://handle.dtic.mil/100.2/ADA417394>

Associations Between Distance Lags, Groundwater Velocities, and Detection Efficiencies in Groundwater Monitoring Networks

Hudak, P.F., Univ. of North Texas, Denton.

Environmental Monitoring and Assessment, Vol 75 No 2, p 215-221, Apr 2002

Effects of distance lags between landfills and monitoring wells on contaminant detection capability

were quantified in several ground-water velocity settings. In general, longer distance lags yielded higher detection efficiencies, but detection efficiencies decreased as monitoring wells approached a buffer zone boundary imposing a maximum permissible contaminant transport distance. Imposing a time limit on contaminant travel substantially reduced detection efficiency in low velocity settings, especially at longer distance lags. Time limits were less significant in high velocity settings.

An Automated Method for Analysis of Inorganic Arsenic Species in Sediments and Tissues by HGAA
Pitts, Leonard C., Woods Hole Group Environmental Laboratories, Raynham, MA.
The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23
October 2003, Univ. of Massachusetts at Amherst.
Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

Methods are presented here to determine inorganic arsenic in tissues and arsenite and arsenate in sediments using an automated Perkin Elmer FIMS 100 Flow Injection Hydride System with atomic absorption detection. Inorganic arsenic is reduced to ASIII prior to hydride generation with NaBH₄, followed by gas liquid separation, decomposition in a 900 degrees C quartz cell, and analysis. A reporting limit of 0.01 mg/kg wet weight is achieved for each matrix. Organic arsenic compounds, which can form volatile hydrides, are removed from the analysis with a trap containing graphitized carbon black. Sample analysis time is about 3 minutes.

Biofilms As Bio-Indicator for Polluted Waters? Total Reflection X-Ray Fluorescence Analysis of Biofilms of the Tisza River (Hungary)
Mages, M. (UFZ Centre for Environmental Research Leipzig-Halle, Magdeburg, Germany); M.V. Ovari; W. Tumpling Jr.; L. Kropfl.
Analytical and Bioanalytical Chemistry, Vol 378 No 4, Feb 2004

This paper reports an investigation of heavy metal accumulation by natural biofilms living in the catchment area of the Tisza river in Hungary, as well as in biofilms cultivated in vitro. Biofilms were cultivated in vitro in natural fresh water from the Saale river, Germany. After reaching the plateau phase, Cu was added to reach a concentration of 100 u/L. An increase of the biofilm mass fraction caused decreased concentration in the water phase. Unfortunately, the reactor wall also acted as a Cu adsorbent. More detailed results of the in vitro experiments will be published in a forthcoming paper. After the infamous cyanide spill, naturally grown biofilm samples from exposed as well as background places at the Hungarian rivers Szamos and Tisza were collected in 2000 and 2002 and analyzed using total reflection X-ray fluorescence analysis (TXRF). Metal mass fraction differences as high as two orders of magnitude were found between polluted and unpolluted (background) sampling points. Extremely high concentration values, e.g., 5600 u/g Zn in biofilm, were found at highly polluted sampling points, indicating an enrichment factor of ~10,000 compared to the water phase.

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies. Ground Water Issue

Newell, C.J. (Groundwater Services, Inc., Houston, TX); H.S. Rifai (Univ. of Houston, TX); J.T. Wilson (U.S. EPA, Ada, OK); J.A. Connor & J.A. Aziz (Univ. of Houston); M.P. Suarez (U.S. EPA, Ada, OK).

U.S. EPA , EPA 540-S-02-500, 28 pp, Nov 2002

This issue paper explains when and how to apply first-order attenuation rate constant calculations in monitored natural attenuation (MNA) studies. First-order attenuation rate constant calculations can be an important tool for evaluating natural attenuation processes at ground-water contamination sites. Specific applications identified in the 1999 U.S. EPA guidelines include use in characterization of plume trends (shrinking, expanding, or showing relatively little change), as well as estimation of the time required for achieving remediation goals. The use of the attenuation rate data for these purposes is complicated as different types of first-order rate constants represent very different attenuation processes: Concentration vs. time rate constants are used for estimating how quickly remediation goals will be met at a site. Concentration vs. distance bulk attenuation rate constants are used for estimating if a plume is expanding, showing relatively little change, or shrinking due to the combined effects of dispersion, biodegradation, and other attenuation processes. Biodegradation rate constants are used in solute transport models to characterize the effect of biodegradation on contaminant migration. Correct use of attenuation rate constants requires an understanding of the different attenuation processes that different first-order rate constants represent.

<http://www.epa.gov/ada/download/issue/540S02500.pdf>

Carbon Isotopes as Indicators of Trichloroethene Degradation under Different Redox Conditions in the Unsaturated Zone

Crowley, O.A., G. Boshoff, K. Redeker, and R.M. Kalin, Queens University, Belfast.

Geophysical Research Abstracts, Vol. 5, 12099, 2003

Chlorinated solvents, in particular trichloroethene (TCE), are very mobile in the subsurface and often exist as volatilized constituents within the vadose zone due to their low water solubility. Limited information is available regarding the fate of TCE in unsaturated conditions. Compound-specific stable carbon isotope measurements for TCE at contaminated sites are useful indicators for the assessment of natural attenuation. Sorption, volatilization, chemical reactions, dispersion, dilution, and biodegradation processes all contribute to natural attenuation and in turn will have a resultant isotope signature. Contaminated site soil and ground water were used in this investigation to set up representative unsaturated microcosms. The microcosms were used to assess the isotopic signature as a result of the natural attenuation processes, under nitrate, sulfate, and methanogenic reducing conditions. The research determined the degradation efficiencies at each of the identified redox conditions. Accurate evaluation of in situ bioremediation of TCE is dependant on accurate identification of degradation occurring. The investigations of carbon isotope signatures as indicators of degradation may provide a novel environmental monitoring tool, allowing for the identification of redox-specific degradation at contaminated sites.

Characterization and Monitoring of Agricultural Contaminant Transport Using Ground Penetrating Radar and Electrical Data

Senechal, P., H. Perroud, D. Rousset, J-B. Daban, and M. Kedziorek, Univ. of Pau, Pau, France.
Geophysical Research Abstracts, Vol. 5, 05392, 2003

A combination of multi-offset Ground Penetrating Radar (GPR) and electrical surveys was used to characterize the physico-chemical properties of soil, in particular those concerning lithology variations, water content, porosity, and water ionic conductivity in agricultural zones. These investigations were completed by independent chemical analyses of soil and water, rainfall, and fertilizers spread data. The experiments were conducted on fields of intensive corn culture (4 x 2 km) where the water table is 1.5 to 5 m deep, in a geological context of alluvial deposits. Analyses of water from various wells in the study area show high concentrations of nitrate coming from the chemical fertilizers spread on the soil surface. The goal of this study was to monitor the variations of water content and water ionic conductivity over twelve months of seasonal variations. GPR and electrical data were recorded at two sites located along a north-south line with one data acquisition per month. These data have been completed by a seismic reflection profile. Velocity analysis of multioffset GPR data were used to estimate lateral and vertical ground-water fluctuations and the combination of radar velocities and electrical conductivities permit to deduce the water ionic conductivity variations. The authors present the GPR, electrical and seismic data, the water content and water ionic conductivity obtained for each data set, and a comparison of these results with the chemical analyses. This study demonstrates the potential of non-destructive geophysical methods for providing information on hydric and solute transfer in the ground and monitoring soil contamination.

Characterization and Speciation of Mercury-Bearing Mine Wastes Using X-Ray Absorption Spectroscopy

Kim, C.S. (Stanford Univ., CA); G.E. Brown Jr.; J.J. Rytuba.
Science of the Total Environment, Vol 261 No 1-3, p 157-168, 16 Oct 2000

The solubility, transport, and potential bioavailability of mercury are controlled by its chemical speciation, which can be directly determined for samples with total mercury concentrations greater than 100 mg/kg (ppm) using X-ray absorption spectroscopy (XAS). This technique has the additional benefits of being non-destructive to the sample, element-specific, relatively sensitive at low concentrations, and requiring minimal sample preparation. This paper discusses a study of Hg L(III)-edge extended X-ray absorption fine structure (EXAFS) spectra collected for several mercury mine tailings (calcines) in the California Coast Range. The speciation results demonstrate the ability of XAS to identify multiple mercury phases in a heterogeneous sample, with a quantitative accuracy of +/-25% for the mercury-containing phases considered. In conjunction with standard microanalytical techniques such as X-ray diffraction and electron probe microanalysis, XAS is useful in the prioritization and remediation of mercury-contaminated mine sites.

Characterization of Contaminated Soil and Groundwater Surrounding an Illegal Landfill (S. Giuliano, Venice, Italy) by Principal Component Analysis and Kriging

Critto, A. (Univ. of Venice, Venice, Italy); C. Carlon; A. Marcomini.
Environmental Pollution, Vol 122 No 2, p 235-244, 2003

The characterization of a hydrologically complex contaminated site bordering the lagoon of Venice (Italy) was undertaken by investigating soils and ground water affected by chemical contaminants originating from wastes dumped into an illegal landfill. Statistical tools such as principal components analysis and geostatistical techniques were applied to obtain the spatial distribution of chemical contaminants. Dissolved organic carbon, SO₄(2-), and Cl⁻ were used to trace the migration of the contaminants from the topsoil to the underlying ground water. A schematic of the conceptual model of the contaminated site supported the formulation of major exposure scenarios.

Characterization of Fe Plaque and Associated Metals on the Roots of Mine-Waste Impacted Aquatic Plants

Hansel, C.M. (Stanford Univ., CA); S. Fendorf; S. Sutton; M. Newville.

Environmental Science & Technology, Vol 35 No 19, p 3863-3868, 1 Oct 2001

Researcher used microscopic and spectroscopic techniques to identify the spatial distributions, associations, and chemical environments of Fe, Mn, Pb, and Zn on the roots of *Phalaris arundinacea*, a common, indigenous wetland plant. Iron forms a continuous precipitate on the root surface composed dominantly of ferrihydrite (~63%) with lesser amounts of goethite (32%) and minor levels of siderite (5%). Pb is juxtaposed with Fe on the root surface, while Mn and Zn exist as discrete, isolated mixed-metal carbonate nodules on the root surface. Hydrated iron oxides, bacterial biofilms, and metal carbonates influence the availability and mobility of metals within the rhizosphere of aquatic plants.

Chlorinated Solvent DNAPL Extent Characterization at the East Gate Disposal Yard (Egdy), Fort Lewis, Washington

Lynch, Kira P., U.S. Army Corps of Engineers, Seattle District, WA.

The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23 October 2003, Univ. of Massachusetts at Amherst.

Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

The EGDY site contains mixed solvent and petroleum hydrocarbon dense nonaqueous phase liquids (DNAPLs) disposed in trenches as drummed waste or directly as liquid waste. The DNAPLs are the source of a TCE plume 13,000 feet in length that contaminates an upper unconfined aquifer and a lower confined aquifer to depths of 220 feet bgs. This presentation describes how the Triad approach was used to develop a conceptual site model for this DNAPL site, and reduce overall uncertainty in the characterization.

Coastal Contaminant Migration Monitoring: The Trident Probe and UltraSeep System. Hardware Description, Protocols, and Procedures

Chadwick, D.B.; B. Harre; C.F. Smith; J.G. Groves; R.J. Paulsen, SPAWAR, San Diego, CA.

Report No: SSC/SD-TR-1902, DTIC: ADA416834, 50 pp, June 2003

Building on historical advances, a collaborative effort between the Environmental Sciences Laboratory at SSC San Diego and the Cornell Cooperative Extension Marine Program set out to develop improved methods for (1) identifying the spatial location where exchange is likely to take place, and (2) accurately measuring the ground-water seepage across the sediment-water interface. This report

describes the initial hardware development, testing, and field protocols for new techniques for identifying potential areas of ground-water impingement into surface waters (the Trident Probe), as well as techniques for quantifying the flow rates and contaminant levels of ground water at the surface water interface (the UltraSeep System).

<http://handle.dtic.mil/100.2/ADA416834>

Commercial Systems for the Direct Detection of Explosives for Explosive Ordnance Disposal Tasks
Bruschini, Claudio, DI-LAP, Ecole Polytechnique Federale de Lausanne (EPFL), Lausanne, Switzerland. ETRO-IRIS, Vrije Univ. Brussel (VUB), Brussels, Belgium
Subsurface Sensing Technologies and Applications, Vol 2 No 3, p 299-336, July 2001

In pursuit of the means to characterize in a non-destructive way the content of unexploded ordnance (UXO), research first concentrated on bulk explosive detection, particularly neutron-based systems exploiting gamma spectroscopy with the potential of detecting the explosive's nitrogen content and/or its other constituents (carbon, oxygen, and hydrogen). Candidate systems exist, though most of them have as primary aim the discrimination of chemical munition. Application of trace explosive detection techniques seem to be less mature due to the large number of parameters influencing the variables of interest (explosive vapor and particle concentration). This paper identifies various existing technologies for the direct detection of explosives and corresponding commercially available systems or advanced prototypes.

Construction of a Portable Piezoelectric Quartz Crystal Sensor Array for Determination of Petroleum Compounds in Contaminated Soil

Bystrom, Emil, Master's thesis, Umea University. 23 pp, 2003

A piezoelectric quartz crystal sensor array, an "electronic nose," was constructed for determination of petroleum compounds at low ppm levels in soil. Six different crystals with five different coating materials, OV-101, DNP, OV-17, OV-225 and Carbowax 1540 (selected based on a classification according to polarity) were applied in a measuring chamber. Different hydrocarbons were injected into the measuring chamber and the characteristic response pattern was recorded. The results show that further improvement is needed before a portable detection device can be used as suggested.

http://www.chem.umu.se/mcn/Exjobb_projrappporter/eNose%20-%20Emil%20Bystr%C3%B6m.pdf

Continuous In Situ Cyanide Monitoring Using a Highly Sensitive and Selective FIA System

Nomura, Y.; K. Nagakubo; H.-S. Ji; A. Watanabe; T. Akimoto; S. McNiven; K. Hayashi; Y. Arikawa; I. Karube.

Environmental Science & Technology, Vol 34 No 12, p 2618-2622, 2003

A flow injection analysis (FIA) system incorporating a gas-diffusion membrane was fabricated for the detection of cyanide anion in aqueous samples. The principle of measurement is based on the reaction of o-phthalaldehyde (OPA) and cyanide in the presence of glycine to produce a fluorescent isoindole derivative. The cyanide concentration of the samples is thus proportional to the observed fluorescence intensity. Although extremely low levels of cyanide could be determined using this system, measurements were affected by the presence of sulfite ion and thiols. After a gas-diffusion membrane was incorporated into the system to separate gaseous hydrogen cyanide from interferences in the sample, the system then displayed high selectivity for cyanide. A device based on this FIA system was

constructed and used for the continuous, in situ monitoring of cyanide concentrations in river water for 5 months, taking readings every 5 minutes and convincingly demonstrating the utility of the sensor. Although the sensitivity of the sensor system tended to decrease over time, replacement of the gas-diffusion membrane restored the sensitivity to its initial level.

Cyanide Assay Based on its Novel Reaction with Resorcinol and Picric Acid

Drochioiu, G. (Al. I. Cuza Univ. of Iasi, Iasi, Romania); C. Oniscu (Gh. Asachi Technical Univ. of Iasi, Iasi, Romania); V. Sunel, K. Popa, C. Cuciuc, and D. Cozma (Al. I. Cuza Univ. of Iasi, Iasi, Romania). *European Journal of Mineral Processing and Environmental Protection*, Vol 3 No 3, 2003

Trace concentrations of cyanides in water and hydrocyanic acid collected in dilute sodium hydroxide solution are determined with a solution of 2 % sodium carbonate containing 110 µg/ml of resorcinol and 229 µg/ml of picric acid when a novel indophenol derivative of 2,6-dinitro-5-hydroxy-4-hydroxylamino-1-cyanobenzene is afforded. The formation of the novel dye was demonstrated by elemental and spectral analyses. After heating the mixture at 100 degrees C for 30 minutes and then cooling it, the absorbance of the red-brown solution is read at 540 nm, where the blank showed a minimum absorption. The detection limit of this method is below 0.01 µg/ml CN⁻. Cyanide in air, cigarette smoke, and waste waters can directly be determined by this selective procedure, without its isolation.

Cyanide Determination in Biological Fluids Using a Microdiffusion Method with a Flow System and Polarographic Detection

do Nascimento, .P.C; D. Bohrer; L.M. de Carvalho, Federal Univ. of Santa Maria, Brazil. *Analyst*, Vol 123 No 5, p 1151-1154, May 1998

The paper describes a method for the automated polarographic determination of cyanide as a tetracyanonickelate (II) anion complex in a gas-diffusion flow system. Volatile cyanide existing in whole blood, plasma and urine samples was measured after gas-diffusion using hexaaminenickel solution as acceptor. The linear range of calibration for measurements at the hanging mercury-drop electrode (HMDE) was from 0.1 to 2.0 ug cyanide with $r = 0.998$. The RSD was, respectively, 3.4 and 1.2% ($n = 5$) for 0.4 ug cyanide measured with and without the flow-system configuration. Detection limits of 7.4 ug/L were calculated.

Defining Groundwater Transport Times near ASR Facilities Using Geochemical Tracers

Clark, J.F., Univ. of California, Santa Barbara.

Eos Trans. AGU, Vol 82 No 47, Fall Meet. Suppl., Abstract H32G-09, 2001

Determining ground-water transport and travel times between recharge facilities and wells has become increasingly important in managing Aquifer Storage and Recovery (ASR) projects. Fundamental geochemical approaches for investigating transport include tritium/helium-3 dating and the addition of sulfur hexafluoride tracer in controlled experiments. When combined, ground-water flow can be imaged with time scales on the order of days to decades. The Orange County Water District used sulfur hexafluoride gas injected into the Santa Ana River over a period of 2 weeks to tag ~3,000 acre-feet of recharged water and have been using it to determine ground-water flow and transport from the river for

more than three years. Results of the gas tracer experiment demonstrate that linear ground-water flow velocities range from less than 1 km/yr to more than 5 km/yr and that the ground-water flow system is stratified. These results will be used to verify and refine numerical models of transport near the ASR facilities in Orange County and have been used to establish flowlines so that in situ water quality changes can be quantified.

Delineation of Groundwater Contamination Around an Ash Pond: Geochemical and GIS Approach
Praharaj, T. (Indian Inst. of Technology, Kharagpur); S.P. Swain; M.A. Powell; B.R. Hart; S. Tripathy.
Environment International, Vol 27 No 8, p 631-638, Mar 2002

The authors investigated the levels of metal contamination in ground water due to particulate matter fallout and leaching from an ash pond. They assigned contamination indices for the adjacent localities around an ash disposal site with the application of geographic information systems (GIS). The exercise delineated zones of attention for Ba, Fe, Cu, Mn, S, and Zn were delineated, though Pb showed no significant attenuation even at a distance of 1200 m.

Detection of Bacteria in Porous Media Using X-Ray Computed Micro Tomography
Polak, A. (Pennsylvania State Univ., University Park, PA); M. Landon (Lock Haven Univ.); A.S. Grader; D. Elsworth.
Geophysical Research Abstracts, Vol. 5, 03800, 2003

Results are reported on experiments to determine if bacteria containing naturally occurring magnetite or magnetite that had been conjugated to the bacteria could be detected with CMT (Computed Micro Tomography). In situ monitoring was done on *Magnetospirillum*, microaerophilic bacteria containing magnetite particles (Fe₃O₄) that were successfully grown in the lab. The bacteria were scanned in MSGM revised medium with and without ferric quinate and in a sample of sand grains. In another experiment, monoclonal anti-*E. coli* antibody that was immobilized onto BSA coated ferromagnetite particles and mixed with an aliquot of x-ray resistant *E. coli* bacteria was used. The sample was scanned in solution and in a Berea rock sample. The researchers found that the *Magnetospirillum* can be detected in the porous media if the concentration of the bacteria is high enough, as the amount of the magnetite particles inside the bacteria is small. In the second experiment, the tagged *E. coli* was detected in a solution and within the Berea sample using CMT.

Determination of Organic Micropollutants in Rainwater Using Hollow Fiber Membrane/Liquid-Phase Microextraction Combined with Gas Chromatography-Mass Spectrometry
Basheer, C.; R. Balasubramanian; H.K. Lee, National Univ. of Singapore, Republic of Singapore.
Journal of Chromatography A, Vol 1016 No 1, p 11-20, 17 Oct 2003

This paper presents a simple and rapid liquid-phase microextraction (LPME) method using a hollow fiber membrane (HFM) in conjunction with gas chromatography-mass spectrometry (GC-MS). The method is applied to quantitative determination of 16 polycyclic aromatic hydrocarbons (PAHs) and 12 organochlorine pesticides (OCPs) in rain water samples. The concentrations of PAHs and OCPs in real rainwater samples were between 0.005-0.162, and 0.063 ug/L, respectively.

Detection of the Variation of Fluid Content in Fractures by Georadar

Liu, L. (Univ. of Connecticut, Storrs, CT); J.W. Lane (US Geological Survey, Storrs, CT); C. Gregoire (Katholieke Univ. Leuven, Belgium).

Geophysical Research Abstracts, Vol. 5, 03006, 2003

Georadar (including ground-penetrating radar (GPR) and borehole radar) has been used in many field studies related to ground-water hydrogeological research. The authors study the effects of fluid content variations in fractured bedrock on radar signal changes to help the assessment of the efficiency of a steam injection technique and biodegradation facilitation technique for remediation of NAPL-contaminated sites in this difficult environment. Numerical simulation with the finite difference time domain (FDTD) method models different scenarios. The electrical and dielectric properties for bedrock (granite, and limestone), fresh and saline water, water-NAPL mix, air, and vegetable oil are used to mimic the remediation process. Then the simulation results are compared with georadar observations and the variation of fluid contents in fractures is estimated. Also examined are the effects of the ratio of fracture aperture/radar signal wavelength, the electromagnetic parameter variations, and their influence to radar performance when steam injection causes temperature changes.

Development of a Continuous In-Situ Zinc Analyzer and Long Term Water Sampler for Monitoring Streams Impacted by Acid Rock Drainage

Chapin, Thomas P. and Richard B. Wanty, U.S. Geological Survey, Denver, CO.

Geological Society of America Annual Meeting, 27-30 October 2002, Denver Colorado. Paper No. 92-10, 2002

A novel instrument, the Zn-DigiScanner, has been developed to examine low and high frequency temporal changes in acid rock drainage areas for hourly in situ monitoring of zinc. The Zn-DigiScanner contains programmable micro pumps that preconcentrate and separate Zn from interfering metals with a strong anion exchange column, add spectrophotometric reagents, and propel the colored reaction product to a photometric detector. A battery-powered logger controls the Zn-DigiScanner and records the data. Reagent consumption currently limits the Zn-DigiScanner deployment duration to 15 days with hourly sampling. The DigiSampler was developed for the long-term daily sampling of biogeochemically active elements. It can be programmed to take 0.1-10 mL sample volumes--either discrete samples every hour, or one sample integrated over 24 hours. The DigiSampler typically injects a 1-mL sample into an acid cleaned, 3.2 mm I.D. by 15 m Teflon coil, which provides the capacity for taking over one hundred samples. A bubble of N₂ gas is injected between water samples to prevent mixing between successive samples. Upon recovery, the 1 mL samples are diluted and run by IC and ICPMS for anions, cations, nutrients, and metals. Physical parameters (temperature, conductivity, dissolved oxygen, pH, turbidity, etc) are measured every 15 minutes with a YSI Sonde 6600. The authors present details of the analytical design of the Zn-DigiScanner and DigiSampler, along with initial monitoring results from the Snake River near Montezuma, CO.

Development of a Long-Term Monitoring System to Monitor Cover System Conditions

Kumthekar, Uday, J.D. Chiou, and Martin Prochaska (Fluor Fernald, Inc., Cincinnati, OH); Craig H. Benson (Univ. of Wisconsin, Madison).

Proceedings of Waste Management '02, Tucson, AZ. 7 pp, 2002

Environmental remediation at the Fernald Environmental Management Project is nearing completion, but long-term technology needs continue to emerge at the site. Remote, real-time, autonomous monitoring technologies are needed to ensure the integrity of the site and its remedy systems once cleanup is complete. The Fernald Post Closure Stewardship Technology Project (PCSTP) has selected technologies to address initial site needs. This paper will explore the monitoring requirements of the Fernald On-Site Disposal Facility final cover system, the parameters selected as critical for comprehensive long-term monitoring, and the process by which technologies were chosen to monitor those parameters.

http://www.uwgeotech.org/pubs/wc_kumthekar_development.pdf

Development of an Innovative Direct Push Sensor System for Long Term Monitoring of Environmental Waste Sites

Eddy-Dilek, C.A., B.D. Riha, S. Bosze, J. Rossabi, Savannah River Technology Center, Aiken, SC. Eos Trans. AGU, Vol 82 No 47, Fall Meet. Suppl., Abstract H32G-04, 2001

DOE scientists have developed and installed a prototype monitoring system that can be used to measure and/or sample multiple parameters appropriate for long term monitoring of environmental waste sites. This system is designed to function as a sentinel system that detects when a significant change in water quality parameters or contaminant concentration occurs in a well-characterized system. The sensor drive configuration is flexible, and the sensor system is installed using direct push methods. Site-specific monitoring scenarios will be need to be developed to address the specific long-term monitoring objectives at a given site. The drive point has a sample port (soil gas or ground water) and windows/ports for additional sensors. A prototype system was installed and studied at the Savannah River Site D-Area. The probes are located in an area where multiple contaminant plumes dominated by volatile organic compounds, metals, and tritium are monitored using standard ground-water wells. The prototype system measures temperature, resistivity, ORP, and pH on a continuous basis, and concentrations of volatile organic compounds and tritium are measured periodically by laboratory analysis of diffusion bag samples deployed in the sample ports of the prototype system. Results are reported for a three-month monitoring interval. The results will be compared with baseline analyses of samples collected from the adjacent ground-water well.

Development of Speciation and Separation Techniques for Radionuclides for the Preassessment of Their Environmental Mobility

Caron, Francois and George Mankarios, Laurentian University, Sudbury, ON, Canada. Proceedings of the Sudbury 2003 Mining and the Environment Conference, 25-28 May 2003, Sudbury, ON, Canada. Laurentian Univ., Sudbury, ON, Canada. Centre for Environmental Monitoring, ISBN: 0-88667-051-9. 2 Vols or 2 CD-ROMs, 7 pp, 2003

Radionuclides of various natural or man-made origins all have the potential to migrate in ground water. Migration, among other factors, depends upon the aqueous speciation of the element. A key component affecting this speciation is natural organic matter (NOM), which consists of a mixture of hydrophilic and hydrophobic compounds and contains weak acidic groups that can complex cationic radionuclides. These complexes can be mobile in soils. A modified separation and speciation scheme is used as a preassessment tool for the mobility of two radionuclides of the actinide series, ²⁴¹Am and U.

<http://www.ott.wrcc.osmre.gov/library/proceed/sudbury2003/sudbury03/19.pdf>

Direct Observation of Alcohol Flooding in Sandy Sediment by MRI

Nestle, N. (Inst. of Hydrochemistry, TU Muenchen) and T. Baumann; A. Wunderlich (Univ. of Ulm); R. Niessner.

Geophysical Research Abstracts, Vol. 5, 03349, 2003

Alcohol flooding has been studied macroscopically as an approach for active remediation of NAPL contaminations in aquifer sediments in pilot- and field-scale experiments. A direct, time-resolved observation of the interaction between the NAPL phase and the alcohol in the sediment has not been reported up to now. In this contribution, the authors present results from MRI studies on column setups with dimensions in the 10 cm range. In the MRI experiments, different contrast modes were used to distinguish between water phase and NAPL. The time resolution in the experiments is about 10 s for the acquisition of a 3D image dataset with a voxel volume of 10 μL , thus enabling the visualization of fast interactions. Using slower imaging protocols, the spatial resolution could be increased to voxel volumes of 1 μL . As the signal intensity recorded in a voxel is an average value over the whole voxel, even smaller quantities of residual NAPL can be localized in such images. The experiments were carried out in steady state columns filled with sandy material. The alcohol phase was injected below the NAPL contamination. Like that, the alcohol is moving upwards by the density difference between alcohol and water. After contact with the NAPL it takes dissolved NAPL with it to the surface. The observation of a water-rich zone around the NAPL contamination during the passage of the flooding alcohol indicates that the contact zone between NAPL and flooding alcohol is crucial to remediation efficiency.

Direct Push Insitu Measurement of Groundwater and Contaminant Flux

Bullock, Paul, University of Florida, Gainesville.

Journal of Undergraduate Research, Aug 2002

The flow of ground water, both volume and direction, affects the spread of in-ground contaminants such as gasoline spilled from an underground tank. An in situ measurement of the ground-water flow or flux would benefit both the remediation design and monitoring for these spills. The movement of contaminants currently is computed from measurements of water pressure head and from pumping tests, inferring rather than actually measuring contaminant flow. Current research at the University of Florida is focused on the development of a material that releases a tracer as water flows through it. A cartridge is constructed from this material, inserted into the ground, and the amount of tracer lost during a given time indicates the volume of water passed. This material can be designed to absorb contaminants and thus measure contaminant concentration as well. Cartridges can be inserted into a well with porous casing, but the excavation of the well and the installation of the casing might affect the flow of ground water near the well. This research project focuses on the development of a direct insertion method for the well casing that limits the potential for installation disturbance. The UF Civil and Coastal Engineering Department owns a cone truck with a 10-ton hydraulic ram that provides a platform for quasi-static insertion of the well casing. A method has been developed and tested for inserting PVC casing using this vehicle. Additional field trials will verify the capability of a measurement cartridge inserted into this casing.

<http://web.clas.ufl.edu/CLAS/jur/0802/howardpaper.html>

Direct-Push-Installed, Gas-Driven Mini-Pumps for Discrete-Point Groundwater Sampling: A New In-Situ Approach to Long-Term Monitoring
Schulmeister, Marcia K.; Steffen M. Birk; John M. Healey; Jim J. Butler; Donald O. Whittemore, Kansas Geological Survey, Lawrence, KS.
Eos. Trans. AGU, Vol 82 No 47, Fall Meet. Suppl., Abstract H22C-0366, 2001.

A new approach to vertical chemical profiling has been developed in which low-volume mini-pump samplers (MPS) are installed in a single borehole using direct-push methods. The positive-displacement, gas-driven minipumps overcome sampling depth limitations of conventional suction pumps. Up to ten pumps can be operated simultaneously using a multi-channel pneumatic controller that drives water to the surface through alternating pressurization and depressurization pulses. By combining direct-push chemical profiling with MPS installation, the pumps can be placed at the most appropriate depths for a particular investigation. The potential of the new approach was assessed in an alluvial aquifer that has been the site of a great deal of previous work. Two sets of mini-pump samplers (four pumps in each) were installed in an interval characterized by a steep chemical gradient. The MPS installations were placed within one meter of conventional multilevel samplers with similar intake depths. Chemical field parameters and dissolved constituent concentrations were measured in the two sets of paired samplers. Although the vertical chemical trends observed in the multilevel samplers also were observed in MPS installed using direct push rods composed of nitrided steel, redox-sensitive measurements from the MPS were affected by installation with standard steel rods. The combination of MPS installation and direct-push characterization allows for repeat sampling of intervals of interest without the need for permanent wells. Ongoing work addresses the long-term performance of the MPS.

Electronic Nose: a Useful Tool for Monitoring Environmental Contamination
Baby, R.E.; M. Cabezas; E.N. Walsoe de Reza, Programa de Investigaciones en Solidos (PRINSO)-CITEFA-CONICET, Buenos Aires, Argentina.
Sensors and Actuators B: Chemical, Vol 69 No 3, p 214-218, 2000

Advances in the technology of multisensor arrays and neural computation have allowed the development of "electronic noses" that can discriminate compounds by their odors and, consequently, can play a role in environmental monitoring. This study examined an electronic nose, MOSES II (MODular SEnsor System), with two arrays of eight tin oxide and quartz microbalance sensors, each one manufactured by Lennartz Electronic/MoTech. The project aimed to discriminate (a) small concentrations (ppm) of lindane and nitrobenzene in water, (b) dry solid insecticides (synthetic pyrethroids) such as permethrin, deltamethrin and cypermethrin, (c) mixtures of different quantities of cypermethrin in an inert substance, and (d) solutions of these pyrethroids in an appropriate organic solvent. [Mentions 1,4-dioxane in the text.]

Elucidation of the 1,4-Dioxane Decomposition Pathway at Discrete Ultrasonic Frequencies
Beckett, M.A. and I. Hua.
Environmental Science & Technology, Vol 34 No 18, p 3944-3953, 2000

The sonolytic decomposition chemistry of the refractory compound 1,4-dioxane in aqueous solution has been investigated at four ultrasonic frequencies: 205, 358, 618, and 1071 kHz. At a frequency of 358

kHz, the observed first-order kinetic rate constants for 1,4-dioxane destruction were highest with a sparge gas ratio of 75% Ar/25% O₂ and lowest in the presence of pure argon. The major intermediates of 1,4-dioxane degradation were ethylene glycol diformate, methoxyacetic acid, formaldehyde, glycolic acid, and formic acid. The highest observed first-order 1,4-dioxane decomposition rate occurred at 358, followed by 618, 1071, and 205 kHz. At each frequency, approximately 85% of the initial carbon is accounted for as the parent compound, as an intermediate, or as CO₂. The major byproducts formation was investigated at all four frequencies, and the results indicate that free radical mechanisms are significant over the entire range of frequencies studied.

Environmental Data Quality and the Search for Representativeness

Crumbling, Deana M., U.S. EPA, Technology Innovation Office, Washington, DC.

The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23

October 2003, Univ. of Massachusetts at Amherst.

Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

The first-generation data quality model that equated environmental data quality with analytical quality is blind to the complexities that collectively are termed “data representativeness.” The environmental data quality model must be updated to explicitly consider those variables that affect the ability to generate data representative from both analytical and sampling standpoints. Because environmental matrices tend to be highly heterogeneous on a variety of spatial, temporal, and chemical scales, measured values can span orders of magnitude within a single site. A variety of decisions typically are made over the course of site investigation and cleanup, and each can require data sets with different representativeness. For example, a data set representative of risk assessment decisions (a statistically random data set representative of an average contaminant concentration over some specified exposure unit) will not be representative of cost-effective remedial design (requiring non-random data representative of contaminant locations, mass, and concentration extremes). EPA has articulated the Triad approach as a practical framework that synthesizes progress in technology and science with the goal of evolving site cleanup practices into second-generation strategies. The Triad approach stresses the importance of systematically identifying and managing project decision uncertainties, including sampling representativeness for data sets. It promotes the contributions of emerging technologies (such as field analysis and decision-support software) and multidisciplinary expertise. Triad project cost savings have ranged up to 50% as compared to traditional process-driven strategies achieving the same decision confidence.

Environmental Geophysical Analysis Utilizing Airborne Electromagnetic and Total Magnetic Field Methods in West Virginia.

Al-Fouzan, Fouzan (King Abdulaziz City for Science and Technology, Riyadh, Saudi); Terry Ackman, Richard Hammack, and Garret Veloski (U.S. DOE, NETL, Pittsburgh, PA); William Harbert (Univ. of Pittsburgh, Pittsburgh, PA).

Geophysical Research Abstracts, Vol. 5, 10456, 2003

Innovative and new environmental geophysical analysis of portions of the Muddy and Roaring Creek watersheds located in northeastern Preston County, WV, has been completed in the region the abandoned T&T subsurface mines. The geophysical data analyzed in this study were collected by making an airborne measurements of frequency-domain electromagnetic (FDEM) conductivity (380,

1400, 6200, 25k and 102k Hz), VLF (VLF1I from Cutler station, VLF2I from Seattle station), and total field magnetics. In the simplest representation, with respect to subsurface acid mine drainage (AMD), the subsurface regions can be thought of as containing three pools of AMD contaminated water. The objectives of this project were to determine the location of these subsurface pools and the lateral extent of a contaminated mine pool located at a depth of about 300 feet. Noise was the significant issue in the lowest frequency EM conductivity data, especially the 380 Hz and 1400 Hz data. The geometry of the high-conductivity pools were imaged using a variety of techniques, including Hue Saturation and Intensity (HSI) algorithms and unsupervised classification. The data are interpreted as showing the geometry of the mine pools and regions of contrasting ground-water conductivity related to discharge. Extraction of cross sections of conductivity was useful to determine the location of anomalies associated with AMD impacted regions. After that, 3-D surface profiles of all the conductivity datasets (380, 1400, 6200, 25000, and 102000 Hz), VLF, and total field magnetics were created for the mine pool (A region only). The conductivities show the largest anomaly in mine pool A. In the deepest penetrating and complex frequency, the 380 Hz, high conductivity and a very high anomaly is seen in the mine pool A region at approximately 280 feet depth. The anomaly is interpreted to represent mine pool A of the AMD. Magnetic result shows that relatively non-magnetic rock unit underlies pool A.

Environmental, Mineralogical, and Genetic Characterization of Ochreous and White Precipitates from Acid Mine Drainages in Taebaeg, Korea
Kim, J.T.; S.J. Kim, Seoul National Univ., Seoul, Korea.
Environmental Science & Technology, Vol 37 No 10, p 2120-2126, 15 May 2003

This paper describes the procedures and results of using X-ray diffraction, energy-dispersive X-ray fluorescence, thermal analysis, scanning electron microscopy, inductively coupled plasma emission spectroscopy, and ion chromatography for the environmental, mineralogical, and genetic characterization of brownish yellow, reddish brown, and white precipitates from acid mine drainage in Taebaeg, Korea.

Environmental Monitoring of Heavy Metals and Arsenic from Ag-Pb-Zn Mining: a Case Study over Two Millennia
Stuben, D. (Univ. Karlsruhe, Germany); Z. Berner; B. Kappes; H. Puchelt.
Environmental Monitoring and Assessment, Vol 70 No 1-2, p 181-200, July 2001

To evaluate the long-term impact of mining wastes on different environmental compartments, a detailed environmental monitoring effort focused on the mineralogical and chemical characterization of the different waste materials. Experiments were carried out with ore fragments, flotation tailings, and medieval metallurgical slags using eluents of different compositions and pHs to assess the conditions governing the mobilization and re-fixation of these species.

Estimate of Heavy Metal Contamination in Soils after a Mining Accident Using Reflectance Spectroscopy
Kemper, T. (Inst. for Environment and Sustainability, Ispra, VA, Italy); S. Sommer.
Environmental Science & Technology, Vol 36 No 12, p 2742-2747, 15 June 2002

In April 1998, the dam of a mine tailings pond in Aznalcollar (Spain) collapsed and flooded an area of more than 4000 ha with pyritic sludge contaminated with high concentrations of heavy metals. After the end of the first remediation campaign, soil samples were collected for chemical analysis and measurement of visible to near-infrared reflectance (0.35-2.4 μm), which predicted six out of nine elements with high accuracy. Most wavelengths important for prediction could be attributed to absorptions features of iron and iron oxides. These results indicate that it is feasible to predict heavy metals in soils contaminated by mining residuals using rapid and cost-effective reflectance spectroscopy.

Estimating Recharge From Soil Water Tension Data

Sisson, J.B. (INEEL, Idaho Falls, ID); G.W. Gee (PNNL, Richland, WA).
Eos Trans. AGU, Vol 82 No 47, Fall Meet. Suppl., Abstract H32G-08, 2001

Effectively managing an aquifer requires accurate estimates of the ambient flux as well as the travel time of annual pulses to pass through the vadose zone. When soil water potential and/or water content data are available together with unsaturated hydraulic properties, the ambient flux can be estimated using Darcy's Law. At the Hanford Buried Waste Test Facility, advanced tensiometers were installed at the site to a depth of 20 ft bgs and data were obtained over a 2-year period. The ambient flux was estimated from the rate of pumpage from the lysimeter to be 55 mm/y. Data from the tensiometers indicated a unit gradient in total water potential at depths greater than 4 m. Thus, the ambient flux was numerically equal to the unsaturated hydraulic conductivity. The data also clearly show the passage of wetting fronts beyond 2.3 m and (with some imagination) to depths beyond 4.3 m. Using the tensiometer data together with previously estimated hydraulic properties resulted in estimates of ambient flux that ranged from about 10 to 120 mm/y. These estimates were found to depend on the length of the period for which soil water potentials were averaged, and on how the hydraulic conductivity was averaged.

Estimation of Chlorophyll Concentration in Lakes and Inland Seas with a Field Spectroradiometer above the Water Surface

Oki, K. and Y. Yasuoka, University of Tokyo, Japan.
Applied Optics, Vol 41 No 30, p 6463-6469, 20 Oct 2002

The estimation of chlorophyll concentration in the water by use of a field spectroradiometer above the water surface is necessary for the removal of the effect of specular reflection at the water surface. The amount of specular reflection from the water surface was assessed on the basis of the spectral signature data that was measured above and below the water surface. Furthermore, a method to remove the effect of specular reflection from spectral signature data that was measured above water surface was proposed. Finally, chlorophyll-a concentration was estimated accurately from the spectral signature measured by field spectroradiometer above water surface with the proposed surface reflection model.

Evaluating Natural Attenuation in a Controlled Field Experiment by Mass Balances, Flux Fences and Snapshots: a Comparison of Results

Devlin, J.F. (Univ. of Kansas, Lawrence); M. McMaster (GeoSyntec Consultants, Guelph, ON); D. Katic (Golder Associates Ltd, Mississauga, ON); J.F. Barker (Univ. of Waterloo, Waterloo, ON).

Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution (Proceedings of the Groundwater Quality 2001 Conference held at Sheffield, UK, June 2001). IAHS Publ. no. 275, p 245-250, 2002

Researchers compared several hydrogeologically based methods of evaluating natural attenuation in a controlled setting in situ and then contrasted the estimated attenuation rates with those from an in situ bioremediation experiment, performed in an identical funnel-and-gate structure. Three volatile organic chemicals, carbon tetrachloride (CT), tetrachloroethene (PCE), and toluene were released into the gate and allowed to migrate its 24 m length, with monitoring conducted at multilevel fences located across the gate. Similar natural attenuation rate trends were indicated by mass balances, flux analysis, and snapshot analysis: CT degraded with a half-life of about 13 days, chloroform with a half-life of 10-23 days, and toluene with a half-life of about 58-62 days, but PCE transformed too slowly to measure with confidence; however, PCE attenuation occurred more rapidly (half-life 35-55 days) in the neighboring bioremediation gate.

Evaluation of Groundwater and Soil Pollution in a Landfill Area Using Electrical Resistivity Imaging Survey

Ahmed, A.M. and W.N. Sulaiman, Univ. Putra Malaysia, Serdang, Selangor, Malaysia.
Environmental Management, Vol 28 No 5, p 655-663, Nov 2001

An electrical resistivity imaging survey was used to investigate the leachate production within a landfill in Malaysia in conjunction with chemical analyses of ground water, surface water, and soil. chemical analysis was performed on soil samples taken from different locations within and around the The resistivity image along line L-L1 indicated the presence of large zones of decomposed waste bodies saturated with highly conducting leachate. Analysis of trace elements indicated their presence in very low concentrations and did not reflect any sign of heavy metal pollution of ground and surface water or of soil. This paper presents the conduct and details of the survey.

Evaluation of In-Situ DNAPL Remediation and Innovative Site Characterization Techniques

Sillan, Randall K.; Michael D. Annable; P. Suresh C. Rao, University of Florida, Gainesville.
Florida Center for Solid and Hazardous Waste Management, Gainesville, FL. 69 pp, 1999.

Researchers evaluated the field-scale performance of in situ cosolvent flushing and innovative tracer techniques for site characterization at a former dry cleaner site. The former Sages dry cleaner site, located in Jacksonville, FL, was contaminated with tetrachloroethene (PCE) that migrated below the water table, where it collected at high saturations in thin, discontinuous layers wherever a change in the soil structure prevented downward migration. An important consequence of this DNAPL distribution is the inefficiency associated with flushing cosolvent through a region where only a small portion in the vertical direction is contaminated. The horizontal flow of alcohol between injection and extraction wells provides limited contact with the contaminants and will require additional time and flushing agent to meet remediation goals. An extensive network of multi-level samplers (MLSs) allowed observation of the link between spatial variability in performance and spatial variability in hydrodynamics and NAPL saturation, but such a network is not likely to be cost-effective for full-scale remediation systems. Material and installation costs for MLSs are small compared to other components, but sample collection and analysis costs can discourage the use of MLSs. A partitioning tracer test conducted prior

to the cosolvent flood proved an estimate of 69 L of DNAPL in the swept zone between the injection and extraction wells. The subsequent cosolvent flood removed 42 L of DNAPL from the remediation zone. Finally, the post-flushing partitioning tracer test indicated approximately 26 L remaining. These results are consistent and are in general agreement with the core data indicating that the cosolvent flood removed approximately 63% of the DNAPL present. Post-flushing concentrations of PCE indicated that concentrations are similar to those prior to the flood. Long-term monitoring will continue to evaluate the impact on the downgradient plume, including the potential for enhanced biodegradation.
<http://www.floridacenter.org/publications/in-situDNAPL.pdf>

Evaluation of Water Content and Ionic Concentrations of Soils via Frequency Domain Analysis of TDR Waveform

Mohamed, A.M.O., R.A. Said, N.K. AlShawawreh, and M.Y. El-Bassiouni, UAE Univ., Al Ain, United Arab Emirates.

Subsurface Sensing Technologies and Applications, Vol 4 No 2, p 159-186, Apr 2003

This study addresses the development of a method for evaluating the water content and ionic concentrations of subsurface polluted soils by analyzing the TDR waveforms in the frequency domain. Soil specimens were prepared with different water contents and NaCl concentrations. A known electrical pulse with multiple harmonics was generated and induced through soil specimens. Reflected signals were then analyzed in the frequency domain and represented in terms of the magnitude and phase shift. Multivariate statistical analysis was performed for various magnitudes and phase shifts, which are dependent on water content and concentrations. Regression equations were obtained; hence, for a known reflected amplitude and phase shift, water content and ionic concentrations could be determined.

Exploring Biological Reduction of Chromate

Idaho National Engineering and Environmental Laboratory (INEEL).

Subsurface Topics, Vol 4 No 1, Mar 2003

At Idaho National Engineering and Environmental Laboratory (INEEL), geophysicist Birsan Canan thinks the process of monitoring subsurface contaminant biotransformation could be simplified. She and a team of biologists and electrical engineers are developing a noninvasive geophysical monitoring technique for biological chromate reduction that could lead to improved field characterization and monitoring techniques. The team's focus is on toxic and highly soluble hexavalent chromium, originally used as a corrosion inhibitor in cooling water and discharged into the INEEL environment. When microbes in the subsurface metabolize hexavalent chromium to trivalent chromium, it is relatively insoluble and much less harmful. Canan and her team conducted an experiment in which they hoped to find a discernible signature of biological chromate reduction using nonlinear complex resistivity. The experiment was performed in a set of sand-packed columns, each containing a different concentration of chromate. Canan measured complex resistivity over time as chromate was reduced chemically and biologically in the columns. In the first test run, the frequencies and phase shifts of the biologically reduced samples were distinct from the control. More tests are needed to determine the lower threshold of chromate concentrations that can be detected using complex resistivity. The microbe population will be sampled every three hours to obtain the necessary data. Contact: Birsan Canan, 208-526-5426, canab@inel.gov.

Exploring Field Vegetation Reflectance as an Indicator of Soil Contamination in River Floodplains
Kooistra, L. (Univ. of Nijmegen, Nijmegen, Netherlands); E.A. Salas; J.G. Clevers; R. Wehrens; R.S. Leuven; P.H. Nienhuis; L.M. Buydens.
Environmental Pollution, Vol 127 No 2, p 281-290, 2004

Investigators examined the relation between vegetation reflectance and elevated concentrations of the metals Ni, Cd, Cu, Zn, and Pb in river floodplain soils. High-resolution vegetation reflectance spectra in the visible to near-infrared (400-1350 nm) were obtained using a field radiometer, and the relations were evaluated using simple linear regression in combination with two spectral vegetation indices: the Difference Vegetation Index (DVI) and the Red-Edge Position (REP). In addition, a multivariate regression approach using partial least squares (PLS) regression was adopted. The three methods achieved comparable results. The best R(2) values for the relation between metals concentrations and vegetation reflectance were obtained for grass vegetation; herbaceous species displayed a larger deviation from the established relationships, resulting in lower R(2) values and larger cross-validation errors. The results corroborate the potential of hyperspectral remote sensing to contribute to the survey of elevated metal concentrations in floodplain soils under grassland using the spectral response of the vegetation as an indicator.

False Cyanide Detection

Analytical Chemistry, Vol 74 No 5, p 134A-141A, 2002

Yasuo Seto of the National Research Institute of Police Science (Japan) uses four real cases of poisoned drink or food, including curried rice served at a festival in Japan, to explain why cyanide detection is so difficult.

Feasibility of Using Dissolved "Excess Air" as an Indicator of VOCs Entrainment in Aquifer Systems Elliot, T. and D. Gibbons, Queen's Univ., Belfast.

Geophysical Research Abstracts, Vol. 5, 09693, 2003

Potentially the study of natural atmospheric gas tracers (e.g., Ar, Kr, Xe, N₂) dissolved in ground waters at recharge can yield information about the dynamics of gas transport in the unsaturated/vadose zone and recharge pathways for other volatile compounds (cf. VOCs, landfill gases). Understanding these processes is a major factor in assessing the natural attenuation budgets and reaction rates for VOCs in both unsaturated and saturated zones. Knowing the ground-water recharge temperature (RT) and amounts of any entrained atmospheric gases or so-called "excess air" (EA) component, the initial dissolved concentrations of any other gases in contact with the water (including VOCs) under equilibrium conditions can be calculated using Henry's Law. If gas concentrations above the water table are greater than the equilibrium concentration, this provides evidence of gas-to-water mass transfer of volatile compounds into the ground water; its corollary suggests (contaminated) ground waters are transferring gases to the unsaturated zone. Ongoing research at QUB initially has focused on developing protocols for and demonstrating the feasibility of monitoring EA development in a range of controlled laboratory column experiments to assess how different modes of unsaturated zone and ground-water recharge affect EA generation in the saturated zone, and whether any characteristic ("fingerprint") signatures in terms of the abundance patterns (Ar, Kr, Xe, N₂) and/or isotopic

compositions (Ar, Kr, Xe) can be used to indicate how volatiles are entrained in ground water. Column packing materials have included sand or gravel (representing single porosity media), and zeolite (representing a dual-porosity system). Initial results are presented both from the column experiments and also from a field case study at a contaminated land site with a shallow gravels aquifer affected by natural tidal forcing of its water table.

Field Tests of a Chemiresistor Sensor for In-Situ Monitoring of Vapor-Phase Contaminants
Ho, C.; L. McGrath; J. Wright, Sandia National Laboratories, Albuquerque, NM.
Geophysical Research Abstracts, Vol. 5, 07510, 2003

An in situ chemiresistor sensor has been developed that can detect volatile organic compounds in subsurface environmental applications. Field tests conducted in 2001 and 2002 tested the reliability, operation, and performance of the in situ chemiresistor sensor system. The chemiresistor consists of a carbon-loaded polymer deposited onto a microfabricated circuit. The polymer swells reversibly in the presence of volatile organic compounds as vapor-phase molecules absorb into the polymer, causing a change in the electrical resistance of the circuit. The change in resistance can be calibrated to known concentrations of analytes, and arrays of chemiresistors can be used on a single chip to aid in discrimination. A waterproof housing was constructed to allow the chemiresistor to be used in air, soil, and water. The integrated unit, which can be buried in soils or emplaced in wells, is connected via cable to a surface-based solar-powered data logger. A cell-phone modem is used to automatically download the data from the data logger on a periodic basis. The field tests were performed at Edwards Air Force Base, CA, the Nevada Test Site, and Sandia's Chemical Waste Landfill near Albuquerque, NM. Results showed that the sensors could be operated continuously for long periods of time (greater than a year) using remote solar-powered data-logging stations with wireless telemetry. The sensor housing, which was constructed of 304 stainless steel, showed some signs of corrosion when placed in contaminated water for several months, but the overall integrity was maintained. The detection limits of the chemiresistors were generally found to be near 0.1% of the saturated vapor pressure of the target analyte in controlled laboratory conditions (e.g., ~100 ppmv for TCE), but fluctuations in environmental parameters and other interferences increased the detection limit by about an order of magnitude in the field tests.

Field Trial of Contaminant Groundwater Monitoring: Comparing Time-Integrating Ceramic Dosimeters and Conventional Water Sampling
Martin, Holger, B.M. Patterson, and G.B. Davis (CSIRO Land and Water, Wembley, Western Australia); P. Grathwohl (Univ. of Tübingen, Tübingen, Germany).
Environmental Science & Technology, Vol 37, p 1360-1364, 2003

Passive sampling with ceramic dosimeters is a new method being developed for long-term, time-integrated monitoring of organic pollutants in ground water. Time-integrated concentration measurements theoretically can be used to quantify exposures for a range of contaminants such as polycyclic aromatic hydrocarbons (PAHs), volatile aromatic compounds such as benzene, toluene, and xylenes (BTEX), and volatile chlorinated hydrocarbons. This paper presents results from lab tests for recovery rates for the extraction of analytes from the adsorbent material Dowex Optipore L-493. The research also examined the long-term stability of adsorbed BTEX and naphthalenes in ceramic dosimeters and results from field tests in ground-water wells comparing BTEX concentrations detected

with ceramic dosimeters to concentrations determined from conventional pumped ground-water samples over different overlapping time periods.

<http://www.uni-tuebingen.de/zag/hydrogeochemie/download/ESTmartinetal3460-3464.pdf>

Final Report for the SEED Project: "Inexpensive Chemresistor Sensors for Real Time Ground Water Contamination Measurement"

Hughes, Robert C.; Chad E. Davis; Michael L. Thomas, Sandia National Lab.

SAND2002-0772, 32 pp, 2002

The purpose of this small program was to demonstrate the effectiveness of the vapor-phase chemiresistor technology to measuring VOC contamination in water. The chemiresistors were found to measure the higher concentrations of VOC quite easily; the rule of thumb is that the best chemiresistor for a particular VOC can measure down to about 0.1 % of the saturated vapor pressure of the liquid VOC at ambient temperature. Depending on the solubility of the VOC in water, this could be a few ppb in the water. For more soluble VOCs like MTBE, it means a few ppm would be the limit of detection. The researchers were able to detect contamination in water actually touching the chemiresistor polymer, but because of slowness of response and long-term instability, they determined that the chemiresistors work best sensing the headspace vapor of contaminated water. The use of a GORE-TEX(R) membrane and small dead volume inside the sensor housing means that equilibration between water and the chemiresistors can be fairly rapid. The fastest response was obtained when active sparging forced contaminated headspace vapor past the chemiresistor, which forces equilibration (partitioning) between the three phases: the water, the headspace, and the chemiresistor polymer.

<http://www.prod.sandia.gov/cgi-bin/techlib/access-control.pl/2002/020772.pdf>

Geochemical and Isotopic Characteristics Associated with High Electrical Conductivities in a Shallow Hydrocarbon-Contaminated Aquifer

Legall, F.D. (DLZ Michigan, Inc. Lansing, MI); E.A. Atekwana (Indiana Univ.-Purdue Univ. Indianapolis, IN); E.A. Atekwana (Univ. of Missouri-Rolla); R.V. Krishnamurthy (Western Michigan Univ.); D.D. Werkema, Jr. (U.S. EPA, Las Vegas, NV); W.A. Sauck (Western Michigan Univ.).
Geophysical Research Abstracts, Vol. 5, 07225, 2003

Data collected from a network of in-situ vertical resistivity probes (VRPs) deployed within a hydrocarbon contaminated aquifer showed high soil conductivities associated with zones where residual and dissolved phase hydrocarbons (RDH) occur and zones where these phases coexist with free phase hydrocarbons (RDFH). Bulk soil conductivities were highest (12 to 30 mS/m) in the RDFH zone compared to the RDH zone (10 to 25 mS/m). Ground water from closely spaced multi-level piezometers (MLPs) installed in the aquifer was analyzed to investigate the role of mineral weathering as the source of ions responsible for the high soil conductivity. Evidence for mineral weathering in the aquifer was assessed using major inorganic ions, dissolved inorganic carbon (DIC), stable carbon isotope ratio of DIC ($\delta^{13}\text{CDIC}$), and bulk soil conductivity. The link between bulk soil conductivity and $\delta^{13}\text{CDIC}$ in contaminant plumes has never been reported in the literature. The results show higher Na, Ca, and Mg in the contaminated zone compared to background. The higher TDS in the contaminated zones is consistent with the weathering of carbonates and Na and Ca feldspars, the dominant minerals in the aquifer. Higher TDS at the contaminated locations was also coincident with higher DIC. The results indicate that the subsurface expression of microbial hydrocarbon mineralization

is recorded in the TDS, DIC, 13CDIC, and bulk soil conductivity. It also appears that the bulk soil conductivity records an integrated summary of process-driven biogeochemical changes reflected in the changing pattern of redox zonation. This suggests that high soil conductivities measured at hydrocarboncontaminated sites could be used to assess the potential for natural attenuation and to monitor intrinsic bioremediation at these sites.

Goelectrical and Colour Tracer Monitoring with Direct Push Observation Wells
Dietrich, P., M. Dietze, and R. Hoffmann, Univ. of Tuebingen, Tuebingen, Germany.
Geophysical Research Abstracts, Vol. 5, 01287, 2003

Borehole/borehole tracer tests are a hydrogeological method to characterize ground-water flow parameters. Breakthrough curves of color tracers, injected in one borehole and measured in one or more observation wells downstream of the first, give exact but locally very limited information about ground-water flow direction and velocity. At heterogeneous subsurface conditions, a large number of investigation wells and frequent sample drawing is necessary to assure recovery of the tracer, which makes the experiments very expensive. Yet, these experiments often fail or do not give sufficient information about the flow regime in the aquifer. Monitoring of salt tracers with goelectrical methods gives an integral information about flow parameters that in most cases is more useful, though especially in deeper aquifers it is a problem to place a high number of electrodes close enough to the moving tracer to gain precise results. To assess the mentioned problems, the authors carried out a combined goelectrical salt and conventional color tracer test. The equipment for both tests was placed in direct push boreholes, which are a lot cheaper than ground-water wells, quickly installed, and much less invasive. The boreholes were installed at 10 meters distance on a 120 m long profile, to form a control plane 25 meters downstream of the tracer injection. The injection took place in three different ground-water wells at a time, to provide for a good overview of the flow regime along the control plane. Integral information from the goelectrical tracer tests can be used to design a refined borehole placement for a successful color tracer test. The results, quite different from ground-water modeling results, reinforce the need to carry out precise field tracer tests for the investigation of ground-water flow parameters.

Goelectrical Methods Applied on a Contaminated Site: the Entressen Landfill Case Study
(South-Eastern France)
Naudet, V., A. Revil, and J.-Y. Bottero, CNRS-CEREGE, Aix-en-Provence, France.
Geophysical Research Abstracts, Vol. 5, 01128, 2003

Redox potential is a controlling parameter in many contaminated site remediation technologies. Its knowledge is crucial to understand the contaminant plume development and risks for ground-water resources. But redox potential is very difficult to measure directly in the field. The researchers performed extensive self-potential (SP) and electrical resistivity measurements downstream the Entressen landfill (south-eastern France in Provence) and obtained a 3D image of the aquifer datum. The image helps the visualization of the pattern of water flow through the channels and estimation of the electrokinetic component of the SP signal. An important negative SP anomaly (-400 mV) is measured near the decantation basins of the landfill, suggesting an hypothetical leak of these basins. The polarity and the great amplitude of this anomaly indicate that the main component of the SP signal is due to electrochemical reactions such as oxido-reduction reactions. The comparison of the SP

measurements and the geochemical data shows that the negative SP anomaly is correlated with the anaerobic zone of the contaminant plume. Redox potential gradients in the contaminant plume may generate a diffusion potential that is responsible for the SP anomaly. Microbial activity also plays a key role in all these processes.

Geoelectrical Stratigraphy and Analysis of a Hydrocarbon Impacted Aquifer

Werkema Jr., D. (U.S. EPA, ORD, Las Vegas, NV); E. Atekwana (Univ. of Missouri-Rolla); A. Endres (Univ. of Waterloo); W. Sauck (Western Michigan Univ.).
Geophysical Research Abstracts, Vol. 5, 13941, 2003

A recently proposed geoelectrical model for hydrocarbon impacted sites predicts anomalously high conductivities coincident with aged contaminated zones. These high conductivities are attributed to an enhancement of mineral weathering resulting from byproducts of microbial redox processes. To evaluate this model, high resolution in situ vertical bulk conductivity measurements were acquired from a mature light non-aqueous phase liquid (LNAPL) contaminated site. The geoelectrical stratigraphy showed conductivity maxima coincident with the free phase LNAPL zone, and occurring within the water table fluctuation zone. This zone is inferred as an active zone of biodegradation suggesting significant microbial degradation under partially saturated conditions. A simple Archie's Law analysis reveals that large pore water saturation and/or large pore water conductivity enhancements are necessary to produce the bulk conductivity observed at the contaminated locations. These results support the conductive model and demonstrate the potential of geoelectrical investigations for assessing microbial degradation of mature LNAPL-impacted soils.

Geostatistical Interpolation of Field Data in Three Dimensions to Assess Nitrate Leaching to Groundwater

Onsoy, S., T. Harter, T. Ginn, J. Hopmans, and W. Horwath, University of California, Davis.
Geophysical Research Abstracts, Vol. 5, 12913, 2003

Groundwater deterioration and associated environmental problems induced by nitrate applications in agricultural areas are a growing concern worldwide. Estimation of downward nitrate flux to ground water is a major concern due to its extensive use, high mobility and persistence in the environment. The overall goal of this research is to better understand the role of deep alluvial unsaturated zone in controlling the long-term impact of California Central Valley agricultural practices on ground-water quality. The quantitative analysis of the subsurface N budget in a 16 m thick vadose zone is described using the data obtained from a 12-year N fertilizer experiment (1982-1995) conducted on an alluvial fan of the Kings River in the Central Valley of California. Three alternative N management practices with an annual fertilizer rate of 0, 100 and 325 lbs N/ac are compared by high-resolution sampling of the vadose zone 12 years after initiation of the applications. The results from directional experimental semivariograms are rather striking. Nitrate data, while widely variable, have a significant spatial continuity in the vertical direction while the sill is identical both in the horizontal and vertical directions. In the case of soil moisture data, however, the sill in the horizontal direction is smaller, while the range is significantly longer than in the vertical direction, indicating that moisture flux is predominantly vertical despite the strong stratigraphic heterogeneity. Two methods estimate the risk of nitrate loss from the root zone: mass balance of the N fluxes in the root zone and deep vadose zone N mass assessment via geostatistical analysis. Both methods identify excess N available in the deep

vadose zone that is susceptible to leaching. The discrepancies between the mass balance and the geostatistical N mass assessment points out that in the absence of measured N data, mass balance is only a rough estimation of N in the system, and thus for the prediction of leachable N to ground water. The physical and chemical processes that control nitrate fate and transport must be identified for better quantification of N leaching to ground water.

Highly Selective and Sensitive Reaction of Cyanide with 2,2-Dihydroxy-1,3-Indanedione.
Drochioiu, G., Al. I. Cuza Univ. of Iasi 11, Carol I, Iasi-6600, Romania.
Analytical and Bioanalytical Chemistry, Vol 372 No 5-6, p 744-747, Mar 2002

A novel reaction of cyanide with 2,2-dihydroxy-1,3-indanedione in the presence of sodium carbonate is highly selective, sensitive, and suitable for the determination of hydrogen cyanide in the environment and free cyanide ions in water, blood, urine, and serum. This paper discusses the analytical properties of the reaction and proposes that the purple color produced under the reaction conditions is that of 2-cyano-1,2,3-trihydroxy-2 H indene.

Identification of a Crystalline Cyanide-Containing Compound in Blast Furnace Sludge Deposits
Mansfeldt, T. and R. Dohrmann, Ruhr-Universitat Bochum, Germany.
Journal of Environmental Quality, Vol 30 No 6, p 1927-1932, Nov-Dec 2001

During blast furnace operation, a cyanide-containing muddy waste referred to as blast furnace sludge is generated that (in Germany) often is pumped into surface deposits. Depending on species, cyanide has very different toxicity. The authors investigated the type of cyanide occurring in blast furnace sludge deposits by means of wet chemical and powder X-ray diffraction analyses of 37 samples of three blast furnace deposits. Wet chemical results indicate that neither the extremely toxic free cyanide (HCN and CN⁻) nor toxic weak metal-cyanide complexes (e.g., [Zn(CN)₄]²⁻) are present in the sludge. Powder X-ray diffraction identified the crystalline cyanide-containing compound potassium zinc hexacyanoferrate(II) nonahydrate as the cyanide-bearing compound. As the iron-cyanide complex [Fe(CN)₆] is not acutely toxic, any direct hazard comes from cyanide occurring in the investigated wastes. Under the predominant pH milieu of the sludge (pH about 8) the solubility of potassium zinc hexacyanoferrate(II) nonahydrate is low, thus minimizing the mobility of cyanide.

In-Situ Characterization of Soil-Water Content Using Gas-Phase Partitioning Tracer Tests: Field-Scale Evaluation
Keller, J.M. and M.L. Brusseau, Univ. of Arizona, Tucson)
Environmental Science & Technology, Vol 37 No 14, p 3141-3144, 15 July 2003

Field-scale tests were performed to evaluate the effectiveness of the gas-phase partitioning tracer method for in situ measurement of soil/water content. The tracer tests were conducted before and after a controlled infiltration event to monitor performance. Nonpartitioning (sulfur hexafluoride) and water-partitioning (difluoromethane) tracers were injected into the test zone, and their effluent breakthrough curves were analyzed using the method of moments to calculate retardation factors for difluoromethane. For the test conducted in drier soil, the soil/water content estimated from the tracer test was identical to the independently measured values obtained with gravimetric core analysis,

neutron scattering, and bore-hole ground penetrating radar, while the test conducted under wetter soil conditions was 81% of the independently measured values. The results indicate that the partitioning tracer method can be an effective technique to measure soil/water content at the field scale, especially for sites with moderate to low soil/water contents.

Investigating the Effects of Microbial Communities on Electrical Properties of Soils: Preliminary Results from a Pilot Scale Column Experiment

Atekwanal, E. (Indiana Univ.); E. Atekwana (Univ. of Missouri-Rolla); D. Werkema, J. Duris, S. Rossbach, C. Koretsky, J. Means, W. Sauck, D. Cassidy, and L. Sherrod (Western Michigan Univ., Kalamazoo).

Geophysical Research Abstracts, Vol. 5, 13832, 2003

The authors describe the results of a mesoscale pilot experiment designed to investigate the influence of biogeochemical processes on electrical conductivity of soils impacted by hydrocarbons. This is an interdisciplinary study integrating geophysics, geochemistry, and microbiology undertaken to 1) verify microbial hydrocarbon degradation by monitoring changes in microbial types, population, and community structure, 2) document temporal changes in the electrical conductivity of soils, and 3) document changes in pore fluid geochemistry using major ions and stable carbon isotopes. Duplicate soil columns were constructed and the results confirm microbial mineralization of diesel within contaminated columns. Electrical conductivity measurements were made using a Wenner array at 2 cm spacing. The electrical measurements show an initial decrease in conductivity. This is consistent with the diesel replacing the more conductive pore waters and changes in water saturation, especially within the unsaturated zone. However, a slow increase in conductivity was observed in column 7 overtime compared to the other columns. The slight increase in electrical conductivity for the contaminated column may be attributed to microbial degradation of hydrocarbon and secondary weathering of the soil minerals. The magnitude in the shift of the pore fluid chemistry does not appear to directly translate to changes in soil electrical conductivity. As the experiment continues, the researchers expect to be able to model the magnitude of the pore fluid chemical change on the soil conductivity as more degradation and mineral weathering occur in the soils columns.

Investigation of Soil Vapor Extraction Mechanisms Using Magnetic Resonance Imaging (MRI)

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Geophysical Research Abstracts, Vol. 5, 02690, 2003

Results from soil vapor extraction models have shown that mass removal rates for nonaqueous phase liquids are controlled by volatilization rates, vapor phase diffusion from unswept zones of low permeability, and/or diffusion through water-filled regions of the pore space. To test these findings magnetic resonance imaging (MRI) was used to measure the location and saturation of the nonaqueous phase liquid, decane, in columns packed with either uniform grain silica gel or a fine grain core surrounded by a coarse grain shell. Columns were contaminated with decane and drained to different decane saturations. Each column was then continuously purged with water saturated nitrogen gas and images were taken intermittently. All images were taken using an inversion recovery spin-echo pulse sequence. This sequence allowed decane protons to be imaged independent of water protons. Results showed that in homogeneous columns at residual decane saturation a sharp volatilization front moved through the columns. Volatilization rates in these columns were fast relative to advection rates. In

heterogeneous columns at residual decane saturation the volatilization front in the core lagged just behind the shell because flow was through the shell and decane in the core diffused outward to the shell. In heterogeneous columns above residual saturation, decane volatilization occurred near the inlet, and decane in the core flowed to the shell to replenish volatilized decane. These results indicate that NAPL trapped in low permeability zones can flow to replenish areas where NAPL is lost due to volatilization. However, when residual NAPL saturation is reached, flow stops and diffusion limits removal from low permeability zones. Existing soil vapor extraction models assume NAPL is distributed as pools and/or as residual NAPL, and NAPL flow does not affect mass removal. These results indicate that this assumption may not always be valid.

Is Method 1664A Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non- Polar Materials) a Measure of Total Petroleum Hydrocarbons?

Miller, Michael (New Jersey Dept. of Environmental Protection, Trenton); Michael Wright (TRC Omni Environmental Corp., Princeton, NJ); A.M. Allen and B. Dubek (ConocoPhillips Bayway Refinery, Linden, NJ).

The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23 October 2003, Univ. of Massachusetts at Amherst.

Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

Total Petroleum Hydrocarbon (TPH) is a non-specific parameter that has been defined by EPA method 418.1 and used for over 20 years to estimate the contamination of the environment by petroleum products. The simple, inexpensive, and straightforward method uses Freon 113 to extract petroleum from the matrix; the petroleum then is treated with silica gel and determined by infrared spectroscopy. Production and importation of Freon 113 is now banned in the United States. U.S. EPA method 1664A Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non- Polar Materials) has been considered as a replacement for method 418.1. This paper reports the results of a study in New Jersey to determine if Method 1664A could replace method 418.1. The study showed that the recovery of petroleum hydrocarbons by method 1664A is temperature-dependent. Petroleum compounds with carbon numbers as low as C12 can be recovered successfully using the Horizon SPEED – VAPTM II 9000 Solvent Evaporation System, at an operational temperature of 28 degrees C. Under this condition, method 1664A Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non- Polar Materials) can replace method 418.1.

Krypton and Sulfur Hexafluoride as Non Aqueous Phase Liquid Partitioning Tracers in the Saturated Zone

Montague, T.E. and T.E. Elliot, Queens University, Belfast.

Geophysical Research Abstracts, Vol. 5, 12162, 2003

Tools to characterize the extent of aquifer contamination by nonaqueous phase liquids (NAPLs) are important in aiding remediation strategies. This preliminary research aims to employ Kr and SF₆ as applied bulk partitioning tracers for the detection and quantification of NAPL volumes in the saturated zone of subsurface environments. These gases potentially are inert, non-toxic, environmentally friendly, and cost-effective tools for assessing NAPL contamination in the subsurface. A protocol has been developed for giving reliable dissolved gas concentration data that can give NAPL water partition coefficients for these gases by simple mass balance. One-dimensional (1-D) column tests are presented

to illustrate the effectiveness of these gases as NAPL partitioning tracers, using dissolved bromide as a comparative conservative tracer. Resultant Break Through Curves (BTCs) are analysed by method of moments and the NAPL volume estimation based on the tracer data compared with known NAPL addition to the columns. Retardation of these tracers compared to the conservative Br tracer is clear evidence that these gases can be effectively employed as bulk partitioning tracers in the saturated zone and are a useful tool for estimating NAPL saturation. Proposals for the use of dissolved Kr and SF₆ gases as novel tracers for other nonaqueous phases (e.g. organic matter) in the saturated zone in conjunction with other intelligent (e.g. interfacial tracers) are discussed.

Measurement of Henry's Law Constant for Methyl tert-Butyl Ether (MTBE) using Solid-Phase Microextraction

Bierwagen, B.G.; A.A. Keller.

Environmental Toxicology & Chemistry, Vol 20 No 8, p 1625-1629, 2001

The design of efficient remediation technologies to remove methyl tert-butyl ether (MTBE) from ground water requires accurate measurement of MTBE's air/water partitioning coefficient (Henry's law constant, H). Previously published data for MTBE appear to have some unusual nonlinearity at lower temperatures (15 to 308 degrees C), and a wide range of values exists for dimensionless H at 258 degrees C, from 0.0216 to 0.1226 in the published literature. H for MTBE was measured using headspace solid-phase microextraction (SPME) and a static method that considers equilibrium partitioning in a closed system, for temperatures between 15 and 408 degrees C. To validate the methods, the authors measured H for benzene, toluene, and trichloroethene and compared the results to previously published values, with excellent agreement.

http://www.esm.ucsb.edu/fac_staff/fac/keller/papers/Abstract31.pdf

Measuring Copper in Seawater: An Automated Detection of Copper Binding Capacity

Kidwell, David A., Naval Research Lab., Washington, DC.

Report No: NRL/MR/6170-03-8729, DTIC: ADA419453, 25 pp, Dec 2003

The mechanism for the detection of copper by ion selective electrodes in seawater has been examined. Contrary to common perception, the direct detection of copper with ion selective electrodes is unlikely to be possible due to the low levels of uncomplexed copper present. Instead, it is proposed that the ion selective electrodes measure the activity of naturally-occurring binding ligands for copper and thereby provide an indirect determination of uncomplexed copper, which is the species most likely to be toxic to organisms. A potentially automated system is described to measure the complexing ability of the seawater system for copper and other metals. This system can allow the determination of excess binding capability for the water system and thereby predict if a water body can absorb extra toxic metals.

<http://handle.dtic.mil/100.2/ADA419453>

Measuring Groundwater, Soil Vapor and Indoor Air to Evaluate Fate and Transport: A Case Study

Kmetzo, Denise A. and Lisa J. Campe, Woodard & Curran, Dedham, MA.

The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23 October 2003, Univ. of Massachusetts at Amherst.

Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

In a study of the transport of chlorinated volatile organic compound (VOC) vapors from ground water into occupied buildings, ground-water samples were collected from various wells around an affected neighborhood, along with two rounds of soil vapor and indoor air data from over 30 residences. Some of the residences were located over the plume; others were not. Ambient air samples were collected on each sampling day from the neighborhood. This paper presents the inter- and intra-medium concentrations detected, as well as the data patterns that describe VOC transport. The authors also describe how the transport conclusions compared to conclusions that would have been made if only fate and transport modeling had been performed.

Measuring Subsurface Water Fluxes Using a Heat Pulse Sensor

Ochsner, T.E. (Iowa State Univ., Ames); Q. Wang (Xian Univ. of Technology, Xian, China); R. Horton (Iowa State Univ., Ames).

Eos Trans. AGU, Vol 82 No 47, Fall Meet. Suppl., Abstract H32G-07, 2001

Heat pulse sensors have been proposed as promising tools for measuring subsurface water fluxes. The heat pulse probe consists of three 4-cm stainless-steel needles embedded in a waterproof epoxy body. The needles contain resistance heaters and thermocouples. The probes are connected to an external datalogger and power supply and then installed in soil. To measure the water flux, a 15-s heat pulse is generated at the middle needle using the power supply and the resistance heater, and the temperature increases at the needles 6-mm upstream and downstream from the heater are recorded using the thermocouples and datalogger. Heat pulse methods have required cumbersome mathematical analysis to calculate soil water flux from this measured data, but the authors present a new mathematical analysis showing that a simple relationship exists between water flux and the ratio of the temperature increase downstream from the line heat source to the temperature increase upstream from the line heat source. The simplicity of this relationship makes heat pulse sensors a more attractive option for measuring subsurface water fluxes.

Measuring Total Flux of Organic Vapors From the Unsaturated Zone Under Natural Conditions:

Design, Laboratory and Field Testing of a Flux Chamber Device

Tillman, F.D. (Univ. of Virginia, Charlottesville); J. Choi; J.A. Smith.

Eos Trans. AGU, 83(19), Spring Meet. Suppl., Abstract H32A-05, 2002

A simple, easy-to-use, and inexpensive device for measuring VOC flux under natural conditions was designed and tested both in the lab and in a natural field setting. The chamber consists of a stainless steel right-circular cylinder open on one end, with a flexible, impermeable membrane allowing for chamber expansion and contraction. Air pumped from inside the chamber through activated carbon traps returns to the chamber, maintaining a net zero pressure gradient from the inside to the outside of the chamber. The traps are analyzed with thermal desorption/GC-FID, and the mass of contaminant is divided by the product of the sampled area and sample time to give VOC flux measured by the chamber. Design parameters for the chamber were selected using continuously stirred tank reactor (CSTR)-equation based modeling under step, sinusoidal and transport-model simulation flux inputs. Laboratory testing of the flux chamber simulated unsaturated zone transport of an aqueous trichloroethene (TCE) solution. The flux chamber measurement was compared to flux prediction based on measured linear concentration data from the simulator and Fick's law. Results from both the diffusion-only and combined advection/diffusion tests indicate the chamber device performs well under

a wide range of fluxes. This paper also presents the results of side-by-side testing of three chamber devices at a TCE-contaminated field site.

Mercury Speciation by X-Ray Absorption Fine Structure Spectroscopy and Sequential Chemical Extractions: a Comparison of Speciation Methods

Kim, C.S. (Stanford Univ., Stanford, CA); N.S. Bloom; J.J. Rytuba; G.E. Brown Jr.
Environmental Science & Technology, Vol 37 No 22, p 5102-5108, 15 Nov 2003

Determining the chemical speciation of mercury in contaminated mining and industrial environments is essential for predicting its solubility, transport behavior, and potential bioavailability as well as for designing effective remediation strategies. This paper describes the results of tests two techniques for determining Hg speciation--X-ray absorption fine structure (XAFS) spectroscopy and sequential chemical extractions (SCE)--applied independently to spiked samples to determine if the two techniques provide comparable Hg speciation results. Statistically significant (>10%) differences were observed in samples containing more soluble Hg-containing phases (HgCl₂, HgO, Hg₃S₂O₄), which might be related to matrix, particle size, or crystallinity effects affecting the apparent solubility of the Hg phases.

Metal Ion Biosensor for Wastewater Discharge

Fierke, Carol A., Michigan Univ., Ann Arbor.
DTIC: ADA417182, 5 pp, June 2003

A carbonic anhydrase-based metal ion biosensor was optimized for measuring copper in wastewater and seawater using molecular biology methods. CA variants were prepared that enhanced the copper ion specificity and/or decreased the copper affinity were incorporated into the sensor. We have also incorporated two additional, commercially available fluorescent labels (Alexa Fluor 660 and Oregon Green) into the transducer by covalently labeling a CAII mutant containing a single cysteine residue. Finally, we have used made fusions with fluorescent proteins (dsRed-CA) as a new method of transducing metal ion concentration. These methods will be useful in the development of sensors to determine the concentration of metal ions in wastewater and the ocean.

<http://handle.dtic.mil/100.2/ADA417182>

Methods for Evaluating Leaching and Transport of Redox-Sensitive Heavy Metals at Contaminated Industrial Sites

Buczko, U. and L. Hopp (Univ. of Bayreuth); W. Durner (Technical Univ. of Braunschweig); S. Peiffer (RWTH Aachen).
Geophysical Research Abstracts, Vol. 5, 01988, 2003

Direct measurements of contaminant entries at the ground-water surface are in most cases infeasible, and indirect methodologies for the percolation immission prognosis are needed. The development of such a methodology for soils contaminated with redox-sensitive heavy metals, such as Cr and As, is the subject of an ongoing research project at the University of Bayreuth. The approach for the percolation immission prognosis consists of three parts: (1) estimation of the emission of metals from the contaminated source soil (using elutions, soil saturation extracts, and column experiments), (2)

transport simulations through the unsaturated zone, and (3) validation of the results gained by those first two steps by analysis of percolation water extracted in situ from undisturbed soil by lysimeters installed at two different soil depths. To quantify the leaching behaviour of contaminated soils, a newly developed unsaturated column test with flow interruption was performed, using materials from eight different industrial sites in northern Bavaria contaminated with Cr, As, Cu, Pb, and Hg. The inverse optimization of the experiments in terms of sorption parameters revealed that desorption of heavy metals can be described with a two-site approach; the kinetically controlled sites, however, prevail over the sorption sites that are in equilibrium with the dissolved concentration. The transport simulations, using a 2-D model to account for spatial variability of soil hydraulic and sorption parameters, resulted in spatially variable contaminant entries at the ground-water table. Locally, heavy metal contaminations would occur in less than 5 years after emission from the source zone.

Microbial Community Structure in a Shallow Hydrocarbon-Contaminated Aquifer Associated with High Electrical Conductivity

Duris, J.W. (U.S. Geological Survey, Lansing, MI); S. Rossbach (Western Michigan Univ.); E.A. Atekwana (Univ. of Missouri-Rolla); D. Werkema Jr. (U.S. EPA, ORD, Las Vegas, NV).
Geophysical Research Abstracts, Vol. 5, 14279, 2003

Little is known about the complex interactions between microbial communities and electrical properties in contaminated aquifers. To investigate possible connections between these parameters, a study was undertaken to investigate the hypothesis that the degradation of hydrocarbons by resident microbial communities causes a local increase in organic acid concentrations, which in turn cause an increase in native mineral weathering and a concurrent increase in the bulk electrical conductivity of soil. Microbial community structure was analyzed using a 96-well most probable number (MPN) method and rDNA intergenic spacer region analysis (RISA). Microbial community structure was found to change in the presence of hydrocarbon contaminants and these changes were consistently observed in regions of high electrical conductivity. The authors infer from this relationship that geophysical methods for monitoring the subsurface are a promising new technology for monitoring changes in microbial community structure and simultaneous changes in geochemistry that are associated with hydrocarbon degradation.

Microelectronic Nose Detects and Recognizes Gases to Save Lives

Greb, Richard, Argonne National Lab.

Argonne National Laboratory: What's New This Week? 21 Mar 2003

The Smart Sensor Development Kit can be used to develop inexpensive devices to detect specific gases. Also known as a microelectronic nose, the sensor is smaller than a dime and detects tiny quantities of airborne chemicals in real time. The sensor is available commercially with measurement and analysis software in a package the size of a cell phone and can save effort, money and human life. The Smart Sensor Developer Kit was one of the winning technologies in the 2002 R&D 100 awards competition. The kit was developed by Argonne's Energy Systems Division and has been licensed to General Atomics of San Diego, CA, and Relative Solutions Corp. of Metairie, LA. The solid-state ceramic-metallic sensors are inexpensive to make using established chip-fabrication techniques. Each chip has a tiny heater on one side and the sensor on the other. The system detects and recognizes substances by their unique "voltammetric" fingerprints. When chemical vapors pass over a chip, small

amounts adhere to the chip's surface. When the chip is heated, the chemical interacts with the testing surface. This interaction changes the electrical resistance of the sensor's components, creating a unique electronic signature that identifies the chemicals and – based on signal intensity – their concentrations. Using distinct signatures from known quantities of chemicals, the computer builds a library of recognizable voltammetric signature patterns. Stored in the detector's software, the library enables the detector to determine the gas's identity and concentration and transmit an alert if needed. The unit can identify the components in a mixture of vapors and even sound an alert when it's exposed to a gas it doesn't recognize. Argonne's Smart Sensor Development Kit is available for licensing to companies who wish to develop, manufacture, and market sensors. As a federally funded research organization, Argonne neither manufactures nor sells commercial products. For licensing information, contact Argonne's Office of Technology Transfer at partners@anl.gov or 800-627-2596.

Mineralogical Characterization of Arsenic in Uranium Mine Tailings Precipitated from Iron-rich Hydrometallurgical Solutions

Moldovan, B.J. (Cameco Corporation, Saskatoon, Saskatchewan, Canada); D.T. Jiang; M.J. Hendry. *Environmental Science & Technology*, Vol 37 No 5, p 873-879, 1 Mar 2003

Arsenic-rich uranium mine tailings from the Rabbit Lake in-pit tailings management facility in northern Saskatchewan, Canada, were investigated to determine the mineralogy and long-term stability of secondary arsenic precipitates formed from iron-rich hydrometallurgical solutions. Total arsenic and iron concentrations in six iron-rich samples of the mine tailings ranged from 56 to 6,000 ug/g and from 12,600 to 30,200 ug/g, respectively. On the basis of stability field diagrams generated from pH, Eh, and temperature measurements on tailings samples, the researchers concluded that arsenic and iron in the tailings were stable as As⁵⁺ and Fe³⁺.

Modeling and Mapping of Sediment Contaminant Distribution: A Univariate Geostatistical Perspective

Ramanitharan, Kandiah and Laura J. Steinberg, Tulane Univ., New Orleans, LA.
The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23 October 2003, Univ. of Massachusetts at Amherst.
Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

This paper presents an exploratory study on the applications of geostatistical techniques in mapping sediment contaminant distributions in water bodies using sediment contaminant concentration data sets from five water bodies (Seal Beach, Tampa Bay, Hudson River, Duwamish River and Lake Geneva). The authors examine how the physical shape of the water bodies, hotspots, and multiple data measurements per data point influence geostatistical modeling and discuss the selection of data to fit a geostatistical model for water bodies with physical barriers.

Monitoring and Quantitative Assessment of Subsurface Solute Transport Using Electrical Resistance Tomography (ERT) and Equivalent Transport Models.

Vanderborcht, J. (Forschungszentrum Juelich GmbH ICG-IV, Juelich, Germany): A. Kemna; H. Vereecken.
Eos Trans. AGU, Vol 82 No 47, Fall Meet. Suppl., Abstract H32G-06, 2001

A NaBr tracer solution was injected in a well in a field-scale tracer test in an unconfined aquifer. Changes in bulk electrical conductivity on a reference plane 6 m downstream from the injection well were monitored over 18 days. With electrical resistance tomography (ERT), spatially resolved images were inverted from a set of transfer resistance data measured in dipole-dipole configuration. Salt tracer concentrations were derived. The maps of tracer concentrations were interpreted using an equivalent convection dispersion model, CDM, that conceptualizes the aquifer as a homogeneous medium with a uniform mean flow velocity. The analytical solution of the CDM was fitted to the observed concentration maps. The fitted equivalent parameters define the mean flow velocity vector and quantify the overall spreading of the plume in the longitudinal and transverse directions. When flow is heterogeneous, the injected tracer plume is distorted by flow heterogeneities, and local concentrations within the plume deviate from predicted concentrations by the equivalent CDM which postulates a maximal homogenization or mixing of solute mass within the plume. A stream tube model, STM, represents transport in the aquifer by a set of 1-D convection dispersion processes to quantify the degree of mixing and the heterogeneity of transport within the plume. The results indicate that the observed tracer plume was fairly well described by the equivalent CDM. Some variability of solute arrival times at the reference plane was evident from the interpretation of the concentration maps by the STM. The equivalent dispersivity in the STM was only slightly smaller than the longitudinal dispersivity of the CDM, which indicates a fairly homogeneous mixing. Since concentration maps are obtained using ERT, this technique bears the potential to determine the spatial structure of the solute arrival times on reference planes, from which the spatial structure of the hydraulic conductivity can be inferred. The concentration maps provide also information about the solute homogenization or mixing due to local scale dispersion processes. The degree of mixing controls the reaction rates between different substances and is therefore a key process for degradation and remediation.

Monitoring of Electrokinetic Removal of Heavy Metals in Tailing-Soils Using Sequential Extraction Analysis

Kim, S.O. (Kwangju Inst. of Science and Technology, Kwangju, South Korea); K.W. Kim.
Journal of Hazardous Materials, Vol 85 No 3, p 195-211, 17 Aug 2001

The researchers monitored the electrokinetic removal of heavy metals from tailing soils and learned that removal efficiencies depend upon their physico-chemical states. The tailings examined contained high concentrations of target metal contaminants (Cd, Cu, Pb, and Zn). The speciation, mobility, and affinity (adsorption capacities) of the different metals in the soil matrix significantly influenced the removal efficiencies. The removal efficiencies of more mobile heavy metals (Cd, Cu, and Zn) were higher than that of the less mobile heavy metal (Pb).

Monitoring of Landfill Leachate Dispersion Using Reflectance Spectroscopy and Ground-Penetrating Radar

Splajt, T. (Univ. of Hull, Hull, England); G. Ferrier; L.E. Frostick.
Environmental Science & Technology, Vol 37 No 18, p 4293-4298, 15 Sep 2003

Strong correlations between red edge inflection position and chlorophyll and heavy metal concentrations have been demonstrated from grassland species affected by leachate contamination of the soil adjacent to a landfill test site. The study demonstrated that reflectance spectroscopy can identify vegetation affected by leachate-contaminated soil at a range of spatial resolutions. To identify the

vegetation affected by leachate contamination, the spectroradiometer must have contiguous bands at sufficient spectral resolution over the critical wave range that measures chlorophyll absorption and the red edge (between 650 and 750 nm). Also demonstrated was the utility of ground-penetrating radar data to identify leachate escaping from breakout points in the contaminant wall.

Mononuclear Cyano- and Hydroxo-Complexes of Iron(III)

Perera, W.N. (Murdoch Univ., Murdoch, Western Australia), G. Hefter.

Inorganic Chemistry, Vol 42 No 19, p 5917-5923, 22 Sep 2003

This paper describes a detailed investigation of the iron(III)-cyanide and iron(III)-hydroxide systems made in NaClO₄ media at 25 degrees C using combined UV-vis spectrophotometric and pH-potentiometric titrations.

An MPN Method for the Enumeration of Iron-Reducing Bacteria

W. D. Gould, W.D. (CANMET, Natural Resources Canada, Ottawa); M. Stichbury (Univ. of Waterloo); M. Francis (NOVA Chemicals Corporation, Calgary, Alberta); L. Lortie; D.W. Blowes.

Proceedings of the Sudbury 2003 Mining and the Environment Conference, 25-28 May 2003, Sudbury, ON, Canada. Laurentian Univ., Sudbury, ON, Canada. Centre for Environmental Monitoring, ISBN: 0-88667-051-9. 2 Vols or 2 CD-ROMs, 5 pp, 2003

Iron-reducing bacteria are a significant biological component of passive systems used to treat acid mine drainage and also play a role in mobilizing other metals. A simple medium containing a readily available iron source, ferric EDTA, has been developed for the enumeration of iron-reducing bacteria. Three cultures of iron-reducing bacteria were used to evaluate various media compositions: *Shewanella putrefaciens* 200 (NCIB 12577), *Shewanella putrefaciens* ESSO 4-1 (NCIB 12580) and a mixed culture of iron-reducing bacteria.

<http://www.ott.wrcc.osmre.gov/library/proceed/sudbury2003/sudbury03/57.pdf>

MSA Instrument Helps Enhance Worker Safety and Homeland Security

Sensor Business Digest, Vol 12 No 8, Nov 2003

The Instrument Division of Mine Safety Appliances Company (MSA, Pittsburgh, PA, 800-MSA-4678) has been designing and manufacturing gas detection equipment for over 70 years. MSA provides gas detection equipment for personal and plant protection, designing and manufacturing sophisticated portable and permanent instruments that monitor workplace environments for toxic and combustible gases and other atmospheric hazards. The new transportable SafeSite™ hazardous gas detection system has been developed for homeland security applications to detect and communicate the presence of chemical warfare agents (CWAs), including nerve and blister agents, VOCs, and numerous toxic industrial chemicals, such as chlorine, ammonia, hydrogen cyanide, and hydrogen chloride, within a wireless network. An innovative modular integrated communications helmet communications system uses an unobtrusive microphone/sound transmission system to provide interface capability with various military and other radio transceivers and intercom systems. The SafeSite hazardous gas detection system integrates multiple sensing technologies, including surface acoustic wave (SAW) for chemical warfare agent detection, photoionization detectors for VOC detection, and electrochemical sensors for

monitoring toxic industrial chemicals. Oxygen and combustible gas monitoring capabilities also can be added to the system.

MSA's Chemgard(tm) monitor uses photoacoustic infrared (PIR) technology to offer high stability and selectivity to the gas(es) of interest, the ability to operate for months without zero drift, enough flexibility to detect a large number of user-selectable compounds, and a broad measuring range--100% by volume down to parts per billion. Gas sensing technologies developed by MSA include the patented Button(tm) sensor, and photoacoustic infrared gas sensors. The Button cell, a small, button-sized electrochemical sensor, is used in MSA's single- and multi-gas instruments, including the Pulsar(tm) single-gas detector, Pulsar Plus single-gas detector, and the Solaris(tm) multi-gas detector. The Button was designed and developed to satisfy a strong market demand for lower-cost, smaller-sized portable instruments.

MTBE and Other Oxygenates: Environmental Sources, Analysis, Occurrence, and Treatment
Deeb, Rula A. (Malcolm Pirnie, Inc., Emeryville, CA); C. Kung-Hui (Univ. of Tennessee, Knoxville); T. Shih (CALEPA, Los Angeles); S. Linder (EPA Region 9); I. (Mel) Suffet (Univ. of California, Los Angeles); M.C. Kavanaugh (Malcolm Pirnie); L. Alvarez-Cohen (Univ. of California, Berkeley).
Environmental Engineering Science, Vol 20 No 5, p 433-447, 2003

This paper provides a review of environmental sources of MTBE and alternative oxygenates, analytical methods available for their detection in environmental samples, their occurrence in the environment with a focus on ground water, and treatment methods for their removal from gasoline-contaminated water. Because of their polar characteristics, oxygenates released to ground water from leaking underground storage tanks migrate through aquifers with minimal retardation, raising widespread concern regarding their potential for reaching drinking water sources. As a group, fuel oxygenates present distinct analytical and sample preparation issues. Conventional procedures for the analysis of gasoline constituents have been shown to be insensitive for fuel oxygenates, and ether hydrolysis to alcohol under acidic conditions has led to a reassessment of conventional handling techniques for ground-water samples. An evaluation of MTBE's occurrence in drinking water sources over time in three states showed that the frequency of MTBE detection since 1999 appears to be stabilizing in ground water and slightly decreasing over time in surface water. Though recent studies have demonstrated the effectiveness of conventional treatment technologies and the promise of emerging technologies for MTBE removal from contaminated media, the removal from water of tert-butyl alcohol (TBA), an impurity in MTBE-blended fuels and an MTBE breakdown product, can be problematic for conventional technologies such as air stripping and granular activated carbon.

Available at <http://www.engr.utk.edu/civil/courses/MTBE-review.pdf>

Networked Sensing in Support of Real-Time Transport Model Parameter Estimation
Kim, J.Y., T. Bendikov, Y. Park, and T.C. Harmon, University of California, Los Angeles.
Geophysical Research Abstracts, Vol. 5, 13740, 2003

This work examines the potential role of embedded networked sensing (ENS) protocols for monitoring the fate and transport of contaminants in the subsurface. The ultimate goal is to deploy a large dense array of chemical sensors for the purpose of identifying key transport parameters that are spatially distributed (e.g., porous media dispersivity) and, in some cases, temporally varying (e.g., nonaqueous phase liquid source zones). While there is clearly a need for further development in chemical sensor

technology, the need to prepare to deploy new sensors in distributed networks is equally great. The researchers first examined heat transfer phenomena as a surrogate for mass transfer in an intermediate scale physical aquifer model. Using a relatively standard data acquisition system (National Instruments A/D converter with Labview software), they continuously monitored water temperature over time and space throughout the model system. For well-defined heat sources, they developed closed-form solutions to the governing differential equations that are suitable for analyzing the data. Then, by embedding these closed solutions into the data-acquisition routines, they were able to identify phenomenological parameters in real time. Moving toward more relevant systems, they next demonstrated the use of a single nitrate sensor placed downgradient of a finite pulse source of nitrate in a 3-D porous medium. Other potential applications and implications of ENS protocols in environmental monitoring networks are discussed in terms of supporting ENS issues of self-adaptation, self-calibration, and coordinated actuation of responses.

A New Approach to Measuring the Direction of Horizontal Groundwater Flow
Klammler, Harald; Kirk Hatfield; Michael Annable, University of Florida, Gainesville.
Eos. Trans. AGU, 84(46), Fall Meet. Suppl., Abstract H21D-0857, 2003

A Passive Flux Meter (PFM) has been developed to simultaneously measure the magnitudes of ground water and contaminant fluxes in porous media. The PFM consists of permeable sorptive media in the shape of a homogeneous cylinder that is inserted into a borehole and that exactly fits the diameter of the well screen. The PFM, which initially contains a known amount of a resident tracer, thus intercepts ground water and contaminant flow, causing the partial elution of the resident tracer from the PFM and the sorption of contaminants onto the PFM. Quantitative analysis of the PFM for the amount of resident tracer remaining on the PFM media and the amount of contaminant sorbed onto the PFM after exposure to ground water and contaminant flow allows for the determination of the magnitudes of ground water and contaminant fluxes. This paper presents two modified configurations of the PFM and compares their capability for measuring the horizontal flow direction simultaneously to the magnitudes of ground water and contaminant fluxes.

A New Specific Method to Detect Cyanide in Body Fluids, Especially Whole Blood, by Fluorimetry
Felscher, D. and M. Wulfmeyer, Carl Gustav Carus der Technischen Univ., Dresden, Germany.
Journal of Analytical Toxicology, Vol 22 No 5, p 363-366, Sep 1998

Fluorimetry provides a simple, rapid, and specific method for the quantitative determination of cyanide ion in body fluids based upon the transformation of cyanide ion into hydrocyanic acid. The hydrocyanic acid then reacts with 2,3-naphthalenedialdehyde and taurine in a self-contained system, and the 1-cyano-2-benzisoindole derivative that forms is suitable for fluorimetric measurement. The fluorescence intensity can be determined by spectrophotometry or by high-performance liquid chromatography (HPLC) with fluorescence detection. The detection limit is 0.002 ug/mL. Linearity was excellent from 0.002 to 1 ug/mL for spectrophotometry and from 0.002 to 5 ug/mL for HPLC with fluorescence detection. Thiocyanate and sulfide did not interfere, even at high concentrations.

Non-Invasive Imaging of NAPL/Partitioning Tracer Interaction in Porous Media
Jones, E.H. (Univ. of Sheffield, UK) and C.C. Smith.

Information about subsurface NAPL distribution can be obtained by comparing the transport of a partitioning tracer to that of a non-partitioning tracer. The NAPL reversibly retains the partitioning tracer, which retards its transport with respect to that of a non-partitioning tracer. The magnitude of retardation is then correlated to the volume of NAPL present. Transport of both partitioning and non-partitioning tracers is influenced significantly by local NAPL distribution, leading to phenomena such as flow bypassing, non-equilibrium partitioning, and dead zone formation. The influence of these phenomena is very difficult to investigate based on breakthrough curves only; full spatial data is required to enable a more complete understanding. A laboratory-based model was developed with a 2-D quartz sand porous medium of nominal thickness and a non-invasive imaging technique with a fluorescent tracer to monitor spatial partitioning tracer behavior and interaction. Fluorescein (0.1g/l concentration) has negligible sorption to quartz sand and was used as both the partitioning (at pH 6.20) and non-partitioning (at pH 9) tracer, with partitioning being independent of tracer concentration. Octanol was employed as a NAPL substitute, with the tracer partitioning into octanol being strongly pH dependent. The physical parameters studied included NAPL entrapment configuration and residual saturation, flow rate, partition coefficient, NAPL zone width, and temperature. Results indicated that the observed retardation factors are sensitive to changes in all these factors with for example increased flow rates leading to an under-prediction of NAPL volume. These influences were not only observable in the breakthrough curves but could also be directly observed in the NAPL contaminated zones using the full spatial data from the imaging system.

A Non-Invasive Imaging Technique to Investigate Solute Transport in Porous Media

Huang, W. (Univ. of Sheffield, Sheffield, UK); D.N. Lerner; C.C. Smith; and S.F. Thornton.

Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution (Proceedings of the Groundwater Quality 2001 Conference held at Sheffield, UK, June 2001). IAHS Publ. no. 275, p 277-282, 2002

The authors report the development and evaluation of a 2-D physical modeling system designed to analyze solute transport in porous media. The lab-based system uses a simulated 2-D porous medium of nominal thickness and a non-invasive imaging technique with a fluorescent dye tracer to monitor solute migration. Under UV illumination, the dye emits visible light that is recorded by a digital camera and processed to produce a 2-D tracer concentration distribution. The system is demonstrated for a contaminant plume within a simulated homogeneous aquifer constructed from high purity quartz sands. The methods presented offer novel advantages for investigating solute dispersion in porous media and for determining the transverse and longitudinal dispersion coefficients without disturbance.

A Novel Aquifer Assessment Tool Using Reactive Tracers

McKnight, D., A.L. Smalley, S.A. Banwart, D.N. Lerner, N.R. Thomson, S.F. Thornton, and R.D. Wilson, Groundwater Protection & Restoration Group, University of Sheffield, UK.

Geophysical Research Abstracts, Vol. 5, 11213, 2003

The dipole flow test that circulates ground water between isolated injection (source) and extraction (sink) chambers within a single borehole has been used successfully by others to delineate heterogeneous hydraulic properties in both highly permeable and fractured rock aquifers. The authors

propose to extend this approach by adding a suite of reactive tracers into a dipole flow field to assess the geochemical properties and biodegradation potential of aquifers. If successful, this approach will provide a method to ascertain site-specific parameters for use in appropriate reactive transport models. The initial phase of this project involves the construction of a laboratory-scale physical model of a dipole probe to investigate the utility of the dipole flow and reactive tracer test (DFRTT) as an aquifer assessment tool. This phase also will serve as the developmental stage between mathematical theory and a host of planned field trials. The development of the laboratory-scale DFRTT including initial scoping calculations, numerical simulation results, chemical and physical properties of the porous medium, and the potential uses and properties of inert and reactive tracers for aquifer assessment are discussed.

A Novel Continuous-Flow Sequential Extraction Procedure for Metal Speciation in Solids
Shiowatana, J.; N. Tantidanai; S. Nookabkaew; D. Nacapricha, Mahidol Univ, Bangkok, Thailand.
Journal of Environmental Quality, Vol 30 No 4, p 1195-1205, July-Aug 2001

A continuous-flow extraction system was developed to speed up, facilitate, and improve the accuracy of the chemical fractionation of metals in solid materials. A three-step sequential extraction scheme was used to evaluate the novel system by analyzing calcium, iron, manganese, copper, and zinc in a certified soil reference material. Apart from the advantages of simplicity, speed, and less risk of the contamination that flow analysis systems usually possess, the continuous-flow system can improve the accuracy of chemical fractionation of metals by sequential extraction. The system ensures that extraction is performed at designated pH values without any need of adjustment.

Novel Microwave Sensors for Detection of Subsurface Moisture and Acid
Werner, M., KDC Technology Corporation, Livermore CA.
Subsurface Sensing Technologies and Applications, Vol 1 No 4, p 441-451, Oct 2000

Certain resonant microwave sensors appear to locate subsurface moisture or acid contamination via the radiation field rather than the near field. The penetration depth is greatly increased. The effect of “lift-off” is correspondingly diminished.

Passive Diffusion Bag Sampler Results From Multiple DoD Installations
Tunks, John P. and John Hicks (Parsons, Denver, CO); Javier Santillan and Raphael Vazquez (AFCEE, Brooks City-Base, TX).
The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23 October 2003, Univ. of Massachusetts at Amherst.
Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

Sample collection with passive diffusion bag samplers (PDBSs) represents a relatively new technology for monitoring volatile organic compounds (VOCs) in ground water. The potential benefits and cost savings associated with using PDBS for long-term monitoring are significant, as no purge waters are generated, and labor requirements for sampler installation and retrieval are minimal. The authors present the results of a field-scale PDBS demonstration performed at 14 DoD installations between May 2001 and May 2002 to assess the effectiveness of the method by comparing ground-water

analytical results for VOCs obtained by conventional sampling with results obtained using the PDBS method. The presentation includes analysis and comparison of method costs.

Petrographic and Spectroscopic Characterization of Phosphate-Stabilized Mine Tailings from Leadville, Colorado

Eusden, J.D. Jr (Bates College, Lewiston, ME); L. Gallagher; T.T. Eighmy; B.S. Crannell; J.R. Krzanowski; L.G. Butler; F.K. Cartledge; E.F. Emery; E.L. Shaw; C.A. Francis.
Waste Management, Vol 22 No 2, p 117-135, 2002

The use of soluble inorganic phosphate and lime as a heavy metal chemical stabilization agent was evaluated for mine tailings from Leadville, CO. The dominant minerals in the tailings are galena (PbS), cerussite, pyromorphite, plumbojarosite, and chalcophanites. The tailings were treated with soluble inorganic phosphate and lime to convert soluble heavy metals (principally Pb, Zn, Cu, Cd) into insoluble metal phosphate precipitates. The treatment process caused bulk mineralogical transformations as well as the formation of a reaction rind around the particles dominated by Ca and P. Within the mineral grains, Fe-Pb phosphosulfates, Fe-Pb sulfates (plumbojarosite), and galena convert to Fe-Ca-Pb hydroxides. The Mn-Pb hydroxides and Mn-(+/-Fe)-Pb hydroxides (chalcophanites) undergo chemical alteration throughout the grains during treatment. Bulk and surface spectroscopies showed that the insoluble reaction products in the rind are tertiary metal phosphate and apatite family minerals. pH-dependent leaching showed that the treatment was able to reduce equilibrium concentrations by factors of 3 to 150 for many metals, particularly Pb²⁺, Zn²⁺, Cd²⁺, and Cu²⁺.

Pharmaceuticals as Groundwater Tracers: Applications and Limitations

Scheytt, Traugott J. (Technical Univ. Berlin, Berlin, Germany); Petra Mersmann; Thomas Heberer.
Eos. Trans. AGU, 84(46), Fall Meet. Suppl., Abstract H21D-0887, 2003

The most important environmental input paths of pharmaceuticals are excretion and disposal into the sewage system. Ground-water contamination is likely to be due to leaky sewage systems, influent streams, bank filtration, and irrigation with effluent water from sewage treatment plants. There are no known natural sources of pharmaceuticals such as clofibric acid, propyphenazone, diclofenac, ibuprofen, and carbamazepine. The use of pharmaceuticals as tracers might include quantification of infiltration from underground septic tanks, detection of leaky sewage systems/leaky sewage pipes, estimation of the effectiveness of sewage treatment plants, identification of transport pathways of other organic compounds, quantification of surface water/ground-water interaction, and characterization of biodegradation potential. The use of pharmaceuticals as tracers is limited by variations in input, the high cost of analyzing trace amounts of pharmaceuticals, and an incomplete understanding of the transport and degradation behavior of pharmaceuticals. Preliminary experiments in the laboratory were conducted using sediment material and ground water to evaluate the transport and sorption behavior of selected drugs. The results of the column experiments show that clofibric acid exhibits no degradation and almost no retardation, whereas ibuprofen is biodegraded (>90 %) under aerobic conditions. Carbamazepine shows no degradation in the soil column experiments but significant retardation under the prevailing conditions. Clofibric acid shows the transport behavior of a conservative tracer, whereas ibuprofen might be used to characterize biodegradation potential in the aerobic zone.

Polarimetric Video Impulse Radar for Landmine Detection

Yarovoy, Alexander G. and Leo P. Ligthart (Delft Univ. of Technology, Delft, The Netherlands); Alexander Schukin and Igor Kaploun (Academic A.L. Mintz Radiotechnical Inst., Moscow, Russia). Subsurface Sensing Technologies and Applications, Vol 3 No 4, p 271-293, Oct 2002

The technical specifications of the a full-polarimetric ultra wideband GPR front-end have been determined based on the analysis of different GPR scenarios and user-oriented demands. The radar has been designed to meet most of these specifications and within a limited budget. The front-end comprises a generator section, a multi-static antenna system, and a receiving unit based on a multi-channel sampling converter. The novel aspects of the radar principally are a new antenna system, multiple pulse generators, and compensation circuits to improve the stability of the system. In comparison with commercially available video impulse GPR systems, the key advantages of the front-end are the considerably larger bandwidth, the ability to measure the polarimetric structure of the scattered field and the high precision of scattered field measurements. The front-end is suitable for subsurface imaging with 3-D resolution sufficient for antipersonnel mine detection and recognition.

Pollution Sleuthing with Environmental Forensics

Idaho National Engineering and Environmental Laboratory News Release, 16 July 2003

Atmospheric scientist Michael Abbott of DOE's Idaho National Engineering and Environmental Laboratory is developing a method of analysis that will decipher the complexity of atmospheric contamination, allowing him to connect downwind air pollution to its source, such as a refinery. The method can identify multiple sources of contamination and how they contribute to the mix. Abbott's approach starts with measuring the contamination as it exists at the downwind locations of interests. He uses statistical software to identify unique combinations of air pollutant constituents that characterize the different natural and man-made emission sources (chemical profiles, or source signatures). His system then uses these profiles to predict how much each source contributed at the measurement location. Experimenting with different statistical software packages, Abbott is homing in on the statistical method or methods that produce the best predictions. Contact: Michael Abbott, 208-526-8596, bot@inel.gov, or visit <http://www.inel.gov/env-energyscience/mercury/>

Pore-Scale Analysis of Mass Transfer from Dense Nonaqueous Phase Liquids Trapped in Low Permeability Zones of an Etched-Silicon Pore Network

Chomsurin, C. and C.J. Werth, Univ. of Illinois at Urbana-Champaign. Geophysical Research Abstracts, Vol. 5, 07224, 2003

Dense nonaqueous phase liquids (DNAPLs) trapped in low permeability zones can prolong cleanup times significantly. The objective of this paper is to quantify the effects of DNAPL saturation in adjacent low and high permeability zones on the mass flux to ground water at the pore scale. Adjacent low and high permeability pore networks were etched into a silicon wafer, saturated with water, and contaminated with tetrachloroethene (PCE) DNAPL. Water was then purged through the system at a constant flow rate and the location, size, and shape of DNAPL blobs were imaged during dissolution. Imaging was performed with an inverted epi-fluorescent microscope equipped with an automated stage, a digital camera, and image acquisition system. The PCE and water were stained with fluorescent dyes for imaging. DNAPL removal in the high permeability zone was controlled by advection and

rate-limited dissolution. DNAPL removal in the low permeability zone was controlled by advection, rate-limited dissolution, and transverse diffusion to the high permeability zone. A continuum-scale analytical solution was developed to describe mass transfer in the low permeability zone. This was fit to the experimental results to obtain the dissolution rate constant. This constant agreed with that determined for PCE dissolution from a low permeability pore network where only advection and rate-limited dissolution controlled DNAPL removal. A model sensitivity analysis showed that as DNAPL saturation in the high permeability zone decreases, the overall rate of DNAPL dissolution from the low permeability zone decreases because more flow is diverted to the high permeability zone. This important result indicates that after removing most of the mass from a high permeability zone, the rate of DNAPL removal from adjacent low permeability zones can decrease. This means cleanup times can increase and averaged ground-water concentrations can decrease in an aquifer after DNAPL is preferentially removed from high permeability zones.

Predicting Leakage Through Composite Landfill Liners

Foose, G.; C. Benson; T. Edil.

Journal of Geotechnical and Geoenvironmental Engineering, ASCE, Vol 127 No 6, p 510-520, 2001

Leakage through composite landfill liners was analyzed using existing analytical and numerical models developed for the study. Three-dimensional numerical models were used to analyze leakage through circular defects and two-dimensional numerical models were used to analyze leakage from defective seams. Leakage rates predicted with the numerical models were compared to leakage rates predicted using existing equations and analytical models currently being used. These comparisons show that existing equations and analytical models all have limitations and no universal equation or method is available for predicting leakage rates. To overcome some of the deficiencies in the existing equations and models, new equations were developed based on results from the numerical models.

Recommendations are made for using the new equations, existing equations, and analytical models to predict leakage rates in thick composite liners having a geomembrane overlaying a compacted soil liner and thin composite liners having a geomembrane overlaying a geosynthetic clay liner.

http://www.uwgeotech.org/pubs/wl_foose_predicting.pdf

Preserving the Distribution of Inorganic Arsenic Species in Groundwater and Acid Mine Drainage Samples

Bednar, A.J. (U.S. Geological Survey, Denver Federal Center, CO); J.R. Garbarino; J.F. Ranville; T.R. Wildeman.

Environmental Science & Technology, Vol 36 No 10, p 2213-2218, 15 May 2002

The distribution of inorganic arsenic species must be preserved in the field to eliminate changes caused by metal oxyhydroxide precipitation, photochemical oxidation, and redox reactions. Several preservatives, such as inorganic acids and ethylenediaminetetraacetic acid (EDTA), were evaluated to minimize metal oxyhydroxide precipitation. EDTA worked best for all sample matrices tested. Storing samples in opaque polyethylene bottles eliminated the effects of photochemical reactions.

Quantitative Method for the Detection of Triethyl Phosphate in Aqueous Solutions

Bagalawis, Rosa L.; J. Carlson; J. Walsh, Army Soldier and Biological Chemical Command, Natick,

MA.

Report No: NATICK/TR-04/002, DTIC: ADA417765, 26 pp, Oct 2003

A gas chromatography (GC) method has been developed to detect and quantify triethyl phosphate (TEP) at the parts per million level in aqueous solution. TEP was used as a chemical agent stimulant to evaluate the penetration characteristics of clothing, gloves, boots, and items of personal equipment. The analytical method, initially developed in 1981, combines gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS) and Fourier-Transform infrared (FTIR) techniques. Quality Assurance and Quality Control (QA/QC) procedures were built into the analytical method to ensure the integrity and reproducibility of the analytical results. The TEP was analyzed directly from aqueous samples without the need for sample extraction or concentration procedures.

<http://handle.dtic.mil/100.2/ADA417765>

Quick X-Ray Absorption Spectroscopy for Determining Metal Speciation in Environmental Samples
Gaillard, J.F. (Northwestern Univ., Evanston, IL); S.M. Webb; J.P. Quintana.
Journal of Synchrotron Radiation, Vol 8 Pt 2, p 928-930, 1 Mar 2001

The authors present a method for determining the chemical speciation of metals in environmental particles based on Quick X-ray Absorption Spectroscopy. The approach can be applied to either the extended or the near edge fine structure. It examines the decomposition of the XAS spectrum of an unknown sample on a reference set of standards' spectra using quadratic linear programming. The analysis accounts for the statistical experimental errors generated during the acquisition of X-ray absorption data, and leads to error estimates on the various fractions determined via a Monte Carlo procedure. The paper contains an application example for the speciation of inorganic Zn in a contaminated sediment sample.

Raman Spectroscopy and Instrumentation for Monitoring Soil Carbon Systems
Stokes, D.L., S. Wullschleger, M. Martin, and T. Vo-Dinh, Oak Ridge National Lab., Oak Ridge, TN.
Advanced Environmental Sensing Technology II.
Proceedings of SPIE - The International Society for Optical Engineering, Vol 4576 [paper 30] 13 pp, 2002

Raman scattering yields very fine spectral features that offer the potential for multicomponent sample analysis with minimal or no sample pretreatment. Although the intensity of Raman scattering is generally extremely low, the surface-enhanced Raman scattering (SERS) effect can greatly enhance Raman signals (106-108 range) through the adsorption of compounds on specially roughened metal surfaces. Lab investigations have assessed copper, gold, and silver as possible substrate metals in the fabrication of SERS substrates. These substrates have included metal-coated microparticles, metal island films, and redox-roughened metal foils. Researchers have evaluated several laser excitation sources spanning the 515-785 nm range for both Raman and SERS analysis. For this particular study, fulvic and humic acids were selected as models for establishing the feasibility of using Raman and SERS in soil carbon analysis. Studies thus far have demonstrated that copper substrates perform best in the SERS detection of humic and fulvic acids, particularly when coupled to electrochemical processes that enhance adsorption of specific compounds. This effect not only yields a stronger signal, but can also impart selectivity in the analysis of complex samples such as soil.

<http://www.ornl.gov/~webworks/cppr/y2001/rpt/119247.pdf>

Rapid Determination of Cyanide and Azide in Beverages by Microdiffusion Spectrophotometric Method

Tsuge, K.; M. Kataoka; Y. Seto, National Research Inst. of Police Science, Kashiwa, Chiba, Japan. Journal of Analytical Toxicology, Vol 25 No 4, p 228-236, May-June 2001

A rapid screening method was developed for the determination of the toxic volatile anions, cyanide and azide, in beverages. This method consisted of a microdiffusion extraction combined with spectrophotometry using the Konig cyanide reaction and ferric azide complex formation in conjugation with cerium azide oxido-reduction. The time required to achieve full recovery in the extraction of hydrogen cyanide and hydrazoic acid from samples was shortened by increasing the diffusion temperature from 25 degrees C to 40 degrees C. The time required to achieve saturated color development in the Konig cyanide reaction also was shortened by increasing incubation temperature to 40 degrees C. The interference in both azide color reactions was examined for volatile compounds. Cyanide interfered only in the case of ferric azide complex formation. Sulfide, sulfate, nitrite, and acetic acid interfered in both the color reactions. The established method gave a detection limit of 6 uM for cyanide and 0.5mM for azide, and it required only 1 hour to determine both anions.

Rapid Quantitation of Cyanide in Whole Blood by Automated Headspace Gas Chromatography

Calafat, A.M. and S.B. Stanfill, Centers for Disease Control and Prevention, Atlanta, GA. Journal of Chromatography B: Analytical Technology Biomedical Life Science, Vol 772 No 1, p 131-7, 25 May 2002

Researchers have developed a sensitive, rapid, simple, and fully automated method for measuring cyanide (CN) in whole blood. The assay is based on the use of gas chromatography (GC) with nitrogen-phosphorus detection and acetonitrile as an internal reference. Following the automated addition of phosphoric acid to the blood sample, the released hydrogen cyanide is analyzed using a fully automated headspace GC system. The assay, validated on human blood samples spiked with potassium cyanide and on clinical samples from fire victims who had smoke inhalation injury, can detect CN at a wide range of concentrations (30 to 6000 ug/L) in about 17 minutes (including incubation and GC run time, and <2 min for manual sample preparation).

Rapid Screening and Analysis of Hazardous Chemical Agents in Public Water Supplies and in-Coming Process Water

Johnson, Robert and Stephen MacDonald, Horizon Technology, Atkinson, NH.

The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23 October 2003, Univ. of Massachusetts at Amherst.

Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

With the recent concerns of hazardous chemical agents possibly being introduced into public water supplies and in-coming process water, the desired goal of one major drinking water facility was to process and analyze 100 samples in a 2-hour turnaround. A study to verify the feasibility of this goal employed an automated SPE disk extractor system, along with a novel drying procedure. The authors

review the analytical conditions used to extract and analyze test samples of acids, neutrals, phenols, hydrocarbons, OCPs, OPPs, and PCBs, identify the detection limits of each compound, and explain the sampling technique.

Real-Time Electrochemical Monitoring: Toward Green Analytical Chemistry

Wang, J.

Accounts of Chemical Research, Vol 35 No 9, p 811-816, 2002

This survey of recent advances in electrochemical sensing technology relevant to green analytical chemistry examines the potential advantages, limitations, and applications of these monitoring devices. New devices and protocols, with negligible waste generation or no hazardous substances and in situ real-time monitoring capability are particularly needed for addressing the challenges of green analytical chemistry. The coupling of modern electrochemical detection principles with recent advances in molecular recognition, microelectronics, and microfabrication has led to powerful, compact, and user-friendly analytical devices that in many instances allow the instrument to be taken to the sample instead of the traditional way of bringing the sample to the laboratory.

Remote Sensing: Engineering and Design

U.S. Army Corps of Engineers. EM 1110-2-2907, 217 pp, 2003

This report provides an introduction to remote sensing, discusses principles of remote sensing systems, and describes sensors and systems, data acquisition and archives, the processing of digital imagery, and remote sensing applications in USACE. The text contains examples of environmental work accomplished with remote sensing tools.

<http://www.usace.army.mil/inet/usace-docs/eng-manuals/em1110-2-2907/toc.htm>

Sample Support and Resistivity Imaging Interpretation

Bentley, L.R. and M. Gharibi, University of Calgary.

Geophysical Research Abstracts, Vol. 5, 01778, 2003

Three-D Electrical Resistivity Imaging (ERI) is a powerful technique that can be used to improve site characterization. In order to integrate ERI with other site characterization measurements such as soil and water chemistry, it is necessary to understand the sample support of various data. The authors studied a decommissioned sour gas processing plant that has experienced releases of glycol and amine. Ammonium and acetic acid are degradation products that cause elevated electrical conductivity (EC) in groundwater and soils. The site is underlain by glacial till that is fractured and has thin sand lenses. 3-D ERI inversion results, direct push tool EC and core EC from the same location are well correlated. However, ground water EC from piezometer installations correlate poorly with ERI EC. The researchers hypothesize that the ERI, direct push, and core EC are mainly measuring relatively immobile porewater EC in the fine grain matrix. Piezometer water is derived from mobile ground water that travels in preferred flow paths such as fractures and higher permeability sand lenses. Due to dewatering and other remediation efforts, the mobile ground water can have a different chemistry, concentration and EC than the immobile pore water. Consequently, the sample support is different for the ground-water samples, and the difference explains the poor correlation between ERI EC and

ground-water sample EC. In this particular case, the potential to monitor the chemical evolution of the source areas is available, but the ERI monitor cannot be used to examine the chemical evolution of mobile ground water.

Searching for Graves Using Geophysical Technology: Field Tests with Ground Penetrating Radar, Magnetometry, and Electrical Resistivity

Buck, S.C., U.S. Army Central Identification Lab., Hickam AFB, HI.

Journal of Forensic Science, Vol 48 No 1, p 5-11, Jan 2003

Field experiments were conducted using three types of geophysical equipment in a variety of situations. The goal of the study was to ascertain the relative utility of this technology for non-geophysical expert forensic professionals searching for buried human remains. The study concludes that the equipment should be used with caution after a critical evaluation of specific field conditions, and more refinement of technical methods and skills should be developed.

Segmented Flow Injection, UV Digestion, and Amperometric Detection for the Determination of Total Cyanide in Wastewater Treatment Plant Effluents

Weinberg, H.S. and S.J. Cook.

Analytical Chemistry, Vol 74 No 23, p 6055-6063, 2002

Segmented flow injection for sample transport and reaction, on-line acidic UV digestion for conversion of complexed cyanide to HCN, and amperometric detection achieved within 4 min of sample injection characterizes a recently developed procedure for the analysis of total cyanide (TCN) in various matrixes that has been demonstrated on chlorinated effluents discharged from municipal wastewater treatment plants. Through a systematic evaluation of the chemistry of the processes involved in this method and an understanding of the complexity of the wastewater matrix, an application was developed that shows consistent reproducibility in measuring TCN in a variety of effluents.

Selective Solid-Phase Extraction of Polycyclic Aromatic Hydrocarbons by the Chemically Modified Polymeric Adsorbents with Protoporphyrin IX

Oh, S.Y., K.P. Kim, H.B. Li, and K.J. Paeng (Yonsei Univ., Wonju, Korea); M.W. Jung (Korea Inst. of Science and Technology, Seoul); D.J. Baek (Hanseu Univ., Seosan, Korea).

Chromatographia, Vol 57 No 9-10, p 665-670, May 2003 [OSTI: DE20397066]

Chemically modified polymeric adsorbents (Amberlite XAD-2 and XAD-4 resins) were evaluated for selective solid-phase extraction of polycyclic aromatic hydrocarbons (PAHs). After the variables that influence the selectivity and recovery of the solid-phase extraction were optimized, the best result was obtained with XAD-4 resins modified with macrocyclic protoporphyrin IX. After the preconcentration and cleanup step, the PAHs were determined by gas chromatography with mass spectrometric detection. The method was used to determine PAHs in soil, with recovery in the range of 79.6 to 94.1%.

Semi-Quantitative "Spot-Test" of Cyanide

Favero, J.A. and M. Tubino, Inst. de Quimica, Univ. Estadual de Campinas, Campinas, SP, Brazil.

Analytical Sciences, Vol 19 No 8, p 1139-1143, Aug 2003

The authors report the development of a selective, sensitive, rapid, and simple analytical method for the determination of cyanide at low detection limits in surface and ground water, soil, and industrial waste samples. The method is based on a reaction proposed by Guilbault and Kramer, where free cyanide reacts with p-nitrobenzaldehyde to form an intermediate cyanohydrin, which reacts with o-dinitrobenzene to give a highly colored purple compound. The original procedure was modified for application in a small device containing a gas-permeable membrane. The cyanide is converted in the volatile hydrogen cyanide, which permeates through a PTFE membrane to reach colorimetric reagents. Printed color scales were built to obtain semi-quantitative results. The method allows rapid, accurate, selective, inexpensive, and easy determinations of free cyanide, even in complex samples. About 150 real samples were analyzed. Less than 10 ng of free cyanide per ml (10 ug/L) can be detected easily. For more concentrated solutions, the results had been compared to those obtained using differential pulse polarography. The standard addition method was used for more diluted solutions.

http://wwwsoc.nii.ac.jp/jsac/analsci/pdfs/a19_1139.pdf

Separation of Inorganic Arsenic Species in Groundwater Using Ion Exchange Method

Kim, M.J., Korea Inst. of Science and Technology, Seoul, Korea.

Bulletin of Environmental and Contaminant Toxicology, Vol 67 No 1, p 46-51, July 2001

Abstract not available.

Simple Method for Determination of Thiocyanate in Urine

Haque, M.R. and J.H. Bradbury, Australian National Univ., Canberra, ACT.

Clinical Chemistry, Vol 45 No 9, p 1459-1464, Sep 1999

A simple kit method is sought for determination of thiocyanate in urine, which could be used to monitor cyanide overload in cassava-consuming populations. The authors describe a method based on the quantitative oxidation of thiocyanate in acid permanganate at room temperature in a closed vial with liberation of HCN, which reacts with a picrate paper. For semiquantitative analysis in the field, the colored picrate paper is matched with a color chart prepared using known amounts of KSCN. In the laboratory, a more accurate result is obtained by elution of the colored complex in water and measurement of the absorbance at 510 nm. The picrate thiocyanate method gives no interference with urine samples containing protein at less than 7 g/L, 21 amino acids, histamine, glucose, NaCl, urea, blood, and linamarin. For 53 urine samples analyzed by an accurate column method and the thiocyanate picrate method, a regression line gave very good agreement. Quantitative recoveries of thiocyanate added to urine samples were obtained with the picrate method.

<http://www.clinchem.org/cgi/content/full/45/9/1459>

A Simple Phase Equilibrium Model for Predicting the Historical Presence of NAPL: a Case Study

Moss, John D. and Daniel D. Titus, HRP Associates, Inc., Plainville, CT.

The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23 October 2003, Univ. of Massachusetts at Amherst.

Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

Using a phase equilibrium partitioning equation, as presented in the Connecticut DEP Remediation Standard Regulations, a theoretical window of potential contaminant concentration ranges in soil (i.e., C_{nap}), as a historical indication of free-phase product (i.e., NAPL) was developed. A sensitivity analysis indicated that C_{nap} is most sensitive to the soil organic carbon/water partition coefficient (K_{oc}), which is a contaminant variable, and the organic carbon fraction (f_{oc}), which is a soil variable. By incorporating possible ranges of K_{oc} and f_{oc} , the model produced a series of curves for predicting the presence or absence of NAPL. The calculated theoretical boundary curves of the model, based on maximum and minimum K_{oc} values, indicate a K_{oc} curve above which NAPL was present, an area between the maximum and minimum K_{oc} curves where NAPL may have been present, and a minimum K_{oc} curve below which NAPL was absent. Site-specific data for a tetrachloroethene (PCE) and high molecular weight cutting oil solution release site were read into the model. The site had been cleaned up, but multiple subsequent investigations had been conducted to determine if residual PCE contamination in excess of 10 mg/kg was due to episodic dissolved phase releases from a septic system or to residual NAPL associated with the release. The model was used to apportion NAPL-related versus dissolved phase contamination.

A Simple, Rapid and Sensitive Semimicro Method for the Measurement of Cyanide in Blood
Vesey, C.J. (St. Bartholomew's Hospital, London, UK); H. McAllister; R.M. Langford.
Annals of Clinical Biochemistry, Vol 36 Pt 6, p 755-758, Nov 1999

A new rapid cyanide measurement procedure can provide a result in 10 min. A sample of blood (100 μ L) is mixed with H_3PO_4 , containing a surfactant, and the HCN is trapped in an alkaline mixture of 1,2-dinitrobenzene and 4-nitrobenzaldehyde in 2-methoxyethanol. The catalytic action of cyanide, which produces purple 2-nitrophenylhydroxylamine, is stopped with acetone after 6 minutes. The absorbance measured at 560 nm shows a linear relationship with the cyanide concentration, but the slope varies with the ambient temperature. Since KCN added to both 50 mmol/L NaOH and blood gives similar assay results, any inaccuracy arising from changes in temperature can be avoided by running standards at the same time as the blood sample.

Simultaneous Determination of Cyanide and Carbonyls in Cyanogenic Plants by Gas Chromatography-Electron Capture/Photoionization Detection.
Curtis, A.J. (Univ. of Colorado, Boulder); C.C. Grayless; R. Fall.
Analyst, Vol 127 No 11, p 1446-1449, Nov 2002

A portable gas chromatograph housing two detectors using a single carrier gas is employed to measure carbonyl compounds (photoionization detector) and cyanide as its cyanogen chloride derivative (electron capture detector) from the headspace of a vegetation sample. This method affords in-field, rapid screening of plants to determine cyanogenicity. Good agreement was seen between this method for cyanide determination and two traditional field cyanide test kits. Detection of both the cyanide and the carbonyl compound(s) allows for confirmation of the presence of cyanogenic glycosides and eliminates the problem of false positives often seen in traditional cyanide test kits.

Simultaneous Determination of Cyanide and Thiocyanate in Blood by Ion Chromatography with Fluorescence and Ultraviolet Detection

Chinaka, S. (Forensic Science Lab., Ishikawa Pref. Police Headquarters, Hirosaka, Kanazawa, Japan); N. Takayama; Y. Michigami; K. Ueda.

Journal of Chromatography B: Biomedical Science & Applications, Vol 713 No 2, p 353-359, 25 Aug 1998

An ion chromatographic method for the simultaneous determination of cyanide and thiocyanate in blood has been developed. After extraction by adding water and methanol to blood, cyanide was derivatized with 2,3-naphthalenedialdehyde and taurine to give a fluorescent product of 1-cyanobenz[f]isoindole. This compound was detected with high sensitivity by fluorometry, and the underivatized thiocyanate was detected by ultraviolet absorption. The detection limits were 3.8 pmol/ml for cyanide and 86 pmol/ml for thiocyanate, and the recoveries from blood were ~83 and 100%, respectively. The method has been applied to the analysis of cyanide and thiocyanate in blood from smokers, non-smokers, and fire victims.

Soil Microbial Parameters and Luminescent Bacteria Assays as Indicators for In Situ Bioremediation of TNT-Contaminated Soils

Frische, T. (Univ. of Bremen, Bremen, Germany); H. Hoper.

Chemosphere, Vol 50 No 3, p 415-427, 2003

During a research project on the in situ bioremediation of topsoil contaminated with 2,4,6-trinitrotoluene (TNT), the authors examined the significance of two bioassays for monitoring purposes. The results of soil microbial assays and luminescent bacteria assays were compared with chemical monitoring data to evaluate changes within different experimental fields during a 17-month remediation period. The luminescent bacteria assays showed a significant reduction of the water-soluble soil toxicants in the treated fields. This bioassay proved to be a sensitive screening indicator of toxicity and could aid the ecotoxicological interpretation of chemical monitoring data. Microbial biomass, the metabolic quotient, and the ratio of microbial to organic carbon showed a highly significant correlation with total concentrations of TNT in the soil, though in contrast to luminescent bacteria assays, this approach did not reveal any recovery of the soil at the end of the remediation period. Due to the persistent adverse effects of chronic TNT contamination on the site-specific microbial community and the local carbon cycle in the soil, useful and complementary data can be gained by using both bioassay approaches for monitoring short-term and long-term effects of soil contamination and the efficiency of remediation.

Solid Phase Microextraction: The Alternative to Purge and Trap

Rossi, Michael, Seth Pitkin, and Kim Watson, Stone Environmental Inc., Montpelier, VT.

The 19th Annual International Conference on Contaminated Soils, Sediments and Water, 20-23 October 2003, Univ. of Massachusetts at Amherst.

Northeast Regional Environmental Health Center, Univ. of Massachusetts, Amherst. CD-ROM, 2003

Solid Phase Microextraction (SPME) is an alternative to the more traditional purge and trap sample preparation technique for volatile organic compound (VOC) analyses. SPME offers a faster, more field friendly, and less expensive technique than the purge and trap method. SPME offers precision and

accuracy equal to the purge and trap technique. SPME consists of a simple and relatively inexpensive phase-coated fiber on which the analytes partition over a specified period of exposure. The fiber then is placed into the GC injection port for thermal desorption and transfer of the analytes onto the GC column. The technique can be applied to water, soil, and air analyses. The relatively inexpensive SPME instrumentation and an extraction time typically under ten minutes make the cost and speed of SPME a fraction of those of purge and trap. Two confirmation studies involved sending duplicate samples to a fixed lab for gas chromatography/mass spectrometry (GC/MS, Method 8260) analyses and comparing the results to the field lab's SMPE/GC results. The paired analytical results for the water and soil samples compared extremely well; the overall average relative percent differences (RPD) for the water and soil analyses were 27 and 25, respectively. A performance-based evaluation of the SPME technique indicated the SPME method can be used to produce fully defensible data, as defined using the EPA's SW-846 8000 guidelines and acceptance criteria.

Spatial and Temporal Observations of Adsorption and Remobilization of Heavy Metal Ions in a Sandy Aquifer Matrix Using Magnetic Resonance Imaging

Nestle, N. (Technische Univ. Munchen, Munchen, Germany); A. Wunderlich; R. Niessner; T. Baumann.

Environmental Science & Technology, Vol 37 No 17, p 3972-3977, 1 Sep 2003

The authors present the results of Magnetic Resonance Imaging (MRI) studies in which submilligram quantities of heavy metal ions were either fed conventionally through the column or locally injected into saturated sand packings. The subsequent transport and mobilization was monitored at a high spatial and temporal resolution. The results of local injection show that column tests under MRI control can be used as a model system for remediation techniques.

Speciation and Characterization of Arsenic in Ketz River Mine Tailings Using X-Ray Absorption Spectroscopy

Paktunc, D. (Canada Centre for Mineral and Energy Technology (CANMET), Ottawa, Ontario, Canada); A. Foster; G. Laflamme.

Environmental Science & Technology, Vol 37 No 10, p 2067-2074, 15 May 2003

The XANES spectra indicate that arsenic occurs as As(V) in tailings, but air-drying prior to analysis may have oxidized lower-valent As. The EXAFS spectra indicate As-Fe distances of 3.35-3.36 Å for the exposed tailings and 3.33-3.35 Å for the saturated tailings with coordination numbers of 0.96-1.11 and 0.46-0.64, respectively. The As-Ca interatomic distances ranging from 4.15 to 4.18 Å and the coordination numbers of 4.12-4.58 confirm the presence of calcium-iron arsenates in the tailings. These results suggest that ferric arsenates and inner-sphere corner sharing or bidentate-binuclear attachment of arsenate tetrahedra onto iron hydroxide octahedra are the dominant form of As in the tailings. EXAFS spectra indicate that the exposed tailings are richer in arsenate minerals whereas the saturated tailings are dominated by the iron oxyhydroxides.

A Spot Test for Aqueous Phosphate by Color Band Formation

Kiso, Y. (Toyohashi Univ. of Technology, Tempaku-cho, Japan); K. Kuzawa; Y. Saito; T. Yamada; M. Nagai; Y.J. Jung; K.S. Min.

Analytical and Bioanalytical Chemistry, Vol 374 No 7-8, p 1212-1217, Dec 2003

Phosphate is generally analyzed by color intensity of phosphoantimonymolybdenum blue (PAMB), especially by a spot test based on spectrophotometric or visual determination. Visual determination is one of the simplest and most inexpensive methods, though also one of low precision. The authors have developed an alternative phosphate spot test, where phosphate concentration is measured by the color band length of PAMB formed in a detection tube similar to a gas detection tube. The color band is formed by the entrapment of the hydrophobic ion pair of PAMB and quaternary ammonium ions in the column; we demonstrated that this color band length correlates quantitatively with the phosphate concentration. Suspended solid (SS) and organic pollutants (COD, TOC) did not interfere with the wastewater analysis. Rapid sample processing with no special instruments required makes this newly developed method suitable for the on-site analysis of wastewater.

Stable Isotope Ratios as a Tool to Assess Biodegradation of Methyl tert-Butyl Ether (MTBE) and tert-Butyl Alcohol (TBA)

Hunkeler, D.; B.J. Butler; R. Aravena; and J.F. Barker, Univ. of Waterloo, Waterloo, Ontario, Canada. Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution (Proceedings of the Groundwater Quality 2001 Conference held at Sheffield, UK, June 2001). IAHS Publ. no. 275, p 283-286, 2002

Compound-specific isotope analysis was investigated for assessing biodegradation of MTBE. The effect of aerobic biodegradation on carbon isotope ratios of MTBE was evaluated using microcosms with MTBE as the only substrate and cometabolic microcosms with 3-methylpentane as the primary substrate. The study results suggest that carbon isotope analysis is a potential tool for tracing in situ biodegradation of MTBE and TBA, and thus to aid better understanding of the fate of these contaminants in the environment.

Static and Push-Pull Methods Using Radon-222 to Characterize Dense Nonaqueous Phase Liquid Saturations

Davis, B.M.; J.D. Istok; L. Semprini, Oregon State Univ., Corvallis.

Ground Water, Vol 41 No 4, p 470-481, July-Aug 2003

Naturally occurring radon in ground water can be used as a partitioning tracer to characterize dense nonaqueous phase liquid (DNAPL) saturations in situ. The static method involves comparing radon concentrations in water samples from DNAPL-contaminated and uncontaminated portions of an aquifer, while the push-pull method involves the injection (push) and extraction (pull) of a radon-free test solution from a single well. During the pull phase, DNAPL retards radon concentration, with retardation manifested in greater dispersion of radon concentrations relative to a conservative tracer. This paper describes a laboratory investigation of these methods using a physical aquifer model and TCE as a model contaminant. The results show that radon is sensitive to changes in DNAPL saturation in space and time; however, the methods are sensitive to DNAPL saturation heterogeneity, test location, sample size, and test design.

Subnanomolar Cyanide Detection at Polyphenol Oxidase/Clay Biosensors

Shan, D.; C. Mousty; S. Cosnier.

Analytical Chemistry, Vol 76 No 1, p 178-183, 2004

The authors describe a novel, inexpensive, and simple amperometric biosensor based on immobilization of polyphenol oxidase (PPO) into Zn-Al-layered double hydroxides, also called anionic clays, applied for determination of cyanide. The detection of cyanide was performed via its inhibiting action on the PPO electrode. Measurement was carried out with 3,4-dihydroxyphenylacetic acid as enzyme substrate, the enzymatically generated quinoid products being electroreduced at -0.2 V. An extremely sensitive detection limit (0.1 nM) was obtained for cyanide.

Technology Overview: an Introduction to Characterizing Sites Contaminated with Dnaps

The Interstate Technology & Regulatory Council Dense Nonaqueous Phase Liquids Team.

Interstate Technology & Regulatory Council (ITRC), 73 pp, Sep 2003

This document discusses scientific approaches and strategies used to characterize sites that are known or suspected to be contaminated with dense, nonaqueous-phase liquids (DNAPLs). It introduces the fundamental concepts of site characterization strategies as they relate to DNAPLs and is meant for the reader who is familiar with the principles of contaminant hydrogeology and conventional characterization approaches but may not be well versed in the issues surrounding the characterization of sites contaminated with DNAPLs. This document is intended to be a primer for characterizing sites contaminated with DNAPLs; it does not attempt to fully discuss and describe the physics and complex behavior of DNAPL flow and fate in the subsurface. That information is readily available in the peer-reviewed scientific literature; however, references to literature describing the multiphase fluid flow concepts required to understand DNAPL physics are included in this document.

Available at <http://www.itrcweb.org/DNAPLS-4.pdf>

Time-Lapse Geophysics for Aquifer Characterization and Remediation Monitoring

Lane, John W., U.S. Geological Survey, Storrs, CT.

Eos. Trans. AGU, 84(46), Fall Meet. Suppl., Abstract H21F-01, 2003

The U.S. Geological Survey, in cooperation with USEPA, DOD, and university researchers, has applied time-lapse geophysics for site characterization and remediation monitoring at several sites: (1) cross-borehole and surface-to-borehole radar methods to monitor vegetable-oil emulsion injections for biostimulation at a Navy site in Fridley, MN; (2) borehole and cross-borehole radar methods to monitor steam injections for remediation of VOCs at the former Loring Air Force Base, ME; (3) electrical resistivity tomography to monitor saline tracer tests at the Massachusetts Military Reservation, MA; (4) borehole and cross-borehole flowmeter and a discrete zone packer system to characterize bedrock aquifer hydraulics and water quality at the University of Connecticut landfill, Storrs, CT; and (5) cross-borehole radar methods to monitor a saline tracer in fractured bedrock at the USGS Mirror Lake Site, NH. These studies provide increasingly quantitative information about the subsurface, which is critical for developing models of aquifer structure, dynamics, and processes, and also identify the spatial and temporal distributions of tracers, contamination, and fluids injected to enhance degradation of contaminants.

Tracing Landfill Gas Migration Using Chlorofluorocarbons
Archbold, M., T. Elliot, K. Redeker, and G. Boshoff, Queens Univ., Belfast.
Geophysical Research Abstracts, Vol. 5, 12235, 2003

Typical landfill gas (LFG) compositions include a wide range of trace-level volatile organic compounds (VOCs). The most mobile VOCs are chlorofluorocarbons (CFCs), and their presence around landfills may reflect the initial flushing out of VOCs during the early aerobic stage when landfills are most active reaching high temperatures, driving off VOCs, and injecting LFG into the surrounding environment. CFCs are aerobically stable and therefore could prove a useful means of characterizing the environmental impact of landfill gas in the unsaturated zone around landfills. As a possible pathfinder or environmental tracer of LFG impacts in the environment, any subsequent changes in the CFCs concentrations after injection potentially reflect natural attenuation (NA) processes, which can affect other VOCs. Tracing the CFCs around a landfill could provide an analog indicator/proxy for other VOCs transport and fate. To assess the feasibility of using chlorofluorocarbons (CFC-11, CFC-12, CFC-113) as proxy tracers, it is imperative to characterize the effects of possible NA processes on both CFC abundances and their overall systematics. In this research, anaerobic biodegradation microcosm studies that mimic the unsaturated zone of a LFG plume are conducted using methanogenic soil samples. Results are discussed in terms of the potential effects on CFCs signatures due to anaerobic biodegradation in the unsaturated zone, and ways of characterizing NA processes by identifying the effects of diffusion on transport processes and degradation products of CFCs are explored. The discussion also includes how stable carbon isotopic signatures can be used to enhance assessments of biodegradation of CFCs in the unsaturated zone around landfills.

Use of Biosensors to Screen Urine Samples for Potentially Toxic Chemicals
Horswell, J. and S. Dickson, ESR, Kenepuru Science Centre, Porirua, New Zealand.
Journal of Analytical Toxicology, Vol 27 No 6, p 372-376, Sep 2003

The authors describe the use of a bacterial biosensor for detecting the presence of commonly encountered potentially toxic chemicals in urine. The biosensor responds to any chemical that causes metabolic stress to the bacterial cell and the response is in direct proportion to the concentration of the stressor. This allows a measure of the concentration of a toxicant in urine, without knowing exactly what the toxic compound(s) may be. A preliminary investigation has shown that this biosensor can indicate the presence, in urine, of herbicides such as glyphosate, 2,4-dichlorophenoxyacetic acid, and 2,4,5-trichlorophenoxyacetic acid; the biocide pentachlorophenol; or inorganic poisons such as arsenic, mercury, and cyanide. The biosensor also is sensitive to a concentration range of these toxicants likely to be found in samples submitted for toxicological analysis.

The Use of Electrokinetics as a Tool to Investigate Bioavailability
Jackman, S.A.; C.J. Knowles (UK and Natural Environment Research Council Centre for Ecology and Hydrology, Mansfield Road, Oxford); G. Maini & A.K. Sharman (Viridian-EHC Ltd, Whitstable, Kent, UK); J.G. Sunderland (C-Tech Innovation Ltd, Chester, UK).
Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution (Proceedings of the Groundwater Quality 2001 Conference held at Sheffield, UK, June 2001). IAHS Publ. no. 275, p 341-346, 2002

Studies of electrokinetics using a radiolabeled model organic contaminant, 2,4-dichlorophenoxyacetic acid, demonstrated movement from a contaminated region into a region inoculated with degradative bacteria. Movement was correlated with biodegradation in situ and recovery of $^{14}\text{CO}_2$. The paper discusses the potential use of these combined techniques to understand the bioavailability of organic contaminants.

Using Advanced Tensiometers to Monitor Temporal Variations in Pore Pressure
Nichols, R.L. (Westinghouse Savannah River Company, Aiken, SC); M.H. Young (Desert Research Institute, Las Vegas, NV); K.L. Dixon, J. Rossabi, W.K. Hyde (Westinghouse Savannah River Company, Aiken, SC); H. Holmes-Burns (Bechtel Savannah River, Aiken, SC).
Eos Trans. AGU, Vol 83 No 47, Fall Meet. Suppl., Abstract H71B-0814, 2002

The Savannah River Site has installed a comprehensive vadose zone monitoring system (VZMS) at its low level radioactive waste disposal facility to collect the necessary information to calculate contaminant flux. The VZMS incorporates water content reflectometers, suction lysimeters, advanced tensiometers (ATs), water flux meters, access ports for neutron probes, and a tipping bucket rain gauge. From 1999 to 2001, 41 ATs were installed at depths ranging from 2 to 60 feet and have been operated continuously. An AT consists of a porous cup installed at a prescribed depth with casing back to the surface and a pressure transducer that is lowered into the casing and connects with the porous cup. The pressure transducer transmits its signal to a datalogger, where the data is stored for future retrieval via a cellular phone communications package. Results from the 2 year operating period show that the AT calibrations are stable and the ATs are capable of extended monitoring of pore pressures. The ATs had sufficient resolution to detect the naturally occurring fluctuations in pore pressure that resulted from infiltration events at the site.

Using Electrical Resistivity Tomography (ERT) for Characterizing Transport Processes in Heterogeneous Aquifers
Vanderborght, J., A. Kemna, and H. Vereecken, Inst. Agrosphere ICG-IV, Forschungszentrum Julich, Germany.
Geophysical Research Abstracts, Vol. 5, 04907, 2003

Besides its mean displacement, the spreading of a pollutant plume and dilution of the local concentrations due to local mixing processes in the subsurface are key parameters for the prediction of the fate of contaminants. Both spreading and dilution are strongly determined by the heterogeneous structure of the subsurface. In classical tracer experiments, the spreading and dilution of an injected tracer solution is derived from a number of local concentration measurements. A characterization of the spatial structure of concentration fluctuations within the plume is mostly not possible due to a limited spatial resolution. With Electrical Resistivity Tomography (ERT), spatial distributions of salt tracer concentrations or concentration maps can be obtained. The authors discuss the potential of these ERT-derived concentration images to characterize the spatial structure of the subsurface and the mixing process. Structure and mixing parameters are derived from the concentration maps using first-order approximations of stochastic flow and transport equations in heterogeneous hydraulic conductivity fields. To illustrate the potential and limitations of the procedure, flow and transport are simulated in a synthetic heterogeneous conductivity field. Concentration maps were converted to electrical

conductivity distributions. Using typical ERT measurement protocols, electric potential data were calculated for a set of current injection dipoles in the electrical conductivity distributions. Noise was added to the individual data sets, which subsequently acted as input to an ERT inversion routine. The inverted images as well as the inferred aquifer characteristics from these images were then compared to the input images and parameters.

Using Soils as Gas-Chromatographs: Diffusive In Situ Gas Tracer Tests for the Investigation of the Unsaturated Zone

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New in situ gas tracer methods were developed for parameter investigation in the unsaturated zone at contaminated sites. The tracer methods rely on the diffusion of gaseous tracers from a soil gas probe into the surrounding porous medium. Diffusive gas tracer tests were first used to quantify the saturation of nonaqueous phase liquids (NAPLs). Conservative and partitioning chlorofluorocarbons as gaseous tracers were injected into the vadose zone to form a point source at the injection point. The quantitative determination of the NAPL saturation is based on a comparison of the concentration decline of the tracers at the probe tip. Experimental investigations of the diffusion of the tracer gases in homogeneous sandy soils with heterogeneous NAPL distribution were demonstrating that the tests give results on mean NAPL saturation on a local scale of a few decimeters around the probe tip. Applications of this test are source delineation and repeated NAPL quantification in situ during remediation at point locations. A similar diffusive test was described to quantify effective and sorption-affected diffusion coefficients of volatile organic pollutants in situ. These diffusion coefficients are required for the prediction of vapor-phase pollutant migration at contaminated sites. Both new tests are performed with similar equipment as used for traditional soil gas monitoring. They are rapid, cheap and thus of potential value for risk assessment at contaminated sites.

Viability of Interceptor Trenches for Monitoring Groundwater Quality near Landfills

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Computer models were used to quantify the detection capability of four alternative ground-water monitoring systems in a shallow aquifer near a 50 x 75-meter landfill oriented oblique to ground-water flow. The monitoring systems included a network of five wells and gravel interceptor trenches. The five-well network detected 81% of contaminant plumes originating within the landfill's footprint before they reached a buffer zone boundary located 50 meters from the landfill's downgradient corner. By comparison, the trenches detected from 77 to 88% of the contaminant plumes, with the wider trenches yielding slightly higher detection efficiencies. Although the well and trench monitoring systems registered similar detection capability, estimated costs for installing the trench systems were more than 10 times those of constructing the wells, which suggests that, even for shallow aquifers, gravel interceptor trenches are not a cost-effective method for detecting leaks from landfills.