

## Measurement & Monitoring: 30th Quarterly Literature Update & Grant Survey

The references selected for this update have been added to the searchable literature database developed for the Measurement and Monitoring Technologies for the 21st Century (21M<sup>2</sup>) Web site: [www.clu-in.org/programs/21m2/litsearch.cfm](http://www.clu-in.org/programs/21m2/litsearch.cfm)

Accurate Mass Screening and Identification of Emerging Contaminants in Environmental Samples by Liquid Chromatography-Hybrid Linear Ion Trap Orbitrap Mass Spectrometry  
Hogenboom, A.C., J.A. van Leerdam, and P. de Voogt.

Journal of Chromatography: A, Vol 1216 No 3, p 510-519, 16 Jan 2009

Screening source waters for the presence of (emerging) contaminants is an essential step in the control of the water cycle from source to tap water. The authors report their experiences with the hybrid linear ion trap (LTQ) FT Orbitrap mass spectrometer for analysis of chemicals in water. A two-pronged strategy in mass spectrometric research was used for exploring effluent, surface-, ground- and drinking-water samples for target compounds and their product ions, and for full-scan screening of water samples in search of unknown or unexpected masses, followed by MS(n) experiments to elucidate the structure of the unknowns. Applications and results are presented for targeted search and analysis of pharmaceuticals, benzotriazoles, and illicit drugs, and for identification of unknown compounds in a groundwater sample and in a polar extract of a landfill soil sample (a toxicity identification evaluation bioassay sample). The applications of accurate mass screening and identification described in this article show that the LC-LTQ FT Orbitrap MS can meet the challenges posed by emerging polar contaminants.

Advances in Integrated and Continuous Measurements for Particle Mass and Chemical Composition

Chow, J.C., P. Doraiswamy, J.G. Watson, L.W. Chen, S.S. Ho, and D.A. Sodeman, Desert Research Inst., Reno, NV.

Journal of the Air and Waste Management Association, Vol 58 No 2, p 141-163, Feb 2008

Efforts are needed to address positive and negative artifacts for organic carbon (OC) and to develop carbon standards to better separate OC versus elemental carbon (EC) under different temperature settings and analysis atmospheres. Advances in thermal desorption followed by gas chromatography/mass spectrometry (GC/MS) provide organic speciation of approximately 130 nonpolar compounds (e.g., n-alkanes, alkenes, hopanes, steranes, and PAHs) using small portions of filters from existing integrated samples. Speciation of water-soluble organic carbon (WSOC) using ion chromatography (IC)-based instruments can replace labor-intensive solvent extraction for many compounds used as source markers. Thermal gas-based continuous nitrate and sulfate measurements underestimate filter ions by 10 to 50% and require calibration against on-site filter-based measurements. IC-based instruments provide multiple ions and report comparable (+/-10%) results to filter-based measurements. Maintaining a greater than 80% data capture rate in continuous instruments is labor intensive and requires experienced operators. Several instruments quantify black carbon (BC) by optical or photoacoustic methods, or elemental carbon (EC) by thermal methods. A few instruments provide real-time OC, EC, and organic speciation. BC and EC concentrations from continuous instruments are highly correlated but the concentrations differ by a factor of two or more. Site- and season-specific mass absorption efficiencies are needed to convert light absorption to BC. Particle mass spectrometers, although semi-quantitative, provide much information on particle size and composition related to

formation, growth, and characteristics over short averaging times. Efforts are made to quantify mass by collocating with other particle sizing instruments. Common parameters should be identified and consistent approaches are needed to establish comparability among measurements.

#### Amperometric Determination of Cyanides at the Low ppb Level by Automated Preconcentration Based on Gas Diffusion Coupled to Sequential Injection Analysis

Zacharis, C.K., P.D. Tzanavaras, A.N. Voulgaropoulos, and B. Karlberg, Aristotle Univ of Thessaloniki, Greece.

Talanta, Vol 77 No 5, p 1620-1626, 15 Mar 2009

A simple, sensitive assay for determining free cyanides is based on automated gas diffusion of the analyte using sequential injection analysis (SIA) coupled to amperometric detection on a silver working electrode. Researchers studied the effects of varying several parameters affecting the analytical procedure (including the flow rates of the donor and acceptor streams, the concentrations of the reagents and the sample volumes) and assessed the validity and quality of the method by examining its linearity, limits of detection and quantitation, precision, and selectivity to potentially interfering substances. The method's sensitivity can be enhanced by applying a simple preconcentration step, after which limits of detection were found to be 0.05 to 0.12 ug/L. Application of the assay to the analysis of tap, mineral, and table water samples spiked at concentrations ranging from 1 to 10 ug/L cyanide yielded recoveries ranging from 88 to 112%.

#### Analytical Method for Perchlorate in Water by Liquid Chromatography-Mass Spectrometry Using an Ion Exchange Column

Kamoshita, M., K. Kosaka, M. Asami, and Y. Matsuoka.

Analytical Science, Vol 25 No 3, p 453-456, Mar 2009

A practical analytical method was developed for the routine analysis of perchlorate in environmental and drinking-water samples by liquid chromatography/electrospray ionization-mass spectrometry (LC/ESI-MS) using an anion exchange column. By using (18)O-enriched perchlorate as an internal standard, the limits of quantification of perchlorate determined by tenfold of the signal-to-noise ratio and tenfold of the standard deviation were 0.1 and 0.03 ug/L, respectively. The perchlorate concentrations in raw and treated water samples from seven water purification plants were determined by LC/ESI-MS. Perchlorate was detected in 12 of 13 samples at concentrations ranging from 0.1 to 36.1 ug/L.

#### Analytical Methods for the Determination of Emerging Organic Contaminants in the Atmosphere

Xie, Z. and R. Ebinghaus, GKSS Research Centre Geesthacht, Inst. for Coastal Research, Geesthacht, Germany.

Analytica Chimica Acta, Vol 610 No 2, p 156-178, 10 Mar 2008

This paper covers developments in the determination in ambient air of emerging organic contaminants, such as polyfluorinated alkyl substances, brominated flame retardants, synthesis musk fragrances, and alkylphenols. Literature from 2002 to 2007 was summarized to identify

new developments in sampling methods, extraction, separation/fractionation, and technology applications for sampling and determination of emerging contaminants.

#### Anthrax Sampling and Decontamination: Technology Trade-Offs

Price, Phillip N., Kristina Hamachi, Jennifer McWilliams, and Michael D. Sohn

LBNL-1519E, 68 pp, Sep 2008

This project addressed the following questions concerning response to a future anthrax release (or suspected release) in a building: 1. Based on past experience, what rules of thumb can be determined concerning: (a) the amount of sampling that may be needed to determine the extent of contamination within a given building; (b) what portions of a building should be sampled; (c) the cost per square foot to decontaminate a given type of building using a given method; (d) the time required to prepare for, and perform, decontamination; (e) the effectiveness of a given decontamination method in a given type of building? 2. Based on past experience, what resources will be spent on evaluating the extent of contamination, performing decontamination, and assessing the effectiveness of the decontamination in a building of a given type and size? 3. What are the trade-offs between cost, time, and effectiveness for the various sampling plans, sampling methods, and decontamination methods that have been used in the past? <http://www.osti.gov/bridge/purl.cover.jsp?purl=/948503-9AToks/>

#### Applicability of Grid-Net Detection System for Landfill Leachate and Diesel Fuel Release in the Subsurface

Oh, M., M.W. Seo, S. Lee, and J. Park.

Journal of Contaminant Hydrology, Vol 96 Nos 1-4, p 69-82, 2008

A grid-net system for estimating electrical conductivity changes was evaluated as a potential detection system for the leakage of diesel fuel and landfill leachate. Electrical conductivity changes varied with the type of contaminant. Electrical conductivity in homogeneous mixtures of soil and landfill leachate increased linearly with the ionic concentration of pore fluid, which became more significant at higher volumetric water contents; however, electrical conductivity in the soil/diesel fuel mixture decreased with diesel fuel content and was more significant at lower water contents. Electrode spacing to enhance electrode sensitivity should be determined by considering the type of contaminant, particularly when 2-electrode sensors are to be used. Electrode sensitivity for landfill leachate remained constant regardless of the electrode spacing, while sensitivity for diesel fuel increased significantly at closer electrode spacing. This effect possibly occurs due to the decreased predominance of the insulating barrier effect of the diesel fuel in a nonaqueous phase at large electrode spacing; electrical current can form round-about paths over a volume with relatively small diesel fuel content. The test results showed that the grid-net detection system can be used to monitor the leakage from landfill and underground storage tank sites.

#### Application of a Luminescence-based Biosensor for Assessing Naphthalene Biodegradation in Soils from a Manufactured Gas Plant

Paton, G.I., B.J. Reid, and K.T. Semple

Environmental Pollution, Vol 157 No 5, p 1643-1648, May 2009

Microbial biosensors have failed in many environmental applications in part because most of these sensors perform in an aqueous phase and a buffered medium, in contrast to the nature of genuine environmental systems. The authors assessed a range of non-exhaustive extraction techniques (NEETs) for compatibility with a naphthalene-responsive biosensor and correlation with naphthalene biodegradation. The NEETs removed a portion of the total soil naphthalene in the order of methanol > 2-hydroxypropyl-beta-cyclodextrin (HPCD) > betaCD > water. In a biodegradation experiment on historically contaminated soils, HPCD extraction was coupled with the biosensor to assess the fraction of the naphthalene capable of undergoing microbial degradation in soil. Exposure of microbial biosensors to cyclodextrin solutions allows the assessment of the degradable fraction of contaminants in soil.

#### Application of High Altitude and Ground-based Spectroradiometry in the Monitoring of Hazardous Waste Derived from Sokolov Open-pit Mine

Chevrel, S., V, Kopacková, A. Bourguignon, P. Rojík, and V. Metelka

10th International Mine Water Association Congress, Technical University of Ostrava, Karlsbad, Czech Republic 2008. International Mine Water Association, Paper 223, 4 pp, 2008

The monitoring of mine sites (abandoned or still-active) is one of the most challenging environmental problems faced worldwide by government and the mining industry. Mineral spectroradiometry, both from airborne or spaceborne sensors and ground measurements, represents an alternative to conventional methods and offers an efficient way to characterize mines and assess the potential for AMD (acid mine drainage). This paper describes how high-altitude spectroradiometry (ASTER, aka Advanced Spaceborne Thermal Emission and Reflection Radiometer satellite data) were applied together with ground-based spectroradiometry (ASD Filedspec spectroradiometer) to define the capability for identifying the locations of the most significant sources of AMD discharge at the Sokolov open-pit mine site.

[http://www.imwa.info/docs/imwa\\_2008/IMWA2008\\_223\\_Chevrel.pdf](http://www.imwa.info/docs/imwa_2008/IMWA2008_223_Chevrel.pdf)

#### Applications of Carboxylesterase Activity in Environmental Monitoring and Toxicity Identification Evaluations (TIEs)

Wheelock, C.E., B.M. Phillips, B.S. Anderson, J.L. Miller, M.J. Miller, and B.D. Hammock. Reviews of Environmental Contamination and Toxicology, Vol 195, p 117-178, 2008

Carboxylesterases are important enzymes that show promise for employment in environmental monitoring with a variety of organisms and testing scenarios.

Acetylcholinesterase has the distinct advantage of a clear biological function, whereas the endogenous role of carboxylesterases is still unclear; however, a combination of activity measurements for the two enzyme systems will provide a much more detailed picture of organism health and insecticide exposure. The main outstanding issues are the choice of substrate for activity assays and which tissues/organisms are most appropriate for monitoring studies. The most logical choice of substrate is PNPA (p-nitrophenyl acetate) as it is commercially available, requires inexpensive optics for assay measurements, and has been used extensively in the literature. None of these beneficial properties indicates, however, that the substrate is an appropriate surrogate for a specific compound, e.g., pyrethroid-hydrolyzing activity, and it most likely will be necessary to use more specific surrogate substrates in assays that require information on the ability to detoxify/hydrolyze specific environmental

contaminants. The use of carboxylesterase activity in TIE protocols appears to have excellent promise, but there are technical issues that should be addressed to increase the utility of the method. The main concerns include the large amount of nonspecific protein added to the testing system, which can lead to undesirable side effects, including nonspecific reductions in observed toxicity, decrease in dissolved oxygen content, and organism growth. The ideal solution would be to have a commercial recombinant carboxylesterase that possessed elevated pyrethroid-hydrolysis activity and is readily available, homogeneous, and inexpensive. The goal is the development of a standardized screen of enzymes with esterase activity to (1) identify environmental contaminants, (2) estimate the potential toxic effects of new compounds on a range of organisms, and (3) monitor organism exposure to agrochemicals (and potentially other contaminants). This approach would provide a multibiomarker integrative assessment of esterase-inhibiting potential of a compound or mixture.

Applied Innovative Technologies for Characterization of Nitrocellulose and Nitroglycerin Contaminated Buildings and Soils: ESTCP Cost and Performance Report  
Environmental Security Technology Certification Program (ESTCP), Project ER-0130, 297 pp, July 2008

The objectives for this demonstration were to evaluate and document the performance of three candidate experimental field analytical methods for detecting and quantifying nitrocellulose (NC) and nitroglycerine (NG) associated with structural concrete pads, underlying soils, and structural building materials, such as framing timbers. The technologies evaluated in the field demonstration were gas chromatography/thermionic ionization detection (GC/TID), DROPEX(Plus)/EXPRAY(tm) colorimetric indicators, and the CRREL RDX colorimetric field screening method. DROPEX(Plus) and EXPRAY(tm) tests were found to be useful tools for screening the presence of significant concentrations of NC and/or NG in the field or on sample extracts. In combination with other field methods, they are beneficial screening tools for identifying areas that contain explosive contamination in buildings above specified limits. Detectable levels are matrix dependent, with low confidence in results at or near the detection limit. The CRREL RDX method of analysis gave a relatively low response for NC compared to NG, and the response was easily affected by matrix interferences. Modifications to the CRREL RDX procedure greatly increased the method response for NC and retained the response for NG. The increase in response made the modified method more robust for NC analysis and allowed analysis of NC on the three sample matrices. The CRREL RDX method was not appropriate for analysis of NC or mixtures of NG and NC, especially in the matrix samples used in this study, whereas the modified CRREL method developed in this study was more suitable. Neither method is specific to NG or NC, and both provide a response to the total of NG and NC.  
<http://www.estcp.org/Technology/upload/ER-0130-C&P.pdf>

Approaches to Assess Biocover Performance on Landfills  
Huber-Humer, M., S. Roeder, and P. Lechner.  
Waste Management, Vol 29 No 7, p 2092-2104, July 2009

When using engineered materials such as compost substrates, biocovers often feature altered, specific properties compared to those of conventional covers with respect to gas permeability, physical parameters (including water retention capacity and texture), and methane

oxidation activity. Existing measuring methods should be carefully evaluated or even modified prior to application of biocovers. This paper discusses possible strategies to be applied in monitoring biocover functionality. An assessment approach has been developed based on experiences derived from investigations and large-scale field trials with compost biocovers in Austria. The authors present a conceptual draft for monitoring biocover performance and recommendations for practical application.

#### Assessing the Influence of Meteorological Parameters on the Performance of Polyurethane Foam-Based Passive Air Samplers

Klanova, J., P. Eupr, J. Kohoutek, and T. Harner, Masaryk Univ., Czech Republic.

Environmental Science & Technology, Vol 42 No 2, p 550-555, 15 Jan 2008

Polyurethane foam (PUF) disk passive air samplers were evaluated under field conditions to assess the effect of temperature and wind speed on the sampling rate for PAHs, PCBs, and organochlorine pesticides. Passive samples integrated over 28-day periods were compared to high-volume air samples collected for 24 h, every 7 days, thus providing a large data set of 42 passive sampling events and 168 high-volume samples over a 3-year period. Average PUF disk sampling rates for gas-phase chemicals were approximately 7 cu m/d and comparable to previous reports. The high molecular weight PAHs, which are mainly particle-bound, experienced much lower sampling rates of approximately 0.7 cu m/d. This small rate was attributed to the ability of the sampling chamber to filter out coarse particles with only the fine/ultrafine fraction capable of penetration and collection on the PUF disk. Passive sampler-derived data were converted to equivalent air volumes ( $V(EQ)$ , cu m) using the high-volume air measurement results. Correlations of  $V(EQ)$  against meteorological data collected on-site yielded different behavior for gas- and particle-associated compounds. For gas-phase chemicals, sampling rates varied by about a factor of 2 with temperature and wind speed. The higher sampling rates at colder temperatures were explained by the wind effect on sampling rates. Temperature and wind were strongly correlated with the greatest winds at colder temperatures. Sampling rates increased greatly at warmer temperatures as the high molecular weight PAH burden was shifted toward the gas phase and subject to higher gas-phase sampling rates. At colder temperatures, sampling rates were reduced as the partitioning of the high molecular weight PAHs was shifted toward the particle phase. More research is needed to develop and test passive air samplers for particle-associated chemicals.

#### Assessment of In Situ Degradation of Chlorinated Ethenes and Bacterial Community Structure in a Complex Contaminated Groundwater System

Imfeld, G., I. Nijenhuis, M. Nikolausz, S. Zeiger, H. Paschke, J. Drangmeister, J. Grossmann, H.H. Richnow, and S. Weber.

Water Research, Vol 42 Nos 4-5, 871-882, Feb 2008

In situ degradation of chlorinated ethenes was investigated using principal component analysis (PCA) in combination with carbon stable isotope analysis in a complex groundwater system consisting of several geological units. The assessment of hydrogeochemistry and chlorinated ethenes distribution using this integrated approach revealed that the chlorinated ethenes biodegraded substantially. Shifts in isotopic values up to 20.4 per thousand, 13.9 per thousand, 20.1 per thousand and 31.4 per thousand were observed between geological units for

PCE, TCE, cDCE, and vinyl chloride, respectively. The use of specific biomarkers (16S rRNA gene) indicated the presence of Dehalococcoides DNA in 20 of the 33 evaluated samples. In parallel, the analysis of changes in the bacterial community composition in the aquifers using canonical correspondence analysis indicated the predominant influence of the chlorinated ethene concentrations (56.3% of the variance,  $P=0.005$ ). The integrated approach could open new prospects for the assessment of spatial and temporal functioning of bioattenuation in contaminated groundwater systems.

#### Assessment of the Value of Reducing Uncertainty by Sampling in a Groundwater Remediation System

Ma, H.W. and C.C. Chang.

Science of the Total Environment, Vol 402 No 1, p 9-17, 25 Aug 2008

It is essential to know how much reduction of uncertainty is needed for the purpose of designing a successful and reliable remediation system. The understanding of the site characteristics is basically increased by site investigation, and thus the uncertainty is decreased by sampling information. A method has been developed to evaluate the value of reducing uncertainty by sampling the hydrogeological parameters in a groundwater remediation system. Hydraulic conductivity being taken as an example of the site characteristics, random field generation and conditional simulation are coupled to obtain a range of hydraulic conductivity fields based on the sampling outputs. A multiple-realization management model that incorporates a chance constraint of health risk is used to find the lowest remediation cost under specific remediation criteria of risk through genetic algorithm. The remediation cost, which is expected to decrease with collection of more samples, serves as the measure of the value of uncertainty reduction by sampling. A case study shows that the variation of the hydraulic conductivity fields among the potential sites as well as the remediation cost is reduced as a result of increase of samples. It also shows that the risk after remediation decreases with the collection of more samples, which suggests that the reduction of risk can also be used to assess the value of sampling.

#### The Benzil-Cyanide Reaction and its Application to the Development of a Selective Cyanide Anion Indicator

Cho, D.G., J.H. Kim, and J.L. Sessler, Univ. of Texas at Austin.

Journal of the American Chemical Society, Vol 130 No 36, p 12163-12167, 10 Sep 2008

The benzil-cyanide reaction is a cyanide-specific reaction that can be exploited to produce a colorimetric indicator for this toxic anion by producing a pi-extended analog of benzil, 7, which is soluble in a 70:30 (v/v) mixture of methanol-water. In this medium, dilute solutions of 7 are yellow but produce colorless products when exposed to low concentrations of cyanide anion ( $\geq 1.7 \mu\text{M}$ ; added as an aqueous NaCN solution), but not to other common anions (e.g.,  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{N}_3^-$ , benzoate-, and  $\text{H}_2\text{PO}_4^-$ ). This promising cyanide anion indicator is attractive in terms of its selectivity, ease of use, water compatibility, and low cyanide detection limit that is discernible to the naked eye.



The Benzil Rearrangement Reaction: Trapping of a Hitherto Minor Product and its Application to the Development of a Selective Cyanide Anion Indicator

Sessler, J.L. and D.G. Cho, Univ. of Texas at Austin.

Organic Letters, Vol 10 No 1, p 73-75, 3 Jan 2008

The isolation and characterization of an intermediate from the benzil-cyanide reaction provides a trapping chemistry that can be used to produce a chemical indicator for the cyanide anion. The indicator relies on the synthesis and reaction of a pi-extended analog of benzil. Addition of tetrabutylammonium cyanide to organic solutions of the species, referred to as compound 3 in the text, gives rise to a dramatic change in both color and fluorescence properties. [See Chapter 4 in Cho's 2008 dissertation for the background information for this paper at <http://repositories.lib.utexas.edu/bitstream/2152/3861/2/chod51559.pdf> ]

Bioluminescent Sensor for Naphthalene in Air: Cell Immobilization and Evaluation with a Dynamic Standard Atmosphere Generator

Valdman, E. and I.G.R. Gutz, Univ. of Sao Paulo, Brazil.

Sensors and Actuators B: Chemical, Vol 133 No 2, p 656-663, 12 Aug 2008

A dynamic atmosphere generator with a naphthalene emission source has been constructed and used for the development and evaluation of a bioluminescence sensor based on the bacterium *Pseudomonas fluorescens* HK44 immobilized in 2% agar gel (107 cell/mL) placed in sampling tubes. A steady naphthalene emission rate was obtained by covering the diffusion unit containing solid naphthalene with a PTFE filter membrane. The maturation time from gelation of the agar matrix to analyte exposure for the bioluminescence assays was most favorable between 1.5 and 3 h. The maximum light emission, observed after 80 min, is dependent on the analyte concentration and the exposure time (evaluated between 5 and 20 min), but not on the flow rate of naphthalene in the sampling tube, over the range of 1.8 to 7.4 nmol/min. Good linear response was obtained between 50 and 260 nmol/L. The limit of detection was estimated at 20 nmol/L, which is far below the recommended threshold limit value for naphthalene in air.

Biomimetic Accumulation of PAHs from Soils by Triolein-Embedded Cellulose Acetate Membranes (TECAMs) to Estimate Their Bioavailability

Tao, Y., S. Zhang, Z. Wang, R. Ke, X.Q. Shan, and P. Christie,

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Chinese Academy of Sciences, Beijing.

Water Research, Vol 42 No 3, p 754-762, Feb 2008

A new passive sampling device, a triolein-embedded cellulose acetate membrane (TECAM), was used biomimetically to accumulate naphthalene, phenanthrene, pyrene, and benzo[a]pyrene from 10 spiked soils, as well as from a soil spiked with different concentrations of these PAHs. TECAM exposure conditions were optimized. The quantities of PAHs accumulated by TECAMs were related positively and linearly to their concentrations in soil. PAHs accumulated by TECAMs were related negatively to soil organic matter and positively to dissolved organic carbon. Aging time (1 to 150 days) had a significant effect on TECAM accumulation of PAHs. A good linear relationship was observed between TECAM-accumulated PAHs and PAHs accumulated by earthworms. The data indicate that TECAM represents a useful surrogate to estimate the bioavailability of PAHs and possibly other hydrophobic organic contaminants in soil.



Characterisation of a DNAPL Source Zone in a Porous Aquifer Using the Partitioning Interwell Tracer Test and an Inverse Modelling Approach

Dridi, L., I. Pollet, O. Razakarisoa, and G. Schaefer, Inst. Franco-Allemand de Recherche sur l'Environnement, Strasbourg, France.

Journal of Contaminant Hydrology, Vol 107 Nos 1-2, p 22-44, 26 June 2009

A partitioning interwell tracer test (PITT) performed in a large-scale experiment with a well-defined TCE spill provided measured concentration profiles within the TCE plume that were used in a combined analytical-numerical inverse modeling approach to predict the distribution of the DNAPL in a virtual vertical plane of the source. The proposed inverse modeling approach assumes local thermodynamic equilibrium of the distribution of TCE between the NAPL phase and the aqueous phase and no decay or sorption of the dissolved TCE concentrations downstream of the spill area. In the first step, the location of the contaminant in a virtual vertical plane of a porous medium is fixed by using measured concentration profiles and considering the dissolution of the organic phase under equilibrium conditions. In the second step, the volume of contaminant entrapped in the source cells is estimated. In the final step, a multiphase advective-dispersive transport model is used to adjust the volumes quantified in the second step. The predictions are highly dependent on the quantity and quality of the data in space and time. From the PITT-breakthrough curves measured at the pumping well, a mean TCE saturation in the sweep zone of 0.0004 was derived, which is very low compared to that determined at the local scale. In a second analysis, tracer breakthrough curves available at measuring points placed closely downstream and upstream of the presumed source zone were used to explain why the globally obtained DNAPL saturation was low compared to the locally evaluated TCE saturations in the source zone. It mainly was caused by the overall travel time compared to the short travel time of the tracers in the source zone; additionally, due to bypassing, only part of the volume of tracer injected was in contact and eventually interacted with the DNAPL. Furthermore, the quantified TCE volume was nearly 30% higher than the spilled volume, which agrees with the conclusions from other studies emphasizing that calculated volumes can overestimate the measured volumes, particularly in the case of an inhomogeneous distribution of the DNAPL within the soil. Good agreement of the measured and inversed concentration profiles was obtained, indicating that it is possible to determine the length-averaged distribution of a residual pollution source from dissolved concentration profiles measured downstream of the source zone.

Characterization of a Fractured Bedrock Groundwater System for Environmental Remediation Using Borehole Geophysics and 3D Seismic Data

Will, R., P. Kaufman, T. Parker, and D. Hiller.

SEG Expanded Abstracts, Vol 27, p 1213-1217, 2008

When the groundwater system comprises fractured and altered metamorphic rock overlain by weathered materials, remediation of DNAPL is particularly challenging. Methods employed for remediation of contaminants either in situ or through extraction require some knowledge of hydrodynamic controlling features, but the nature of fracture systems defies localized description using conventional geological characterization methodologies. To overcome this problem, sparse borehole-based characterization methods have been supplemented

with high-resolution 3D seismic data. The 3-D seismic data have provided critical information regarding key bedrock morphologic features that can be used to optimize remediation activities.

Characterization of Oil Sands Tailings Using Nuclear Magnetic Resonance (NMR) Technique  
Motta, C., J. Bryan, and A. Kantzas.

10th International Mine Water Association Congress, Technical University of Ostrava, Karlsbad, Czech Republic 2008. International Mine Water Association, Paper 56, 4 pp, 2008

In the oil sands mining industry in Alberta, Canada, large volumes of tailings are produced as waste from the recovery of bitumen. Investigators used the nuclear magnetic resonance (NMR) technique to characterize tailings samples and their settling behavior in the presence of flocculant. An estimation of the water, oil, and solids content and the variations in the settling rate were analyzed over time. NMR is used to establish if flocculant addition is successful in breaking down suspensions, or if additional chemical is required. The results show the NMR technique has potential as a fast on-site measurement of tailings settling characteristics for determining process modifications.

[http://www.imwa.info/docs/imwa\\_2008/IMWA2008\\_056\\_Motta.pdf](http://www.imwa.info/docs/imwa_2008/IMWA2008_056_Motta.pdf)

Collection of Pyrethroids in Water and Sediment Matrices: Development and Validation of a Standard Operating Procedure

Hladik, M.L., J.L. Orlando, and K.M. Kuivila.

U.S. Geological Survey Scientific Investigations Report 2009-5012, 22 pp, 2009

Loss of pyrethroid insecticides onto surfaces during sample collection can confound the interpretation of analytical and toxicity test results. Sample collection devices, container materials, and water matrix composition have a significant influence on the association of pyrethroids to container walls, which can be as high as 50%. Any sample collection method involving transfer through multiple containers or pieces of equipment increases the potential for pyrethroid loss. This loose surface-association with container walls can be reversed through agitation. When sampling water matrices with pumps or autosamplers, no pyrethroids were lost as long as the water was moving continuously through the system. When collecting water matrices in containers, the material with the least amount of pyrethroid sorption is as follows: glass < plastic < Teflon. Additionally, pyrethroids re-suspended more easily from the glass container walls. Since the amount of surface association is proportional to the ratio of volume to contact area of the sample, taking larger-volume field samples (greater than 3 liters) reduced pyrethroid losses to less than 10%. The amount of surface association cannot be predicted easily because of the dependence on water matrix composition; samples with higher dissolved organic carbon or suspended-sediment concentrations were observed to have lower percent loss. Sediment samples were not affected by glass-container sorption (the only containers tested). Standardized sample-collection protocols are critical to yield accurate pyrethroid concentrations for assessment of potential effects, and have been summarized in an accompanying standard operating procedure. <http://pubs.usgs.gov/sir/2009/5012/>

Comparative Assessment of Gene Quantification Using Real-Time PCR and Water Quality Parameters in Unsanitary Landfill

Han, J.S. and C.G. Kim, Inha Univ., Namgu, Incheon, South Korea.

Water Science & Technology, Vol 59 No 2, p 331-338, 2009

To gain a better understanding of the fates of contaminants in association with groundwater quality parameters, groundwater was seasonally sampled from four closed unsanitary landfills in which microbial diversity was simultaneously obtained by 16S rDNA methods. Subsequently, specific genes of representative bacteria and encoding enzymes were quantified by real-time PCR. The relationship between water quality parameters and gene quantification were compared based on correlation factors. Correlation between DSR gene and BOD was greater than 0.8, while NSR gene and nitrate were related more than 0.9. For MTOT, it was at the highest related at 100% over BOD/COD, and Dde genes were correlated over 0.8. Anaerobic genes and DO also were related more than 0.8, showing anaerobic reactions generally were dependent upon DO. This work demonstrates that molecular biological investigation and water quality parameters are highly co-linked, such that quantitative real-time PCR results could be used for assessing landfill stabilization in association with the conventional monitoring parameters.

Comparative Evaluation of Dy(III) Selective Poly(Vinyl) Chloride Based Membrane Electrodes of Macrocyclic Tetraimine Schiff's Bases

Gupta, V.K., M.K. Pal, and A.K. Singh, Indian Inst. of Technology Roorkee, India.

Talanta, Vol 79 No 2, p 528-533, 15 July 2009

Three different derivatives of macrocyclic tetraimine Schiff's base have been synthesized and explored as a neutral ionophores for preparing PVS-based membrane sensors selective to Dy(3+). The addition of sodium tetraphenyl borate and various plasticizers--o-NPOE, DBP, DBBP, DOP, and CN--were found to improve sensor performance. The best-performing sensor functioned satisfactorily over a wide pH range (2.8 to 7.2) with a fast response time (10 s). The sensor also performed in partially nonaqueous media with up to 20% (v/v) content of acetonitrile, methanol, or ethanol. The sensor can be used over a period of 1.5 months without significant drift in potentials. The sensor has been also utilized for the determination of Dy(3+) level in different soil samples.

A Comparative Study of AgX (X = Cl(-), Br(-), I(-) and N(3)(-)) Solid-Phase Reactors for Flow-Injection Determination of Cyanide in Electroplating Wastewater

Noroozifar, M., M. Khorasani-Motlagh, A. Taheri, and R. Zare-Dorabei, Univ. of Sistan & Baluchestan, Zahedan, Iran.

Analytical Sciences, Vol 24 No 5, p 669-672, May 2008

In the development of rapid-flow injection-flame atomic absorption spectrometry for cyanide detection, different AgX (X = Cl(-), Br(-), I(-), and N(3)(-)) solid-phase reagents (SPR) were tested for indirect determination of cyanide. In a single-line FIA system, the cyanide was allowed to react with AgX SPR, which in turn changed Ag ions in AgX to silver cyanide complexes in a sodium hydroxide carrier stream. The eluent containing the analyte as silver cyanide complexes was measured by FAAS. The calibration curve was linear up to 30 mg/L with a detection limit of 0.05 mg/L for cyanides. The sampling rate and the relative standard deviation

were <1.09% and >200/h, respectively. The method was applied to the determination of cyanide in electroplating wastewater.

[http://www.jstage.jst.go.jp/article/analsci/24/5/24\\_669/article](http://www.jstage.jst.go.jp/article/analsci/24/5/24_669/article)

#### Comparison of an Assay for Dehalococcoides DNA and a Microcosm Study in Predicting Reductive Dechlorination of Chlorinated Ethenes in the Field

Lu, X., J.T. Wilson, and D.H. Kampbell.

Environmental Pollution, Vol 157 No 3, p 809-815, Mar 2009

This work compares the detection of the 16S rRNA gene of Dehalococcoides species with a microcosm study for biotransformation in predicting reductive dechlorination of chlorinated ethenes in groundwater at hazardous waste sites. Groundwater samples collected from 12 PCE- or TCE-contaminated sites in the United States were analyzed and used to construct microcosms in the laboratory. The results showed that the presence of Dehalococcoides DNA was associated with dechlorination to ethene in the field. Nearly half the wells in which Dehalococcoides DNA was detected had ethene as a dechlorination end product. For groundwater samples from 16 wells where ethene was detected, ethene was produced in 11 of the corresponding microcosms. During two years of incubation, dechlorination for most microcosms was less extensive than that observed in the field.

#### A Comparison of Two MGP Site Remediation Perimeter Ambient Air Monitoring Programs

Gendron, L.J., ENSR Corporation.

Third International Symposium and Exhibition on the Redevelopment of Manufactured Gas Plant Sites, 23-25 September 2008, Mystic, Connecticut. 9 pp, Sep 2008

This presentation compares design specifications and operational protocols of two MGP perimeter monitoring programs in the following areas: monitoring objectives, parameters measured, risk-based action levels, instrumentation, data telemetry/action-level alarms, frequency of sampling, number of monitoring sites, costs of air monitoring programs, and advantages/disadvantages of both programs. Program A is a 17-acre MGP site in New Jersey with sensitive receptors in all directions (day care center, elderly housing, residential housing development, etc.). This site represents a fairly complex and conservative approach to fenceline monitoring. Program B is 6-acre MGP site in Rhode Island in a primarily industrial area. This site calls for a more simplistic and manual approach to fenceline monitoring

[http://proceedings.instep.ws/2008\\_09\\_23\\_MGPUSA2008/content/pdf/03\\_Gendron.pdf](http://proceedings.instep.ws/2008_09_23_MGPUSA2008/content/pdf/03_Gendron.pdf)

#### Completely Automated Open-Path FT-IR Spectrometry

Griffiths, P.R., L. Shao, and A.B. Leytem, Univ. of Idaho, Moscow.

Analytical and Bioanalytical Chemistry, Vol 393 No 1, p 45-50, Jan 2009

Atmospheric analysis by open-path Fourier-transform infrared (OP/FT-IR) spectrometry has been possible for over two decades but has not been widely used because of the limitations of the software of commercial instruments. This paper covers the current state of the art of the hardware and software that constitutes a contemporary OP/FT-IR spectrometer and describes laboratory advances that have enabled many of the limitations of this type of instrument to be overcome. These advances include not having to acquire a single-beam background spectrum

that compensates for absorption features in the spectra of atmospheric water vapor and carbon dioxide. Instead, an easily measured "short path-length" background spectrum is used for calculation of each absorbance spectrum that is measured over a long path-length. To accomplish this goal, the algorithm used to calculate the concentrations of trace atmospheric molecules was changed from classical least-squares regression to partial least-squares regression. For calibration, OP/FT-IR spectra are measured in pristine air over a wide variety of path lengths, temperatures, and humidities; ratioed against a short-path background; and converted to absorbance. The reference spectrum of each analyte then is multiplied by randomly selected coefficients and added to these background spectra. Automatic baseline correction for small molecules with resolved rotational fine structure, such as ammonia and methane, is effected using wavelet transforms. A novel method of correcting for the effect of the nonlinear response of mercury cadmium telluride detectors is also incorporated. Finally, target factor analysis can be used to detect the onset of a given pollutant when its concentration exceeds a certain threshold. In this way, the concentration of atmospheric species has been obtained from OP/FT-IR spectra measured at intervals of 1 min over a period of many hours with no operator intervention.

<http://eprints.nwisrl.ars.usda.gov/1304/1/1281.pdf>

#### Continuous and Semicontinuous Monitoring Techniques for Particulate Matter Mass and Chemical Components: a Synthesis of Findings from EPA's Particulate Matter Supersites Program and Related Studies

Solomon, P.A. and C. Sioutas, U.S. EPA, Las Vegas, NV.

Journal of the Air and Waste Management Association, Vol 58 No 2, p 164-195, Feb 2008

U.S. EPA established the Particulate Matter (PM) Supersites Program to provide key stakeholders (government and private sector) with significantly improved information needed to develop effective and efficient strategies for reducing PM on urban and regional scales. The methods tested include a variety of continuous and semicontinuous instruments typically having a time resolution of an hour or less. These methods often overcome many of the limitations associated with measuring atmospheric PM mass concentrations by daily filter-based methods (e.g., potential positive or negative sampling artifacts). Semicontinuous coarse and ultrafine mass measurement methods also were developed and evaluated. Other semicontinuous monitors tested measured the major components of PM--nitrate, sulfate, ammonium, organic and elemental carbon, trace elements, and water content of the aerosol--as well as methods for other physical properties of PM, such as number concentration, size distribution, and particle density. Particle mass spectrometers, although unlikely to be used in national routine monitoring networks in the foreseeable future because of their complex technical requirements and cost, are discussed because of the wealth of new information they provide on the size-resolved chemical composition of atmospheric particles on a near-continuous basis. The improvements in time resolution achieved by the reported semicontinuous methods have proven to be especially useful in characterizing ambient PM, and are becoming essential in allowing scientists to investigate sources of particulate pollution and to probe into the dynamics and mechanisms of aerosol formation in the atmosphere.

## Continuous Determination of High-Vapor-Phase Concentrations of Tetrachloroethylene Using On-Line Mass Spectrometry

Fine, D., M.C. Brooks, M. Bob, S. Mravik, and L. Wood.

Analytical Chemistry, Vol 80 No 4, p 1328-1335, 15 Feb 2008

A method was developed to determine the vapor concentration of PCE at and below its equilibrium vapor-phase concentration, 168,000 ug/L (25 degrees C). Vapor samples were drawn by vacuum into a 6-port sampling valve and injected through a jet separator into an ion trap mass spectrometer (MS). This on-line MS can continuously sample a vapor stream and provide vapor concentrations every 30 seconds. Calibration of the instrument was done by creating a saturated stream of PCE vapor, sampling the vapor with the on-line MS and with thermal desorption tubes, and correlating the peak area response from the MS with the vapor concentration determined by automated thermal desorption gas chromatography mass spectrometry. Dilution of the saturated stream provided lower concentrations of PCE vapor. The method was developed to monitor the vapor concentration of PCE sparged from a 2-D flow chamber and to determine the total PCE mass removed during each sparge event. The method has potential application for analysis of gas-phase tracers.

## Demonstration and Evaluation of Solid Phase Microextraction for the Assessment of Bioavailability and Contaminant Mobility: Laboratory Study Report

Reible, D., G. Lotufo, A. Skwarski, D. Lampert, and X.-X. Lu.

Environmental Security Technology Certification Program (ESTCP), Project ER-0624, 101 pp, June 2008

The basic parameters of routine field deployment of solid-phase microextraction (SPME) have been defined as a tool for the assessment of in situ contaminant migration processes and bioavailability of polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) contaminants. The detection limit of the SPME fibers used in these studies was in the low ng/L level or less for the contaminants of concern using 1 cm of fiber. Detection limits were roughly inversely proportional to hydrophobicity (i.e., lower detection limits were observed for more hydrophobic compounds) since the sorption onto the fiber was more or less proportional to hydrophobicity. Reproducibility of the SPME measurement was tested by comparison of independent replicates. Reproducibility generally was above 90%. The characteristic time for achievement of steady state was less than a day for PAH in water, about a week for PAH with bare fiber in sediments, but as long as a month for more hydrophobic PCB in sediments. The slow achievement of equilibrium for PCB may be the cause of the increased variability in reported fiber/water partition coefficients for PCB. Experimental results show that uptake kinetics are relatively insensitive to temperature. A field-deployable SPME system was developed with a protective sheath over a slotted rod containing the fiber. The dynamics of uptake on fiber within the field deployable system was essentially identical to that for the bare fiber. A model of chemical uptake will be applied to define equilibrium times in the field-deployable system. The existing data will be used to define the mass-transfer resistance associated with the sheath layer. The vertical resolution of the field-deployable system was assessed by evaluation of pore-water concentration gradients in a layered system (sand over contaminated sediment). Sharp concentration gradients (~1 cm resolution or better) were observed for all contaminants evaluated except for the least hydrophobic, phenanthrene, presumably due to greater vertical spreading of this compound. The laboratory studies have

shown the potential for SPME to correlate with and predict bioaccumulation in benthic organisms. The high resolution possible also suggests that the field-deployable system might be used effectively to identify and evaluate in-bed transport processes. Field demonstration of these capabilities is currently under way.

<http://www.estcp.org/Technology/upload/ER-0624-Lab-Rep.pdf>

#### Design of Fluorescent Assays for Cyanide and Hydrogen Peroxide Based on the Inner Filter Effect of Metal Nanoparticles

Shang, L. and S. Dong, Chinese Academy of Sciences.

Analytical Chemistry, Vol 81 No 4, p 1465-1470, 15 Feb 2009

A new type fluorescent assay based on the inner filter effect (IFE) of metal nanoparticles (NPs) is conceptually different from previously reported metal NPs-based fluorescent assays. Two proof-of-concept examples are based on the IFE of Au NPs by choosing MDMO-PPV as a model fluorophore; the fluorescence could be tuned by the absorbance of Au NPs with a much higher sensitivity than the corresponding absorbance approach. While the first assay worked in a turn-on mode upon the etching of Au NPs by cyanide, the second one functioned in a turn-off mode upon the catalytic growth of Au NPs by hydrogen peroxide. As a result, the present IFE-based approach can detect cyanide ranging from  $1.0 \times 10^{-6}$  to  $6.0 \times 10^{-4}$  M with a detection limit of  $6.0 \times 10^{-7}$  M and hydrogen peroxide ranging from  $1.5 \times 10^{-7}$  to  $2.2 \times 10^{-5}$  M with a detection limit of  $8.5 \times 10^{-8}$  M, respectively. The IFE-based approach allows the design of fluorescent assays in a simpler, time-saving, and economical approach when compared with conventional metal NPs-based fluorescent assays as no modification step of the fluorophore is required.

#### Design of Groundwater Monitoring Networks Considering Conceptual Model and Parametric Uncertainty

Hassan, A., H. Bekhit, Y. Zhang, and J. Chapman.

Abstracts: American Geophysical Union (AGU) 2008 Fall Meeting, San Francisco, California, December 11-15, 2008

Uncertainty built into conceptual groundwater flow and transport models and associated parametric uncertainty should be appropriately included when such models are used to develop detection monitoring networks for contaminated sites. The authors compare alternative approaches of propagating such uncertainty from the flow and transport model into the network design. The focus is on detection monitoring networks where the primary objective is to intercept the contaminant before it reaches a boundary of interest (e.g., compliance boundary). Different uncertainty propagation approaches identify different well locations and different well combinations (networks) as having the highest detection efficiency. It is thus recommended that multiple uncertainty propagation approaches are considered. If several approaches yield consistent results in terms of identifying the best performing candidate wells and the best performing well network for detecting a contaminant plume, this would provide confidence in the suitability of the selected well locations.



#### Detection of Arsenic (As) in Mine Tailing Soils Using Laser Induced Breakdown Spectroscopy (LIBS)

Park, K., J.H. Kwak, C. Lenth, C. Salb, E.J. Ko, and K.W. Kim.

GREAT 2008: Proceedings of the International Symposia on Geoscience Resources and Environments of Asian Terranes, 4th IGCP 516, and 5th APSEG, 24-26 November 2008, Bangkok, Thailand. [abstract only] 2008

Laser-induced breakdown spectroscopy (LIBS) was used to determine arsenic (As) concentration in 16 soil samples from four different mine tailing sites in Korea. The use of a double-pulse laser in the LIBS led to enhancement of the intensity and peak-to-base ratio of the As emission lines with smaller relative standard deviation compared to a single-pulse laser approach. An internal standardization was used to minimize matrix effects by other chemical components in soils. Data showed that the double-pulse approach with internal standardization by iron (Fe) provided a good correlation between As concentration and the LIBS signal ( $r=0.95-0.96$ ), which can be used to quantify the As concentration by the LIBS. Furthermore, the As concentrations determined by the LIBS were compared with those obtained by off-line atomic absorption spectrometry (AAS) to evaluate the current LIBS system. They are correlated well with a correlation coefficient of  $r=0.85$  and a linear regression slope of 0.85. The ratio of As concentration by AAS to one by LIBS ranged from 0.6 to 2.4 with an average value of 1.0, except in three samples having low As concentrations.

#### Detection of Hexavalent Uranium with Inline and Field-Portable Immunosensors

Melton, S.J., H. Yu, M.F. Ali, K.H. Williams, M.J. Wilkins, P.E. Long, and D.A. Blake.

Uranium, Mining and Hydrogeology. Springer, Berlin. ISBN: 978-3-540-87745-5, p 27-36, 2008

An antibody that recognizes a chelated form of hexavalent uranium was used in the development of two different immunosensors for uranium detection. The sensors were utilized for the analysis of groundwater samples collected during a 2007 field study of in situ bioremediation in a aquifer located at Rifle, CO. The antibody-based sensors provided data comparable to that obtained using kinetic phosphorescence analysis. These novel instruments and associated reagents should provide field researchers and resource managers with valuable new tools for on-site data acquisition.

#### Detection of Indoor Biological Hazards Using the Man-Portable Laser Induced Breakdown Spectrometer

Munson, C.A., J.L. Gottfried, E.G. Snyder, F.C. De Lucia, Jr., B. Gullett, and A.W. Miziolek. Applied Optics, Vol 47 No 31, p G48-G57, 1 Nov 2008

The performance of a man-portable laser induced breakdown spectrometer was evaluated for the detection of biological powders on indoor office surfaces and wipe materials. Identification of pure unknown powders was performed by comparing against a library of spectra containing biological agent surrogates and interferents, such as dusts, diesel soot, natural and artificial sweeteners, and drink powders, using linear correlation analysis. Simple models constructed using a second technique, partial least squares discriminant analysis, successfully identified *Bacillus subtilis* (BG) spores on wipe materials and office surfaces. The models also were able to identify BG on materials not used in the training of the model.

Determination of 10 Particle-Associated Multiclass Polar and Semi-Polar Pesticides from Small Streams Using Accelerated Solvent Extraction

Schaefer, R.B., R. Mueller, W. Brack, K.D. Wenzel, G. Streck, W. Ruck, and M. Liess, UFZ-Helmholtz Centre for Environmental Research, Leipzig, Germany.  
Chemosphere, Vol 70 No 11, p 1952-1960, Feb 2008

A new analytical method using accelerated solvent extraction was developed for determination of 10 particle-associated polar and semipolar pesticides. Six deuterated analogs of the target compounds were evaluated as internal standards. The method yielded acceptable accuracy (73 to 103% recovery) and precision (<25% relative standard deviation) for 8 compounds. Using size exclusion chromatography as cleanup step resulted in higher recoveries compared to solid-phase extraction cleanup. Deuterated standards with 10 or more deuterium atoms performed well as internal standards concerning similar recovery and correlation with the target analytes. The method was employed to extract particle-associated pesticides from 16 streams located in an area with intense agriculture. Acetochlor, pirimicarb, tebuconazole, fenpropidin, alpha-endosulfan, and chlorfenvinphos were detected at concentrations up to 1 mg/kg dry weight.

Determination of Perchlorate in River by Ion-Pair Hollow-Fiber Liquid-Phase Microextraction Coupled with Electrospray Ionization Tandem Mass Spectrometry

Chen, H.C., W.T. Chen, and W.H. Ding, National Central Univ., Taiwan.  
Talanta, Vol 79 No 2, p 442-445, 15 July 2009

Analysis of perchlorate in surface water samples has been achieved by a rapid and reliable ion-pair hollow-fiber liquid-phase microextraction (HF-LPME) method coupled with flow-injection electrospray ionization tandem mass spectrometry (ESI-MS/MS) technique. The authors investigated and optimized the effects of the type and concentration of ion-pairing reagents, extraction time, temperature, and pH value on the quantitative extraction of perchlorate by ion-pair HF-LPME. Di-n-hexyl ammonium acetate (DHAA) was employed to form an extractable ion-pair complex with aqueous perchlorate. The characteristic ions were observed in the ESI negative-ionization mode. The predominant product ions were used for quantitation and to maximize the detection selectivity and sensitivity. The limit of detection was 0.5 ug/L.

Determination of Total and Available Fractions of PAHs by SPME in Oily Wastewaters: Overcoming Interference from NAPL and NOM

Gomes, R.B., R. Nogueira, J.M. Oliveira, J. Peixoto, and A.G. Brito, Univ. of Minho, Braga, Portugal.

Environmental Science and Pollution Research, 2009 Mar 17. [Epub ahead of print]

This paper describes the development of a simple and suitable methodology for the determination of the freely dissolved and the total fraction of PAHs present in oily wastewaters. Headspace SPME was used for analyzing PAH. Four model PAHs--anthracene, fluorene, phenanthrene, and pyrene--were analyzed by GC-MS. Negligible depletion SPME technique was used to determine the free fraction. Total PAH was determined by enhancing the mass transfer from the bonded phase to the freely dissolved phase by temperature optimization and the use of the method of standard additions. The PAH absorption kinetics were determined to define the

optimal sampling conditions for this method. The fitting of the experimental data to a mathematical model was accomplished using Berkeley Madonna software. Humic acid and silicon oil were used as model NOM and NAPL, respectively, to study the effect of these compounds on the decrease of SPME response. The method then was evaluated with wastewater from a fuel station spill retention basin. The SPME kinetic parameters were determined from experimental data modeling. The determination of the free fraction required 15-min sampling to ensure that PAH depletion from sample was below 1%. For total PAH, a 30-min extraction at 100 degrees C ensured the maximum signal response in the GC-MS. For the determination of free and total PAHs, extractions were performed before reaching the SPME equilibrium. The wastewater used in this study had no free fraction of the analyzed PAHs; however, the four model PAHs were found when the method for total PAH was used. The addition of NOM and NAPL dramatically decreased the efficiency of the SPME. This decrease was the result of a greater partition of the PAHs to the NAPL and NOM phases and was also observed in the analysis of the fuel station spill retention basin, where no free PAH was measured. Using the method of standard addition for the determination of total PAH, it was possible to quantify all four PAHs.

#### Determining Bioavailable PAHs in Sediment Pore Waters

Thal, Dave.

The Business of Brownfields Conference, April 2008, Pittsburgh, PA. 18 slides, 2008  
EPA's narcosis model predicts toxic effects to benthic wildlife from PAH-impacted sediments. Toxicity is predicted when the sum of bioavailable concentrations expressed as toxic units exceeds the benchmark value. The Bioavailable Concentration equals the freely dissolved fraction as given by equilibrium partitioning theory. The model assumes that OC/Water equilibrium position equals Octanol/Water. A proof of concept study for a new method was completed in October 2006. ASTM approved the provisional method as work product WK10122. Following publication of that standard, 5 years is allowed to complete the full interlab study with 7 laboratories. The EPA interlab validation study for EPA Draft Method 8272 was completed in summer 2007 under the guidance of Mr. Barry Lesnik. Three non-development labs participated, TestAmerica, UMBC, and Meta. Results will be published in a peer reviewed paper. The new method was posted by EPA in Jan 2008 as SW-846 Method 8272 at its "Test Methods for Evaluating Solid Waste" page ([www.epa.gov/epawaste/hazard/testmethods/sw846/](http://www.epa.gov/epawaste/hazard/testmethods/sw846/)). Method 8272 covers the separation of pore water from PAH-impacted sediment samples, the removal of colloids, and the subsequent measurement of dissolved concentrations of the 10-parent PAHs and two alkylated daughter PAHs in the pore water samples. This method directly determines the concentrations of dissolved PAHs in environmental sediment pore water, groundwater, and other water samples. <http://www.eswp.com/brownfields/Thal.pdf>

#### Development and Field Trial of a Household Surface Lead Loading Rate Sampling Device in a Lead-Contaminated Community of Southern Thailand

Untimanon, O., A. Geater, V. Chongsuvivatwong, S. Thoumsang, P.K. Verkasalo, and W. Saetia, Ministry of Public Health, Nontaburi, Thailand.

Environmental Monitoring and Assessment, 2009 May 5. [Epub ahead of print]

A new dust-collecting device was developed to assess surface lead loading rates in houses in communities contaminated with lead oxide dust used for caulking in nearby boat-repair yards. The device consists of two small glass sheets with total area of 1,200 sq cm placed in two plastic trays suspended from the ceiling in the house for 3 months before wiping and sending the dust specimen for determination of lead content using flame atomic absorption spectrophotometry. After a pilot study in four households, additional data were collected from 43 matched pairs of boat-caulkers' and neighboring control households. All devices were retained in the house for 3 months without any complaint. Static measurements of lead dust levels were also assessed in all households. The values significantly discriminated high from low lead exposure households ( $p = 0.015$ ) and provided good correlations with floor lead loading (Spearman rank correlation coefficient,  $r = 0.39$  to  $0.62$ ) and dust lead content ( $r = 0.53$  to  $0.64$ ). This sampling method is an alternative to others which consume more household space or require a longer collection period.

#### Development of a Bioactive Paper Sensor for Detection of Neurotoxins Using Piezoelectric Inkjet Printing of Sol-Gel-Derived Bioinks

Hossain, Z., R.E. Luckham, A.M. Smith, J.M. Lebert, L.M. Davies, R.H. Pelton, C.D.M. Filipe, and J.D. Brennan.

Analytical Chemistry, Vol 81 No 13, p 5474-5483, 2009

This paper describes a novel, paper-based, solid-phase biosensor that utilizes piezoelectric inkjet printing of biocompatible, enzyme-doped, sol-gel-based inks to create colorimetric sensor strips. To create the sensor, polyvinylamine (PVAm, which captures anionic agents) was first printed and then AChE was overprinted by sandwiching the enzyme within two layers of biocompatible sol-gel-derived silica on paper. AChE inhibitors, including paraoxon and aflatoxin B1, were detected successfully using this sensor by measuring the residual activity of AChE on paper (Ellman's colorimetric assay) with capture of the 5-thio-2-nitrobenzoate (TNB-) product on the PVAm layer. The assay provided good detection limits (paraoxon, 100 nM; aflatoxin B1, 30 nM) and rapid response times ( $<5$  min). Detection could be achieved either by eye or using a digital camera and image analysis software, avoiding the need for expensive and sophisticated instrumentation. The bioactive paper strip can be used either as a dipstick or as a lateral flow-based biosensor. The use of sol-gel-based entrapment produced a sensor that retained enzyme activity and gave reproducible results after storage at 4 degrees C for at least 60 days, making the system suitable for storage and use in the field.

#### Development of a Gas-Phase Chemiluminescence Detection System for the Measurement of Arsenic in Environmental and Biological Samples

Assegid, Kirubel, Master's thesis, George Mason Univ., VA. 107 pp, 2008

Measurement of trace arsenic at parts per billion (ppb) levels in environmental and biological samples is a key component for the mitigation and understanding of this crisis. This project deals with the development of an analytical technique for the measurement of arsenic based on a gas-phase chemiluminescence reaction between ozone ( $O_3$ ) and arsine ( $AsH_3$ ) as the detection principle. The approach is capable of analyzing arsenic concentration in a 1.0 mL sample in one minute. The determination of As(III) and As(V) was achieved based on the different pH dependence and the reducibility of these species to arsine gas by sodium

borohydride ( $\text{NaBH}_4$ ). The intense chemiluminescence formed in a reflective glass reaction cell from the reaction of  $\text{AsH}_3/\text{O}_3$  is detected by a sensitive photomultiplier tube (PMT). The signal is further amplified, digitalized, and recorded with a complete data acquisition computer-controlled system. The limit of detection is 0.146  $\mu\text{g/L}$  (ppb, or 146 ppt) for total arsenic concentration in 10 determinations. To validate the performance of the gas-phase chemiluminescence-based arsenic analyzer, results were compared with hydride generation atomic absorption spectroscopy and atomic fluorescence spectroscopy techniques. The chemiluminescence detection system was also coupled with a flow injection system to enhance its efficiency. Sequential procedures, including direct chemical and data analysis methods and step by step development of the analyzer, are described in depth. The system has been effectively tested using standard and unique field water samples from several regions of Ethiopia.

<http://mars.gmu.edu:8080/dspace/handle/1920/3000>

#### Development of MWNT Based Disposable Biosensor on Glassy Carbon Electrode for the Detection of Organophosphorus Nerve Agents

Jha, N. and S. Ramaprabhu.

Journal of Nanoscience and Nanotechnology, Vol 9 No 9, p 5676-5680, Sep 2009

A disposable acetylcholinesterase (AChE)-based biosensor has been developed using synthesis, purification, and further functionalization with oxygen-containing hydrophilic functional groups of carbon nanotubes. The biosensing activity of functionalized multi-walled carbon nanotubes (MWNTs) for the detection of an organophosphorus compound, paraoxon, was tested using the amperometric method. Functional groups on the surface of MWNTs create a favorable surface for enzyme immobilization and enhance the enzyme electrode interaction by increasing the electron transfer rate via the high electrical conductivity of the MWNTs. Upon exposure to paraoxon, a decrease occurs in the catalytic activity of AChE, which results in lower production of the enzymatic product thiocholine, which leads to reduction in the electrooxidation current. The ability of the MWNT-based sensor to measure concentration reliably in the 7 to 0.5 nM range has been demonstrated, with a detection limit as low as 0.5 nM.

#### Development of Two Novel Pore Water Sampling Techniques to Reduce Confounding Field Variables

Clough, S.R. (Haley & Aldrich, Inc.), M. Shupe (GeoTrans, Inc.), M. Avakian (TG&B Marine Services, Inc.), and P.G. Bucens (Remedium Group, Inc.).

Third International Symposium and Exhibition on the Redevelopment of Manufactured Gas Plant Sites, 23-25 September 2008, Mystic, Connecticut. Poster, Sep 2008

Recent seminal research on the bioavailability of PAHs strongly suggests that pore water (PW), not bulk sediment chemistry, is the primary medium of concern to evaluate in terms of PAHs presenting a hazard to benthic macroinvertebrates. Confounding field variables in PW collection include too much silt, currents or tidal movement, and PW dilution due to "short-circuiting" of surface water. Using available technologies, the authors developed two in situ PW samplers that help reduce confounding environmental variables. Both samplers use a portable peristaltic pump to obtain PW samples. The first sampler, employed in a marine setting, has an upper stainless steel pipe, and the lower section essentially is a modified stainless steel well head (slotted for the top 10 cm of substrate) welded to a horizontal flange. The well head/flange has a

small ID sample port that allows pumping of PW, along with the upper 2 cm of surface water, which is more realistic in terms of macroinvertebrate exposure. The device effectively prevents short-circuiting of the overlying surface water column into the underlying PW sample.

[http://proceedings.instep.ws/2008\\_09\\_23\\_MGPUSA2008/content/p\\_29C.htm](http://proceedings.instep.ws/2008_09_23_MGPUSA2008/content/p_29C.htm)

#### Diffusive Partitioning Tracer Test for the Quantification of Nonaqueous Phase Liquid (NAPL) in the Vadose Zone: Performance Evaluation for Heterogeneous NAPL Distribution

Werner, D., H.K. Karapanagioti, and P. Hoehener, Univ. of Newcastle, UK.

Journal of Contaminant Hydrology, 2009 May 19. [Epub ahead of print]

A partitioning tracer test based on gas-phase diffusion in the vadose zone gives estimates of the residual nonaqueous-phase liquid (NAPL) saturation. The technique was investigated further by examining diffusive tracer breakthrough curves in the vadose zone for a heterogeneous NAPL distribution. Tracer experiments were performed in a lysimeter with a horizontal layer of artificial kerosene embedded in unsaturated sand. Tracer disappearance curves at the injection point and tracer breakthrough curves at some distance from the injection point were measured inside and outside of the NAPL layer. A numerical code was used to generate independent model predictions based on the physicochemical sand, NAPL, and tracer properties. The measured and modeled tracer breakthrough curves agreed well, confirming the validity of modeling assumptions such as negligible sorption of chlorofluorocarbon (CFC) tracers to the uncontaminated sand and their fast reversible partitioning between the soil air and the NAPL phase. The model was used to investigate different configurations of NAPL contamination, and experimental and model results show that the tracer disappearance curves of a single-well diffusive partitioning tracer test (DPTT) are dominated by the near-field presence of NAPL around the tip of the soil gas probe. In contrast, breakthrough curves of inter-well tracer tests reflect the NAPL saturation in between the probes, although the interpretation of the tracer signals is not unique if the NAPL distribution is heterogeneous. Numerical modeling is useful for the planning of a DPTT application. Simulations suggest that several cubic meters of soil can be investigated with a single inter-well partitioning tracer test of 24-hour duration by placing the injection point in the center of the investigated soil volume and probes at up to 1 m distance for the monitoring of gaseous tracers.

#### Direct Screening of Ground Water Samples for Fuel Oxygenates by Headspace Liquid Phase Microextraction-Gas Chromatography

Kaykhaei, M. and M.R. Mirbaloochzahi.

Environmental Monitoring and Assessment, Vol 147 Nos 1-3, p 211-222, Dec 2008

The authors investigated the applicability of headspace liquid-phase microextraction and gas chromatography (HS-LPME/GC) for the rapid and reliable screening of 68 well-water samples for selected fuel oxygenate compounds (i.e., MTBE, TAME, ETBE, and n-BEE). The method used 3  $\mu$ L of 1:1 benzyl alcohol/1-octanol as extraction solvent, 20 min extraction time with stirring at 1,250 rpm at 20 degrees C, and salt addition of a mixture of 0.3 g/mL sodium sulphate/0.1 g/mL sodium chloride. Limits of detection were in the range of 77 to 110 ng/L. The relative standard deviations at 0.05, 0.50 and 10.0 mg/L of spiking levels were in the range of 1.28 to 6.80%, with recoveries between 96.2 and 106.0%. Groundwater wells located near different gasoline reservoirs in the eight largest cities of the Sistan and Balouchestan province

were screened by the method. Eight contaminated wells were identified that contained MTBE at levels between 0.3 and 1.7 mg/L. In all cases, other target analytes were at low concentrations or not detected.

#### DNAPL Distribution in the Source Zone: Effect of Soil Structure and Uncertainty Reduction with Increased Sampling Density

Pantazidou, M. and K. Liu.

Journal of Contaminant Hydrology, Vol 96 Nos 1-4, p 169-186, 19 Feb 2008

This paper focuses on parameters describing the distribution of DNAPL contaminants, investigates the parameter variability that results from soil heterogeneity, and quantifies the uncertainty reduction that can be achieved with increased density of soil sampling. Numerical simulations of DNAPL releases were performed using stochastic realizations of hydraulic conductivity fields generated with the same geostatistical parameters and conditioning data at two sampling densities, thus generating two simulation ensembles of low and high density (a three-fold increase) of soil sampling. The results showed that DNAPL plumes in aquifers identical in a statistical sense exhibit qualitatively different patterns, ranging from compact to finger-like. The corresponding quantitative differences were expressed by defining several alternative measures that describe the DNAPL plume and computing these measures for each simulation of the two ensembles. The uncertainty in the studied plume features was affected to different degrees by the variability of the soil, with coefficients of variation ranging from about 20 to 90% for the low-density sampling. Meanwhile, the increased soil sampling frequency resulted in reductions of uncertainty varying from 7 to 69% for low- and high-uncertainty variables, respectively. In view of the varying uncertainty in the characteristics of a DNAPL plume, remedial designs that require estimates of the less uncertain features of the plume might be preferred over those that need a more detailed characterization of the source zone architecture.

#### Effect of Sampling Method on Contaminant Measurement in Pore-Water and Surface Water at Two Uranium Operations: Can Method Affect Conclusions?

Robertson, E.L. and K. Liber.

Environmental Monitoring and Assessment, 2008 Aug 24. [Epub ahead of print]

Two methods of sediment pore-water sampling and two methods of surface water sampling were used and compared in an investigation of cause(s) of adverse effects on benthic invertebrate communities at two Saskatchewan uranium operations (Key Lake and Rabbit Lake). Ammonia, pH, DOC, and trace metals were measured and compared. For pore water, centrifuged and 0.45- $\mu$ m filtered sediment core samples were compared against 0.2- $\mu$ m dialysis (peeper) samples. For surface water, 53- $\mu$ m filtered Van Dorn horizontal beta samples were compared against 0.2- $\mu$ m dialysis (peeper) samples. Results showed that 62% of the sediment core pore-water values were higher than the corresponding peeper pore-water measurements and that 63% of the Van Dorn surface water measurements were lower than corresponding peeper surface water measurements. Only 24 and 14% of surface water and pore-water measurements, respectively, fell within  $\pm 10\%$  range of one another; 73 and 50%, respectively, fell within  $\pm 50\%$ . Although different filtering methods were used, the observed differences nonetheless are believed to be related primarily to small, vertical differences in the environment sampled. Despite observed differences in concentrations of toxicologically relevant variables generated by



the different sampling methods, the weight-of-evidence conclusions drawn from each set of exposure data on the possible cause(s) of in situ toxicity to *Hyaella azteca* from a related study were the same at each uranium operation; however, this concurrence was due largely to other dominant lines of evidence. The weight-of-evidence conclusions at Key Lake were dominated by the toxicity response of *H. azteca* in relation to exposure chemistry, whereas the weight-of-evidence conclusions at Rabbit Lake were informed by exposure chemistry, the toxicological response of *H. azteca*, and whole-body contaminant concentrations in the test organisms. Had these multiple lines of evidence not been available, differences in exposure chemistry generated by the different sampling methods could have influenced the identification of potential causes of in situ toxicity substantially.

#### Electrical Leak Location Surveys for Landfill Caps

Hansen, R. and A. Beck, Vector Engineering Inc., Grass Valley, CA.

Proceedings of the Environmental and Water Resources Institute (EWRI) Conference: An International Perspective on Environmental and Water Resources, 5-7 January 2009, Bangkok, Thailand. EWRI, 7 pp, 2009

Electrical leak location surveys are a proven technology for locating holes in installed geomembrane liners. Typically, leak detection surveys are specified for landfill expansion cells on the bottom lining system. Landfill capping systems often incorporate a geomembrane designed to avoid infiltration into the waste and subsequent leakage through or overflowing of the bottom liner. Protective cover soil is placed over the geomembrane as part of closure construction. Placement of cover material on landfill caps is particularly difficult due to the orientation of the heavy equipment on steep slopes. Damage to the underlying geomembrane typically goes unnoticed since the damage usually is covered quickly after it has occurred. The authors performed two leak locations surveys on two landfill geomembrane capping systems after the placement of the protective cover soil using the dipole method (ASTM D7007-03). One survey was specified as part of closure construction quality control while the other was specified forensically after poor closure construction. The survey methods for each survey are discussed, along with site preparations conducted to maximize the sensitivity of the surveys. Results of the surveys are presented along with practical suggestions for future landfill cap surveys. Leak detection testing of landfill caps proved a viable tool to ensure the integrity of the geomembrane capping systems.

[http://www.vectoreng.com/content/Document/pdf/papers/Electrical%20Leak%20Location%20Surveys%20for%20Landfill%20Caps\\_THAI%20PROCEEDINGS\\_HansenBeck2.pdf](http://www.vectoreng.com/content/Document/pdf/papers/Electrical%20Leak%20Location%20Surveys%20for%20Landfill%20Caps_THAI%20PROCEEDINGS_HansenBeck2.pdf)

#### Electrical Resistivity Characterization of a Reclaimed Gold Mine to Delineate Acid Rock Drainage Pathways

Rucker, D.F., D.R. Glaser, T. Osborne, and W.C. Maehl.

Mine Water and the Environment, Vol 28 No 2, p 146-157, June 2009

An electrical resistivity survey completed at the Landusky mine consisted of 15 lines on the surface of the reclaimed Surprise pit, Queen Rose pit, and the region immediately south of Swift Gulch. Additionally, wells and seeps were used by energizing electrodes in direct contact with groundwater to increase the sensitivity of the resistivity method at depth. The survey was conducted to locate potential acid mine drainage (AMD) pathways that are contaminating Swift

Gulch. The lowest resistivity values were coincident with the Queen Rose pit, and the low resistivity feature appeared to trend northeast along a known fault. A scatter plot of resistivity values versus total dissolved solids (TDS) showed a strong correlation. A linear regression model suggests TDS at the lowest resistivity region to be ~2.5 times greater than that measured in groundwater wells.

#### Estimating the Spatial Scale of Herbicide and Soil Interactions by Nested Sampling, Hierarchical Analysis of Variance and Residual Maximum Likelihood

Price, O.R., M.A. Oliver, A. Walker, and M. Wood, Univ. of Warwick, UK.

Environmental Pollution, Vol 157 No 5, p 1689-1696, May 2009

An unbalanced nested sampling design was used to investigate the spatial scale of soil and herbicide interactions at the field scale. A hierarchical analysis of variance based on residual maximum likelihood was used to analyze the data and provide a first estimate of the variogram. Soil samples were taken at 108 locations at a range of separating distances in a 9 ha field to explore small- and medium-scale spatial variation. Soil organic matter content, pH, particle size distribution, microbial biomass, and the degradation and sorption of the herbicide, isoproturon, were determined for each soil sample. A large proportion of the spatial variation in isoproturon degradation and sorption occurred at sampling intervals less than 60 m; however, the sampling design did not resolve the variation present at greater scales. A sampling interval of 20 to 25 m should ensure that the main spatial structures are identified for isoproturon degradation rate and sorption without a detrimental loss of information in this field.

#### Estimation of Uncertainty Arising from Different Soil Sampling Devices: the Use of Variogram Parameters

de Zorzi, P., S. Barbizzi, M. Belli, M. Barbina, A. Fajgelj, R. Jacimovic, Z. Jeran, S. Menegon, A. Pati, G. Petruzzelli, U. Sansone, and M. Van der Perk.

Chemosphere, Vol 70 No 5, p 745-752, Jan 2008

Within the international SOILSAMP project, funded and coordinated by the National Environmental Protection Agency of Italy (APAT), uncertainties due to field soil sampling were assessed. Three different sampling devices were applied in an agricultural area using the same sampling protocol. Cr, Sc and Zn mass fractions in the collected soil samples were measured by k(0)-instrumental neutron activation analysis (k(0)-INAA). For each element/device combination, the experimental variograms were calculated using geostatistical tools. The variogram parameters were used to estimate the standard uncertainty arising from sampling. The sampling component represents the dominant contribution of the measurement uncertainty with a sampling uncertainty/measurement uncertainty ratio ranging between 0.6 and 0.9. The approach based on the use of variogram parameters leads to uncertainty values of the sampling component in agreement with those estimated by replicate sampling approach.

#### Evaluating Ground-Water/Surface-Water Transition Zones in Ecological Risk Assessments: ECO Update/Ground Water Forum Issue Paper

EPA-540-R-06-072, OSWER 9285.6-17, 30 pp, July 2008

Numerous hydrogeological and ecological methods and tools are available for delineating groundwater discharge areas in a rapid and cost-effective manner, and for evaluating the effects of contaminant exposure on transition zone biota. These tools and approaches, which are

commonly used in hydrogeological and ecological investigations, can be readily employed within the existing EPA framework for conducting screening- and baseline-level ecological risk assessments in Superfund to identify and characterize the current and potential threats to the environment from a hazardous substance release. This document applies equally to recharge zones and to evaluation of advancing plumes that have not yet reached the transition zone. [http://www.epa.gov/oswer/riskassessment/ecoup/pdf/eco\\_update\\_08.pdf](http://www.epa.gov/oswer/riskassessment/ecoup/pdf/eco_update_08.pdf)

#### Evaluating the Fate of Chlorinated Ethenes in Streambed Sediments by Combining Stable Isotope, Geochemical and Microbial Methods

Abe, Y., R. Aravena, J. Zopfi, B. Parker, and D. Hunkeler, Univ. of Neuchatel, Switzerland. *Journal of Contaminant Hydrology*, Vol 107 Nos 1-2, p 10-21, 26 June 2009

The occurrence of chlorinated ethene transformation in a streambed was investigated using concentration and carbon isotope data from water samples taken at different locations and depths within a 15 x 25 m study area across which a PCE plume discharges. The investigators also evaluated how the degree of transformation is related to groundwater discharge rates, redox conditions, solid organic matter content (SOM), and microbial factors. The degree of chlorinated ethene transformation was highly variable, from no transformation to transformation beyond ethene. Complete reductive dechlorination to ethane and ethene occurred at locations with at least sulfate-reducing conditions and with a residence time in the samples streambed zone (80 cm depth) of at least 10 days. Dehalococcoides were detected using a PCR method where SOM contents were >2% w/w and where transformation proceeded beyond ethane, but were not detected at locations with low SOM, which may cause an insufficient H<sub>2</sub> supply to sustain a detectably dense Dehalococcoides population. It also is possible that other organisms are responsible for the biodegradation. A microcosm study with streambed sediments demonstrated the potential of VC oxidation throughout the site even at locations without a pre-exposure to VC, consistent with the detection of the epoxyalkane:coenzyme M transferase (EaCoMT) gene involved in the degradation of chlorinated ethenes via epoxidation. In contrast, no aerobic transformation of cDCE in microcosms over a period of 1.5 years was observed. The study results demonstrated that carbon isotope analysis is a sensitive tool to identify the degree of chlorinated ethene transformation even in hydrologically and geochemically complex streambed systems. The investigators observed that the degree of transformation is related to redox conditions, which in turn depend on groundwater discharge rates.

#### Evaluation of Geochemical Tests in Predicting Acid Mine Drainage Potential in Coal Surface Mine

Gautama, R.S. and G.J. Kusuma.

10th International Mine Water Association Congress, Technical University of Ostrava, Karlsbad, Czech Republic 2008. International Mine Water Association, Paper 48, 4 pp, 2008

Geochemical tests generally conducted to predict AMD potential have been studied using samples from a coal mine area in Kalimantan, Indonesia. Acid-base accounting and net acid generation (NAG) tests were used to classify whether the samples were potentially acid forming or non acid forming material. A modified free-draining column leach test was conducted on the potentially acid forming samples to understand the kinetics of acid generation. This paper presents the results of more than 200 days of observation, with analysis of the findings and

comparisons. Some deviations were noted between the result of acid base accounting analysis and the result of kinetic tests. This study could be used to revisit the interpretation of test results for a better prediction on AMD potential in coal mines.

#### Evaluation of the Suitability of Sampling on Tenax TA and Polydimethylsiloxane for the Analysis of Combustion Gases

Desmet, K., M. Schelfaut, T. Gorecki, and P. Sandra, Ghent Univ., Belgium.

Talanta, Vol 79 No 3, p 967-970, 15 Aug 2009

Two sorbents commonly employed for air sampling--Tenax TA as adsorbent and polydimethylsiloxane (PDMS) as absorbent--were selected for an evaluation of suitability for the analysis of combustion gases. Target compounds were selected among the gaseous combustion products of polyurethane foam and fire-retarded polystyrene. The combustion gases were generated by burning test materials in the flame of a Bunsen burner. Gaseous combustion products were sampled simultaneously with the two sorbents using a two-way adapter, thereby exposing each sorbent to the same combustion gas atmosphere. Special attention was given to the deterioration encountered in the Tenax TA performance upon repeated combustion gas exposure, limiting its use for sampling reactive atmospheres.

#### Experiences in Long-Term Evaluation of Mercury Emission Monitoring Systems

Cheng, C.-M., H.-T. Lin, Q. Wang, C.-W. Chen, C.-W. Wang, M.-C. Liu, C.-K. Chen, and W.-P. Pan.

Energy and Fuels, Vol 22 No 5, p 3040-3049, 2008

Six mercury continuous emission monitoring (CEM) systems provided by two leading mercury (Hg) CEM system manufacturers were tested at five coal combustion utilities. The linearity, response time, day-to-day stability, efficiency of the Hg speciation modules, and ease of use were evaluated by following procedures specified in 40 CFR Part 75. Mercury monitoring results from Hg CEM systems were compared to an EPA-recognized reference method. A sorbent trap sampling system was also evaluated in this study to compare the relative accuracy to the reference method as well as to Hg CEM systems. A conceptual protocol proposed by U.S. EPA (Method 30A) for using an Hg CEM system as the reference method for the Hg relative accuracy (RA) test was also followed to evaluate the workability of the protocol. This paper discusses the operational experience obtained from these field studies and the remaining challenges to overcome while using Hg CEM systems and the sorbent trap method for continuous Hg emission monitoring. <http://www.wku.edu/ICSET/Experiences.pdf>

#### Explosive Detection Using Infrared Laser Spectroscopy

Hildenbrand, J., J. Herbst, J. Woellenstein, and A. Lambrecht.

Quantum Sensing and Nanophotonic Devices VI. Proceedings of SPIE--The International Society for Optical Engineering, Vol 7222, Paper 72220B, 2009

Stand-off and extractive explosive detection methods for short distances were investigated using mid-infrared laser spectroscopy. A quantum cascade laser (QCL) system was developed for explosives (i.e., TNT and TATP) detection by open-path absorption spectroscopy in the gas phase. A detection limit of 5 ppm/m was achieved in lab measurements. For explosives

with lower vapor pressure, an extractive hollow fiber-based measurement system was investigated. Gaseous TATP or TNT is introduced into a heated fiber by thermal desorption. The small sample volume and a fast gas exchange rate enable fast detection. TNT and TATP detection levels below 100 ng are feasible even in samples with a realistic contaminant background.

#### Field Analysis of Total PCBs in Soils by Thermal Desorption/GC and Determination of the Individual PCB Congeners by GC X GC - TOF-MS

Li, Xiaojing, Master's thesis, Univ. of Waterloo, 133 pp, 2009

Environmental field analysis can allow real-time decisions, interactive sampling, and cost-effective solutions to problems faced during a site investigation. Gas chromatography (GC), a widespread technique for the determination of organic pollutants in the environment, is useful in environmental field analysis. Thermal desorption of solid environmental sample provides a technique for liberation of volatile analytes from the samples without the need for solvent extraction. Combining the thermal desorption technique with a field gas chromatograph (GC) thus provides the possibility of on-site determination of organic contaminants in soils. Comprehensive 2-D gas chromatography (GC X GC) is a powerful analytical tool that provides enhanced separation and resolution capacity for analyses. The project presented here involved the development and validation of a field method for the analysis of total polychlorinated biphenyls (PCBs) in soil, followed by determination of individual PCB congeners in the same samples via laboratory analysis. The developed field analytical system was a field-portable GC interfaced with a thermal desorber. The identification of PCB congeners was realized by a GC X GC system with a time-of-flight mass spectrometer as the detector. The field method was developed by optimizing and characterizing the method using PCB standards. After total PCBs in environmental soil samples were determined using the thermal desorption/GC method, PCB contents (i.e., individual congeners) in the environmental soil samples were characterized further in the laboratory using a Soxhlet extraction/GCxGC/TOF-MS method.

<https://uwspace.uwaterloo.ca/handle/10012/4195>

#### Field Calibration of Polyurethane Foam (PUF) Disk Passive Air Samplers for PCBs and OC Pesticides

Chaemfa, C., J.L. Barber, T. Gocht, T. Harner, I. Holoubek, J. Klanova, and K.C. Jones, Lancaster Univ., UK.

Environmental Pollution, Vol 156 No 3, p 1290-1297, Dec 2008

Passive air sampler (PAS) strategies have been developed for sampling in remote areas and for cost-effective simultaneous spatial mapping of persistent organic pollutants (POPs) over differing geographical scales. The widely used polyurethane foam (PUF) disk generally is mounted inside two stainless steel bowls to buffer the air flow to the disk and shield it from precipitation and light. A field study was conducted to compare performance of 3 different designs of sampler, calibrate the sampler against the conventional active sampler, and gather more information on field-based uptake rates and equilibrium times of the samplers. Samplers were deployed at different locations across the field site and at different heights up a meteorological tower to investigate the possible influence of sampler location. Samplers deployed <5m above ground and not directly sheltered from the wind provided similar uptake

rates. Small differences in dimensions between the 3 designs of passive sampler chamber had no discernable effect on accumulation rates, allowing comparison with previously published data.

#### Field Evaluation of Resistivity Sensors for in Situ Moisture Measurement in a Bioreactor Landfill

Kumar, D., S. Jonnalagadda, P. Jain, N.A. Gawande, T.G. Townsend, and D.R. Reinhart, Univ. of Florida, Gainesville.

Waste Management, Vol 29 No 5, p 1547-1557, May 2009

The ability of resistance-based sensors to measure in situ waste moisture content in a landfill was examined via the installation of 135 resistance-based sensors in a leachate recirculation well field at a bioreactor landfill in Florida. For the 78% of sensors that worked successfully in the field during the study period (>6 yrs), the initial spatial average moisture content determined by the sensor readings was 42.8% compared to 23% from gravimetric readings. Eighteen sensors (13%) showed that they were saturated before liquid addition, and no change in moisture content was observed in these sensors during the study period. Lab-derived calibration methods resulted in an over-estimation of moisture content. An alternate field-calibration method, where wetted sensor output was assumed equal to the average of gravimetric measurements for wet samples, was evaluated. The final spatial average moisture contents were 64.2 and 44.4% for the laboratory- and field-derived calibration methodologies, respectively, compared to 45% measured gravimetrically from excavated waste samples. When moisture content was determined using a mass-balance approach, the result was 34.6%. The results suggest that when appropriately calibrated, resistivity-based sensors can be used to obtain a reasonably accurate estimate of local moisture content, although caution should be taken to extend moisture content values that are representative of waste surrounding the sensors to estimate the overall moisture content on a landfill-wide scale.

#### Field Testing a Flow-Through Sampler for Semivolatile Organic Compounds in Air

Xiao, H., H. Hung, T. Harner, Y.D. Lei, and F. Wania, Univ. of Toronto Scarborough.

Environmental Science & Technology, Vol 42 No 8, p 2970-2975, 15 Apr 2008

A flow-through sampler (FTS) can collect gaseous and particle-bound SVOCs from large volumes of air by turning into the wind and having the wind blow through a porous sampling medium. To test performance under field conditions, a traditional pumped high-volume air sampler and an FTS, both using polyurethane foam (PUF) as sampling medium, were co-deployed on the campus of the University of Toronto Scarborough from August 2006 to June 2007. Quantitative relationships between the wind speed outside the sampler and after passage through the PUF were established for estimation of sampling volumes under conditions of low and high wind speed. PCBs and PAHs were quantified in the samples taken by both air samplers. Separate analysis of 7 PUF disks arranged sequentially within the FTS confirm that even relatively volatile SVOCs do not experience serious breakthrough. Theoretical plate-number analysis of the breakthrough curves yields an understanding of the effect of temperature and wind speed on FTS sampling efficiency and reveals different behavior of gaseous and particle-bound compounds on the PUF. Air concentrations of PCBs and PAHs obtained with the FTS compare favorably with those obtained by averaging the concentrations of several 24-h active high-volume samples taken during the same time period.

Flexibility of Solid-Phase Microextraction for Passive Sampling of Atmospheric Pesticides  
Wang, J., L. Tuduri, M. Millet, O. Briand, and M. Montury, CNRS-Univ. Bordeaux, France.  
Journal of Chromatography A, Vol 1216 No 15, p 3031-3037, 10 Apr 2009

For pesticides of low volatility, applications of solid-phase microextraction (SPME) for air sampling have been reported with sampling time chosen in the linear stage of the sorption kinetics because of long equilibrium time. In pre-equilibrium conditions, sampling rates (SRs) expressed as the volume of air sampled by the SPME sampler per unit of time were used to estimate analyte concentrations in air. In the present work, the sorption kinetics of several pesticides with SPME were investigated in detail to achieve good extraction performance and accurate calibration, with a focus on parameters influencing SRs. Linear air velocity was found to be the main parameter affecting SRs. For exposed fibers, with air velocities below 20 to 25 cm/s, SRs increased with increasing air velocity. When linear air velocity was equal to or greater than 25 to 30 cm/s, it had little effect on SRs. To improve the flexibility of SPME, different configurations of SPME were compared: different lengths of fibers exposed, retracted fibers, and exposed fibers with grids. SRs were linearly proportional to exposed lengths of fibers. Lower SRs and wider calibration time range were achieved with grids. SRs for retracted fibers were the lowest among the different experimental configurations.

A Fluorescence Turn-on Detection of Cyanide in Aqueous Solution Based on the Aggregation-Induced Emission

Peng, L., M. Wang, G. Zhang, D. Zhang, and D. Zhu.  
Organic Letters, Vol 11 No 9, p 1943-1946, 7 May 2009

The nucleophilic addition of cyanide to the trifluoroacetyl amino group in **2** yields an amphiphilic species that induces the aggregation of silole **1**, which significantly increases the fluorescence of the ensemble. Thus, a fluorescence turn-on detection of cyanide in aqueous solution can be established with an ensemble of silole **1** and compound **2**. This ensemble also displays good selectivity toward cyanide over other common inorganic anions.

Functional Genes Reveal the Intrinsic PAH Biodegradation Potential in Creosote-Contaminated Groundwater Following in Situ Biostimulation

Nyyssonen, M., A. Kapanen, R. Piskonen, T. Lukkari, M. Itavaara, Technical Research Centre of Finland, Espoo.  
Applied Microbiology and Biotechnology, 2009 May 21. [Epub ahead of print]

Researchers used a small-scale functional gene array containing 15 functional gene probes targeting aliphatic and aromatic hydrocarbon biodegradation pathways to investigate the effect of a pilot-scale air sparging and nutrient infiltration treatment on hydrocarbon biodegradation in creosote-contaminated groundwater. Using the functional gene array to detect genes involved in the different phases of PAH biodegradation indicated the presence of intrinsic biodegradation potential in the contaminant plume, although the low aerobic fluorescein diacetate hydrolysis, the polymerase chain reaction (PCR) amplification of 16S rRNA genes closely similar to sulfate-reducing and denitrifying bacteria, and the negligible decrease in contaminant concentrations showed that aerobic PAH biodegradation was limited in the anoxic groundwater. Increased abundance of PAH biodegradation genes was detected by functional



gene array in the monitoring well located at the rear end of the biostimulated area, which indicated that air sparging and nutrient infiltration enhanced intrinsic aerobic biodegradation of PAHs. Ten times higher naphthalene dioxygenase gene copy numbers were detected by real-time PCR in the biostimulated area, which agreed well with the functional gene array data. The results indicate the potential of using functional gene array analysis as a tool for evaluating the efficiency of hydrocarbon bioremediation in field-scale applications.

#### GASSYS: Direct In-Situ and Passive Gas Sampling from Unsaturated Soil and from Groundwater

Weyer, K.U. (WDA Consultants Inc.); H. Kaiser (KaiserGEOconsult, Erlangen, Germany). WaterTech 2009: Water Technologies Symposium, 29 April - 1 May 2009, Fairmont, Banff Springs, Alberta, Canada. 66 presentation slides, 2009

GASSYS is a passive gas sampling system developed by KaiserGEOconsult GmbH, Erlangen, Germany. The system can sample repeatedly and over many years from exactly the same position and under exactly the same sampling conditions within saturated and unsaturated soil, and it can determine the actual gas concentration per volume of soil gas. Sampling intervals can be installed at depths of 30 m and greater. This method opens the door to controlling gas sampling conditions in the subsurface and to monitoring gas components of chemical and biochemical processes in groundwater and soil air as they occur during (for example) natural attenuation. GASSYS collects quantitative gas samples by diffusion through a permeable ethylene vinyl acetate membrane from unsaturated soil into a tube. Because the membrane is permeable to gas but not to water, it also collects qualitative gas samples from groundwater. The installed membrane tube stays in the ground and, as indicated in case histories of leak detection, can function for more than 20 years in collecting volatile and less volatile hydrocarbon gases. Within each tube, up to four sealed sampling intervals can be installed at different depths. Diffusion processes collect gas samples from the space immediately surrounding the collection chamber. During sampling, gas collected in the chamber is transferred from each segment by means of fine stainless steel tubes and calibrated syringes into a headspace vial. These vials are subjected to laboratory analyses. A new variant of GASSYS is under development to provide 10 or more chambers stacked vertically. The new device has an outer diameter 65 mm and a chamber volume of 160 ml (at 1 m length). The presentation provides 4 case histories of the use of GASSYS in site investigation: (1) monitoring of methane content in unsaturated soil and groundwater at the Langenfeld Waste Disposal site; (2) monitoring of hydrogen gas content in groundwater at the Terrania site; (3) sampling of BTEX, H<sub>2</sub>S, and methane gases during remediation of benzene/toluene plumes in groundwater at Schwarze Pumpe; and (4) sampling of chlorinated hydrocarbons (CHCs), vinyl chloride, ethane, ethene, and hydrogen gases in groundwater at Dusseldorf/Hilden for investigation and remediation of CHC plumes.

<http://www.esaa-events.com/watertech/2009/pdf/Presentation10.pdf>

#### Geochemical Sampling Scheme Optimization on Mine Wastes Based on Hyperspectral Data

Ting, Z., P. Debba, and A. Stein.

The International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences, Beijing, 2008. Vol. XXXVII, Part B7, p 1529-1532, 2008

The authors present a spatial simulated annealing method using hyperspectral data. This sampling method was applied in an environmental assessment of the Dexing Copper Mine. Mine

waste contains high concentrations of metals, mostly of a non-economic value. Most of them are discharged without any decontamination. Acid rock drainage can adversely impact the quality of drinking water and the health of riparian ecosystems. To assess or monitor the environmental impact of mining, sampling of mine waste is required. Optimal geochemical sampling schemes, which focus on ground verification of mine wastes extracted from hyperspectral data, were derived automatically from a JAVA program. Hyperspectral data help to identify ground objects by a larger spectral range. Spectral angle-mapper classification technique was carried out to obtain rule images. A rule image provides weights that are utilized in defining the objective function for the sampling scheme, which then are optimized by means of simulated annealing. The simulated annealing uses the Weighted Means Shortest Distance (WMSD) criterion between sampling points. The scaled weight function intensively samples areas where an abundance of mine waste weathering occurs. A threshold is defined to constrain the sampling points to specific areas of interest. [http://www.isprs.org/congresses/beijing2008/proceedings/7\\_pdf/9\\_ThS-17/22.pdf](http://www.isprs.org/congresses/beijing2008/proceedings/7_pdf/9_ThS-17/22.pdf)

#### Geographic Sampling of Urban Soils for Contaminant Mapping: How Many Samples and from Where

Griffith, D.A., Univ. of Texas at Dallas.

Environmental Geochemistry and Health, Vol 30 No 6, p 495-509, Dec 2008

As spatial autocorrelation increases in an urban landscape, the amount of duplicate information contained in georeferenced data also increases, whether an entire population or some type of random sample drawn from that population is being analyzed, resulting in conventional power and sample size calculation formulae yielding incorrect sample size numbers for model-based inference. Spatial statistical model specifications have been exploited to formulate equations for estimating the necessary sample size needed to obtain some predetermined level of precision for an analysis of georeferenced data when implementing a tessellation stratified random sampling design, a "model-informed" approach, since a model of latent spatial autocorrelation is required. This paper addresses issues of efficiency associated with these model-based results and summarizes findings from a data collection exercise (soil samples collected from across Syracuse, NY), as well as from a set of resampling and from a set of simulation experiments. Guidelines are suggested concerning appropriate sample size (i.e., how many) and sampling network (i.e., where).

#### A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants Using Compound Specific Isotope Analysis (CSIA)

Hunkeler, D., R.U. Meckenstock, B. Sherwood-Lollar, T.C. Schmidt, and J.T. Wilson.

EPA 600-R-08-148, 82 pp, Dec 2008

When organic contaminants are degraded in the environment, the ratio of stable isotopes often will change, and the extent of degradation can be recognized and predicted from the change in the ratio of stable isotopes. Recent advances in analytical chemistry make it possible to perform compound-specific isotope analysis (CSIA) on dissolved organic contaminants, such as chlorinated solvents, aromatic petroleum hydrocarbons, and fuel oxygenates, at concentrations in water that are near their regulatory standards. The traditional approach for monitoring contaminant concentrations at sites often does not offer adequate information about the processes

responsible for removal of the contaminants. Stable isotope analyses can provide an in-depth understanding of biodegradation or abiotic transformation processes in contaminated aquifers. Because CSIA is a new approach, neither widely accepted standards have been established for accuracy, precision, and sensitivity, nor approaches to document accuracy, precision, sensitivity and representativeness. This text provides general recommendations on good practice for sampling, measurement, data evaluation and interpretation in CSIA. This guide is intended for managers of hazardous waste sites who must design sampling plans that will include CSIA and specify data quality objectives for CSIA analyses, for analytical chemists who must carry out the analyses, and for staff of regulatory agencies who must review the sampling plans, data quality objectives, and the data provided from the analyses.

<http://www.epa.gov/ada/pubs/reports/600r08148/600R08148.html>

#### A Highly Sensitive and Selective Chemosensor for Cyanide

Ren, J., W. Zhu, and H. Tian.

Talanta, Vol 75 No 3, p 760-764, 15 May 2009

A fast, highly sensitive, and selective cyanide chemosensor has been based on fused indoline and benzooxazine fragment. The detection of cyanide is performed via the nucleophilic attack of cyanide anion on the oxazine, i.e., the cleavage of the C-O bond of oxazine and the binding of cyanide to the spiro center of oxazine. The specific reaction results in high selectivity for cyanide ion. Addition of cyanide anion to the oxazine in a cyanomethane/water solution results in a loss in absorbance at 343 nm and an increase in new absorbance at 411 nm, with obvious changes in color. Cyanide can be detected down to 1  $\mu$ M levels in less than 30 seconds with no interference from other anionic species.

#### Identification of Novel Perchloroethene-Respiring Microorganisms in Anoxic River Sediment by RNA-Based Stable Isotope Probing

Kittelman, S. and M.W. Friedrich, Max Planck Inst. for Terrestrial Microbiology, Germany.

Environmental Microbiology, Vol 10 No 1, p 31-46, Jan 2008

The authors report on the detection of a novel group of dehalorespiring bacteria that reductively dechlorinate PCE to cis-DCE by RNA-based stable isotope probing. Pristine river sediment was incubated at 15 degrees C with PCE at low aqueous concentration. Upon formation of dechlorination products, the microbial community was probed with C-13 labeled acetate as electron donor and carbon source. Terminal restriction fragment length polymorphism (T-RFLP) analysis of density-separated 16S rRNA revealed a predominantly radiolabeled bacterial population only in the microcosm with PCE in high-density gradient fractions, whereas in the control without PCE, bacteria-specific rRNA was restricted to light gradient fractions. By cloning and sequence analysis of 16S rRNA, the predominant population was identified as a novel group of bacteria within the phylum Chloroflexi. The results show that stable isotope probing allows the targeting of dehalorespiring bacteria as a functional guild and identification of previously unrecognized PCE-respiring populations.

#### Identifying Abiotic Chlorinated Ethene Degradation: Characteristic Isotope Patterns in Reaction Products with Nanoscale Zero-Valent Iron

Elsner, M., M. Chartrand, N. Vanstone, G.L. Couloume, and B.S. Lollar.

Environmental Science & Technology, Vol 42 No 16, p 5963-5970, 15 Aug 2008

Carbon isotope fractionation was used to distinguish the effectiveness of an implemented abiotic degradation remediation scheme from intrinsic biotic degradation. A study of the transformation of TCE and daughter products with two types of nanoscale iron materials showed different reactivity trends but relatively consistent carbon isotope enrichment factors. Products of the dichloroelimination pathway (ethene, ethane, and acetylene) were consistently 10 per thousand more isotopically depleted than those of the hydrogenolysis pathway (cis-DCE from TCE, VC from cis-DCE), displaying a characteristic pattern that might serve as an indicator of abiotic dehalogenation reactions and as a diagnostic parameter for differentiating the effects of abiotic versus biotic degradation. In contrast, the product-related enrichment factors of each respective pathway varied significantly in different experiments, which suggests that the two pathways may share an irreversible first reaction step with subsequent isotopically sensitive branching.

#### Improved Quantification of Dehalococcoides Species by Fluorescence In Situ Hybridization and Catalyzed Reporter Deposition

Fazi, S., F. Aulenta, M. Majone, and S. Rossetti.

Systematic and Applied Microbiology, Vol 31 No 1, p 62-67, Mar 2008

There is a general consensus in the literature that members of the genus *Dehalococcoides* (Dhc) are required for complete dechlorination of halogenated compounds. These microorganisms have been successfully visualized by fluorescence in situ hybridization (FISH) in highly active dechlorinating cultures, but FISH detection of Dhc under low-activity conditions can be hampered owing to their small cell size and low ribosome content. When catalyzed reporter deposition (CARD)-FISH was employed as an alternative detection method in a TCE-dechlorinating enrichment culture, CARD-FISH (using proteinase K as a permeabilization pre-treatment) was found to be significantly superior to conventional FISH in terms of both microscopic visualization and quantification efficiency (about 30%). The application of this method to contaminated aquifer samples is discussed.

#### Integration of Traditional and Innovative Characterization Techniques for Flux-Based Assessment of Dense Non-Aqueous Phase Liquid (DNAPL) Sites

Basu, N.B., P. Suresh, C. Rao, I.C. Poyer, S. Nandy, M. Mallavarapu, R. Naidu, G.B. Davis, B.M. Patterson, M.D. Annable, and K. Hatfield.

Journal of Contaminant Hydrology, Vol 105 Nos 3-4, p 161-172, 1 Apr 2009

Key attributes of the source zone and the expanding dissolved-phase TCE plume at a site in Australia were evaluated using trends in groundwater monitoring data with data from on-line VOC samplers and passive flux meters (PFMs) deployed in selected wells. The data indicate that residual TCE source mass in the saturated zone, estimated using two innovative techniques, is small (~10 kg), which is also reflected in small source mass discharge (~3 g/day). The plume is disconnecting, based on TCE concentration contours and TCE fluxes in wells along a longitudinal transect. Biodegradation is minimal, based on TCE mass discharge of ~6 g/day at a

plume control plane approximately 175 m from source, which is also consistent with aerobic geochemical conditions observed in the plume. Residual TCE in the vadose zone provides episodic inputs of TCE mass to the plume during infiltration/recharge events. TCE flux data also suggest that the small residual TCE source mass is present in the low-permeability zones, which makes source treatment difficult. Based on a synthesis of the archived data and new data, analysis suggests that source treatment is unwarranted, and that containment of the large TCE plume (1.2 km long, 0.3 km wide, 17 m deep, ~2,000 to 2,500 kg TCE mass) or institutional controls, along with a long-term flux monitoring program, is preferred. The flux-based site management approach outlined in this paper provides a novel way of looking beyond the complexities of groundwater contamination in heterogeneous domains to make site decisions based on strategic measurement of the appropriate metrics.

#### Integrative Approach to Delineate Natural Attenuation of Chlorinated Benzenes in Anoxic Aquifers

Stelzer, N., G. Imfeld, M. Thullner, J. Lehmann, A. Poser, H.-H. Richnow, and I. Nijenhuis. Environmental Pollution, Vol 157 No 6, p 1800-1806, June 2009

Biodegradation of chlorobenzenes was assessed at an anoxic aquifer by combining hydrogeochemistry and stable isotope analyses. In situ microcosm analysis evidenced microbial assimilation of chlorobenzene-derived carbon and laboratory investigations showed mineralization at low rates. Due to simultaneous depletion and enrichment of C-13 (which complicates the evaluation of degradation), sequential dehalogenation of chlorinated benzenes can affect the isotope signature of single chlorobenzene species; hence, the compound-specific isotope analysis was interpreted based on an isotope balance. The enrichment of the cumulative isotope composition of all chlorobenzenes indicated in situ biodegradation. Investigation of the relationship between hydrogeochemistry and degradation activity by principal component analysis highlighted variable hydrogeochemical conditions associated with degradation activity at the plume scale. Although the complexity of the field site did not allow straightforward assessment of natural attenuation processes, the application of an integrative approach appeared relevant to characterize in situ biodegradation potential. Lines of evidence for in situ biodegradation of chlorinated benzenes in an anoxic aquifer were achieved by combining hydrogeochemical and stable isotope data with multivariate statistics.

#### An Investigation on the Environmental Effects of Sulphide Mines Using Geophysical Studies

Moradzadeh, A., F.D. Ardejani, and S.F. Pisheh. 10th International Mine Water Association Congress, Technical University of Ostrava, Karlsbad, Czech Republic 2008. International Mine Water Association, Paper 60, 4 pp, 2008

Low-grade wastes produced by mining activities, particularly in sulfide deposits, can cause detrimental impacts on the environment as sulfide minerals within the waste dump release various toxic elements during oxidation. Where the transportation of metallic pollutants by different physical and geochemical mechanisms changes the conductivity of the affected zones, electric and electromagnetic geophysical methods can be used to map these zones. The authors investigated the pollution potential of a sulfide mine located in northeastern Iran using very low frequency electromagnetic (VLFEM), resistivity (RES), and induced polarization (IP) geophysical methods. The investigators also performed numerical modeling using VLF data to

provide geoelectrical sections along different profiles so that the capability of this cost-effective and fast method could be evaluated relative to the results produced by the time-consuming and expensive RES and IP methods. The results of modeling indicate that VLF data could provide geoelectrical sections that are in good agreement with those provided by the RES and IP data. The obtained results further show that the drainage emanating from the waste dump contaminated an area with a dimension of 70x40 sq m to depths more than 30 m downgradient. [http://www.imwa.info/docs/imwa\\_2008/IMWA2008\\_060\\_Moradzadeh.pdf](http://www.imwa.info/docs/imwa_2008/IMWA2008_060_Moradzadeh.pdf)

Laser-Induced Breakdown Spectroscopy for the Classification of Unknown Powders  
Snyder, E.G., C.A. Munson, J.L. Gottfried, F.C. De Lucia, Jr., B. Gullett, and A. Miziolek.  
Applied Optics, Vol 47 No 31, p G80-G87, 1 Nov 2008

Laser-induced breakdown spectroscopy (LIBS) was used to discern between two biological agent surrogates (*B. atrophaeus* and ovalbumin) and potential interferent compounds (mold spores, humic acid, house dust, and Arizona road dust). Multiple linear regression and neural network analysis models were constructed using *B. atrophaeus* and ovalbumin spectra and limits of detection were calculated. Classification of the agent surrogates' LIBS spectra was attempted using a neural network model. False negative rates of zero percent were observed for *B. atrophaeus* (100 colony forming units-cfu) spore spectra using the neural network model for classification.

Localized Surface Plasmon Resonance of Gold Nanoparticle-Modified Chitosan Films for Heavy-Metal Ions Sensing

Praig, V.G., H. McIlwee, C.L. Schauer, R. Boukherroub, and A. Szunerits.  
Journal of Nanoscience and Nanotechnology, Vol 9 No 1, p 350-357, Jan 2009

Gold nanoparticles (Au NPs) were entrapped in and between a cross-linked thin chitosan film cast on a glass substrate. The glass/chitosan/Au NPs interface was formed by casting Au NPs/chitosan solutions onto flat glass supports, followed by exposure to Au NPs in solution, and repeating the casting procedure for the desired number of layers. The optical properties of the resulting interfaces and their ability to sense various heavy metal ions, such as Fe<sup>3+</sup> and Cu<sup>2+</sup>, were investigated utilizing the phenomenon of localized surface plasmon resonance visualized by UV/V is absorption spectroscopy. The interfaces showed different optical behavior to the presence of the different metal ions. Fe<sup>3+</sup> showed a detection limit of 0.5  $\mu$ M and a linear range up to ~2  $\mu$ M, whereas for Cu<sup>2+</sup>, the detection limit is 0.5 mM with a linear range up to ~5 mM due to a lower binding capability.

Locating Oil Spills under Sea Ice Using Ground-Penetrating Radar

Bradford, J.H., L.M. Liberty, and D.F. Dickins.  
The Leading Edge 2008 27: 1424-1435

As development in the Alaska oilfields increases, so does the potential for accidental oil spills in the arctic marine environment. The need for reliable systems to detect oil trapped in a range of ice conditions remains at the forefront of continued efforts to improve response to ocean spills.

### Long-Path Supercontinuum Absorption Spectroscopy for Measurement of Atmospheric Constituents

Brown, D.M., K. Shi, Z. Liu, and C.R. Philbrick, Pennsylvania State Univ.  
Optics Express, Vol 16 No 12, p 8457-8471, 9 June 2008

A supercontinuum source has been proposed as a new tool for measurement of minor species concentrations on long paths through the atmosphere. This paper describes results from recent experiments that demonstrate the potential for differential absorption spectroscopy and spectral pattern-recognition/differential-absorption lidar measurements utilizing a supercontinuum source. As an initial example of this measurement approach, the results feature the quantification of water vapor concentration through indoor and outdoor path absorption measurements using a collimated supercontinuum source. Experimental spectra were compared with equivalent simulations from MODTRAN versions 4 and 5 to examine the water-vapor band between 1300 and 1500 nm to demonstrate the feasibility of the approach.

### Luminescent Lanthanide Nanoparticles as Labels in DNA Microarrays for Quantification of Methyl Tertiary Butyl Ether Degrading Bacteria

Son, A., M. Nickkova, D. Dosev, I.M. Kennedy, and K.R. Hristova, Univ. of California Davis.  
Journal of Nanoscience and Nanotechnology, Vol 8 No 5, p 2463-2467, May 2008

Lanthanide nanoparticles were applied for DNA quantification in a microarray platform as a substitute for conventional organic fluorophores in a demonstration of a non-PCR-based DNA microarray assay for quantifying bacteria capable of biodegrading MTBE. Probe DNA was immobilized on a glass surface, hybridized with biotinylated target DNA, and subsequently incubated with Neutravidin-biofunctionalized nanoparticles. The fluorescence spot intensities, measured by a commercial laser scanner, showed a linear relationship with bacterial 16S rDNA over a range of target DNA concentrations, while the background fluorescence remained low. The present sensitivity of the assay is 10 pM of target DNA. The exercise showed the selectivity of the DNA/nanoparticle probes to discriminate a non-target DNA with two base-pairs mismatch in the 16S rDNA gene sequence. The use of Eu:Gd<sub>2</sub>O<sub>3</sub> nanoparticles as biolabels provides a relatively non-toxic, inexpensive, rapid, and sensitive alternative to the materials currently used in DNA microarrays.

### Mapping the Nitrate Plume at Hanford's BC Cribs with Electrical Resistivity Rucker, D.F.

SEG Expanded Abstracts, Vol 27, p 2704-, 2008

At DOE's Hanford Site, a geophysical characterization project was conducted at the BC Cribs and Trenches (BCCT) Area, which consists of 26 waste disposal trenches and cribs that received 30 million gallons of liquid waste from the uranium recovery and ferrocyanide processes associated with reprocessing nuclear fuel. Geophysical characterization at the 50 acre site primarily involved electrical resistivity applied using a pole-pole array from the surface along a series of linear transects oriented orthogonally. The site was characterized by a network of 55 lines ranging in length from about 400 to 850 meters with a total of approximately 24.4 line kilometers. The data were compiled and inverted in three dimensions. Low resistivity (or high conductivity) is indicative of soil and porewater of high ionic strength resulting from the



migration of nitrate and other inorganic constituents through the vadose zone. High spatial density soil data from several boreholes, which included coincident nitrate concentrations, electrical conductivity, and Tc-99, were used to form field-based petrophysical relations that could transform the electrical resistivity data into a nitrate concentration. The nitrate plume was shown to extend laterally beyond the original boundaries of the waste sites. Through the mapping exercise, investigators postulated that the waste did not reach the water table approximately 105m below ground surface.

#### Mass Recovery Methods for Trichloroethylene in Plant Tissue

Gopalakrishnan G, C. Werth, and M. Negri

Environmental Toxicology and Chemistry, Vol 2009 Jan 21:1. [Epub ahead of print]

The use of plants as monitoring devices is a novel method that could result in significant cost savings at contaminated groundwater sites. This paper presents a simple, robust, inexpensive technique to recover most of the contaminant (i.e., TCE) in plant branch tissue, irrespective of the age or species of the plant. Headspace and solvent extraction techniques in the literature were evaluated, including headspace extraction at different incubation times and temperatures, and solvent extraction using hexane or hot methanol. Extraction using hot methanol was found to be a relatively fast, simple, and reliable method that recovered more than 89% of TCE present in branches of 5 different tree species.

#### Measurement of Freely Dissolved PAH Concentrations in Sediment Beds Using Passive Sampling with Low-density Polyethylene Strips

Fernandez, L.A., J.K. MacFarlane, A.P. Tcaciuc, and P.M. Gschwend, MIT, Cambridge, MA.

Environmental Science & Technology, Vol 43 No 5, p 1430-1436, 1 Mar 2009

A method to assess hydrophobic organic chemical contamination in sediments was developed using polyethylene (PE) passive samplers inserted directly in the intact sediment beds to measure freely dissolved concentrations of the contaminants. Performance reference compounds (d10-phenanthrene, d10-pyrene, and d12-chrysene) impregnated into the PE before use, allowed porewater concentrations to be deduced in days instead of months--exposure times much shorter than would be required for sampler equilibration. Three different sediments were used in the laboratory, and PE-deduced porewater concentrations of six native PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, and chrysene) matched results from air/bridge testing and from direct porewater extractions after correcting for colloid effects. PE strips, deployed from a boat in Boston Harbor, yielded concentrations that were like those measured in porewaters from a sediment core collected nearby. Equilibrium partitioning estimates were always much higher (up to 100 times higher) than those measured using the other methods, suggesting the large inaccuracy of that approach. The results indicate that PE passive sampling can improve the accuracy of assessing the hazards posed by PAHs in sediment beds.

#### Measuring Mercury with Nanotechnology

Royal Melbourne Institute of Technology (RMIT) University News Release, 27 May 2009

RMIT's research on mercury monitoring through nano-engineered gold surfaces has been featured on the cover of Physical Chemistry and Chemical Physics. The research team behind the

publication was led by Professor Suresh Bhargava with Dr Prashant Sawant, Dr Vipul Bansal, Dr Samuel Ippolito and Dr Ylias Sabri. RMIT researchers have used breakthrough nanotechnology to create a pioneering sensor that can measure mercury with precision. The mercury sensor developed by RMIT's Industrial Chemistry Group uses tiny flecks of gold that are nano-engineered to make them irresistible to mercury molecules. In the effort to reduce mercury contamination in the environment and the associated health risks, accurately measuring the toxin has become a priority for mercury-emitting industries like coal-burning power generators and alumina refineries. The complex mixtures of VOCs, ammonia, and water vapor emitted from stacks can interfere with the monitoring systems of the present generation of mercury sensors. Sensors are needed that are robust enough to cope with the industrial environment but also sensitive enough to give precise readings of the amount of mercury vapor in the emissions. The mercury sensor was developed with the use of patented electrochemical processes that enabled the RMIT researchers to alter the surface of the gold, forming hundreds of tiny nano-spikes, each one about 1,000 times smaller than the width of a human hair. These nano-engineered surfaces are used with existing technologies, such as quartz crystal microbalances -- a finely tuned set of scales that measure weight down to molecular levels -- to determine the levels of mercury in the atmosphere. Although gold attracts mercury and vice versa, a regular gold surface doesn't absorb much vapor, and any measurements it makes are inconsistent. The nano-engineered gold surfaces are 180% more sensitive than non-modified surfaces and are unaffected by the usual gases found in effluent gas streams. The sensors the team has created so far using the nano-engineered surfaces have worked successfully at a range of extreme temperatures over many months. Funded through an Australian Research Council Linkage grant, the project was supported by industry partners who now have engaged RMIT to develop a mercury sensing device for a pilot plant trial at an Australian refinery. The Industrial Chemistry Group's multidisciplinary team will extend its work on mercury removal technology through an international collaboration with the Indian Institute of Chemical Technology at Hyderabad, focusing on putting the nano-engineered gold surfaces to use in a system that can absorb and remove mercury vapor from the air. A description of this technology has been published in *Physical Chemistry & Chemical Physics* 11(14):2374-8(2009) as "In-depth nano-scale analysis of complex interactions of Hg with gold nanostructures using AFM-based power spectrum density method," by P. Sawant, et al.

#### Method 314.2: Determination of Perchlorate in Drinking Water Using Two-Dimensional Ion Chromatography with Suppressed Conductivity Detection

Wagner, H.P., B.V. Pepich, D. Later, C. Pohl, K. Srinivasan, B. De Borja, R. Lin, and D.J. Munch.

EPA 815-B-08-001, Version 1, 42 pp, July 2008

Water samples are collected in the field using a sterile filtration technique. A 2.0 to 4.0-mL sample aliquot is injected onto a 4-mm ion chromatographic (IC) column. Separation of perchlorate is achieved in the first dimension (1-D) using 35 mM KOH at a flow rate of 1.0 mL per minute. Approximately 5-6 mL of the suppressed eluent containing the perchlorate is diverted from the 1-D column to a concentrator column used in place of the sample loop of the second dimension (2-D) injection valve. The concentrator column has low backpressure but sufficient capacity to trap the perchlorate ions quantitatively in the suppressed eluent. In this manner, perchlorate is separated from other matrix ions and concentrated on a trapping column. The heart-cut portion of the 1-D chromatogram is eluted off the concentrator column and onto a

smaller diameter (2 mm diameter) guard and analytical column that have different selectivity from the 1-D columns to facilitate the 2-D separation using 65 mM KOH at a flow rate of 0.25 mL per minute. Perchlorate is quantitated using the external standard method.

[http://www.epa.gov/safewater/methods/analyticalmethods\\_ogwdw.html](http://www.epa.gov/safewater/methods/analyticalmethods_ogwdw.html)

Method 522: Determination of 1,4-Dioxane in Drinking Water by Solid Phase Extraction (SPE) and Gas Chromatography/Mass Spectrometry (GC/MS) with Selected Ion Monitoring (SIM)  
Munch, J.W. and P.E. Grimmett.

EPA 600-R-08-101, Version 1, 41 pp, Sep 2008

A water sample that has been dechlorinated and preserved with a microbial inhibitor is fortified with the isotopically labeled surrogate analyte (SUR), 1,4-dioxane-d(8). The sample is extracted by one of two SPE options. In option 1, a 500-mL sample is passed through an SPE cartridge containing 2 g of coconut charcoal to extract the method analyte and SUR. In option 2, a 100-mL sample is extracted on a Waters AC-2 Sep-Pak or Supelco Supelclean ENVI-Carb Plus cartridge. In either option, the compounds are eluted from the solid phase with a small amount of dichloromethane, approximately 9 mL or 1.5 mL, respectively. The extract volume is adjusted, and the internal standard (IS), tetrahydrofuran-d(8), is added. Finally, the extract is dried with anhydrous sodium sulfate. Analysis of the extract is performed by GC/MS. The data provided in this method were collected using splitless injection with a high-resolution fused silica capillary GC column that was interfaced to an MS operated in the selected ion monitoring (SIM) mode. The analyte, SUR, and IS are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical GC/MS conditions. The concentration of the analyte is determined by comparison to its response in calibration standards relative to the IS. Although the performance data presented in Section 17 of this method were obtained in the SIM mode for maximum method sensitivity, the sample extract analysis also can be performed in full scan mode if the sensitivity achieved meets the data user's requirements.

<http://www.epa.gov/nerlcwww/ordmeth.htm>

Method Development for the Analysis of 1,4-Dioxane in Drinking Water Using Solid-Phase Extraction and Gas Chromatography-Mass Spectrometry  
Grimmett, P.E. and J.W. Munch.

Journal of Chromatographic Science, Vol 47 No 1, p 31-39, Jan 2009

U.S. EPA's National Exposure Research Laboratory (NERL) has developed a method for the analysis of 1,4-dioxane in drinking water at ng/L concentrations. The method consists of an activated carbon solid-phase extraction of 500-mL or 100-mL water samples using dichloromethane as the elution solvent. The extracts are analyzed by gas chromatography/mass spectrometry in selected ion monitoring mode. In the NERL laboratory, recovery of 1,4-dioxane ranged from 94 to 110% in fortified laboratory reagent water, and recoveries of 96 to 102% were demonstrated for fortified drinking water samples. The relative standard deviations for replicate analyses were less than 6% at concentrations exceeding the minimum reporting level.

Molecularly Imprinted Nanoporous Polyacrylate Surface for Benzo(a)Pyrene Recognition  
Krupadam, R.J., B. Bhagat, M.S. Khan, and P.S. Wate.

Journal of Nanoscience and Nanotechnology, Vol 9 No 9, p 5441-5447, Sep 2009

Molecularly imprinted polymers (MIPs) were synthesized using co-polymerization of methacrylic acid with the cross-linking agent ethylene glycol dimethacrylate in the presence of benzo(a)pyrene (BAP), followed by the extraction of BAP from the cross-linked polymer matrix. This MIP contains nanopores that are geometrically specific to the BAP molecule. The adsorption capacity of BAP onto MIP was determined using equilibrium experiments. Cross-reactivity (CR) experiments conducted to assess the selectivity of BAP in the presence of 5 other PAHs showed that the PAH molecules smaller in molecular length than BAP (i.e., pyrene), showed higher interference (up to 40%) compared with other PAH compounds. By increasing the concentration of other PAH compounds (100 ug/mL), the selectivity of MIP was reduced from 3.5 to 1.6. The value of the equilibrium binding constant for BAP was larger than for other PAH compounds, for which  $K_E$  values ranged from 0.011 to 0.028 ug/mL. The prepared MIP shows greater binding capacity and selectivity due to the creation of homogenous nanopores patterned uniformly in the polymer matrix.

Monitoring Aromatic Hydrocarbon Biodegradation by Functional Marker Genes

Nyyssönen, M., R. Piskonen, and M. Itävaara, Technical Research Centre of Finland, Espoo.  
Environmental Pollution, Vol 154 No 2, p 192-202, July 2008

In an investigation of the potential of functional gene array analysis to monitor changes in the amount of functional marker genes as indicators of contaminant biodegradation, a prototype functional gene array was developed for targeting key functions in the biodegradation of naphthalene, toluene, and xylenes. Internal standard probe based normalization was introduced to facilitate comparison across multiple samples. Coupled with one-color hybridization, the signal normalization improved the consistency among replicate hybridizations, resulting in better discrimination for the differences in the amount of target DNA. During naphthalene biodegradation in a PAH-contaminated soil slurry microcosm, the normalized hybridization signals in naphthalene catabolic gene probes agreed well with the amount of naphthalene-degradation genes and the production of (14)CO<sub>2</sub>. Gene arrays can provide an efficient means for monitoring contaminant biodegradation in the environment.

Multi-Incremental Sampling, Part 1: Impacts on Sampling and Sample Processing

Hewitt, A.D., M.E. Walsh, M.R. Walsh, and S.R. Bigl (U.S. Army ERDC-CRREL, Hanover, NH); M.A. Chappell (U.S. Army ERDC-EL, Vicksburg, MS); C.A. Ramsey (EnviroStat, Inc., Fort Collins, CO).

The Business of Brownfields: 2009 Conference Proceedings, 15-17 April, abstract only, 2009

Very little guidance has been available for site characterization activities that address the concentration and mass of energetic residues in military training range soils. As a consequence, the characterization of energetic residues depends heavily on sampling and analysis plans adopted by different branches of the government. Experiences gained through more than 25 training range studies conducted by ERDC-CRREL and others under SERDP projects ER-1155 and ER-1481 and the Corps of Engineers Distributed Source Program has led to modifications of EPA Method 8330 in which techniques are described that allow scientifically defensible project

data quality objectives to be achieved. See Method 8330B in EPA's "Test Methods for Evaluating Solid Waste" (SW-846) at <http://www.epa.gov/epawaste/hazard/testmethods/sw846/>. See also the "Guide to Implementing EPA SW-846 Method 8330B," DoD Environmental Data Quality Workgroup, June 2008, at [http://www.itrcweb.org/Documents/TeamResources\\_MIS/Final8330BImplementationGuide061708.pdf](http://www.itrcweb.org/Documents/TeamResources_MIS/Final8330BImplementationGuide061708.pdf)

Multi-Incremental Sampling, Part 2: Laboratory Support for Multi-Increment Sampling  
Bruce, M. (TestAmerica, Inc, North Canton, OH); L. Penfold (TestAmerica, Inc, Arvada, CO).  
The Business of Brownfields: 2009 Conference Proceedings, 15-17 April. 27 slides, 2009

The U.S. Army Corp of Engineers has adapted sample collection techniques from the mining and agricultural fields for use on military training ranges, which have heterogeneous distributions of energetic contaminants. These multi-increment sampling procedures have also been applied to both metals and organics. Large samples in the 1- to 5-kg range typically are sent to the lab for processing and sub-sampling prior to analysis. The laboratory process for energetics is described in SW-846 Method 8330B. The same principles have also been adapted for other analyte groups. This presentation summarizes the various laboratory processing options for multi-increment samples and covers the advantages and limitations of each. These processing options include drying, sieving, chopping, grinding, and wet and dry mixing. Sub-sampling techniques, such as multi-increment and line & scoop, also are covered.

[http://www.itrcweb.org/Documents/TeamResources\\_MIS/BruceMarkTALNEMC2008LaboratorySupportforMultiIncrementSampling.pdf](http://www.itrcweb.org/Documents/TeamResources_MIS/BruceMarkTALNEMC2008LaboratorySupportforMultiIncrementSampling.pdf)

A Multi-Stage Sampling Strategy for the Delineation of Soil Pollution in a Contaminated Brownfield

Verstraete, S. and M. Van Meirvenne, Ghent Univ., Belgium.  
Environmental Pollution, Vol 154 No 2, p 184-91, July 2008

A multi-stage sampling strategy based on sequential Gaussian simulation was developed to optimize the step-wise selection of a small number of additional samples to delineate soil pollution. This strategy was applied to a Pb-contaminated Belgian brownfield of 5.2 ha. Starting from an initial number of 240 samples in stage 1 (20 stages were used), additional samples were added at 25 per stage, and the reduction of uncertainty in the Pb delineation was monitored. By stage 6, a local optimum was found based on the median conditional coefficient of variation. An independent validation confirmed that this index was to be preferred over the median conditional variance. At the Belgian brownfield, the procedure indicated that 365 selected samples would have been sufficient, representing a gain of 70.7% in sampling effort compared to current practice, which required 1,245 samples.

A Multiscale Stratigraphic Analysis of Shallow Unconsolidated Sediments: A New Approach for Hydrogeophysical Characterization in Heterogeneous Environments for Contaminant Remediation

Cameron-Gonzalez, A.E., C. Knapp, A. Addison, and M. Waddell.  
SEG Expanded Abstracts, Vol 27, p 2714-2718, 2008

The identification of porous layers and assessment of their saturation, the characterization of sediments, the identification of bedrock, and the analysis of shallow stratigraphy are examples

of topics of primary interest in near-surface applications, especially in areas with near-surface contaminants. The authors discuss work conducted to integrate geophysical methods with geological and hydrological data at the P Reactor Area at the Savannah River Site to develop new approaches for hydrogeophysical characterization in heterogeneous environments.

Nano Level Detection of Cd(II) Using Poly(Vinyl Chloride) Based Membranes of Schiff Bases  
Gupta, V.K., M. Al Khayat, A.K. Singh, and M.K. Pal, Indian Inst. of Technology at Roorkee.  
*Analytica Chimica Acta*, Vol 634 No 1, p 36-43, 16 Feb 2009

The authors describe the construction and performance characteristics of polymeric membrane electrodes based on two neutral ionophores for quantification of cadmium ions. The influences of membrane compositions on the potentiometric response of the electrodes were found to improve the performance characteristics substantially. The best performance was obtained with the electrode having a membrane composition (w/w) of (L(1)) (2.6%):PVC (31.6%):DOP (63.2%):NaTPB (sodium tetraphenyl boron) (2.6%). The electrode performs satisfactorily over a wide pH range (2.0 to 8.5) with a fast response time of 11 seconds. The electrode works in partially nonaqueous media up to 40% (v/v) content of methanol, ethanol, and acetonitrile and remains effective for a period of 2.5 months. The analytical usefulness of the proposed electrode was evaluated by its application to the determination of cadmium in cigarette samples, and its practical utility has been observed in the presence of surfactants.

A New Scheme for Biomonitoring Heavy Metal Concentrations in Semi-Natural Wetlands  
Batzias, A.F. and C.G. Siontorou, Univ. of Piraeus, Greece.  
*Journal of Hazardous Materials*, Vol 158 No 2-3, p 340-358, 30 Oct 2008

A wetland biomonitoring framework for heavy metal concentrations is based on the dynamic integration of biological assemblages and biosensors. This synergistic scheme minimizes uncertainty and monitoring costs and increases the reliability of pollution control and abatement. The initial network consists of both biosensors and species. Once the monitoring efficiency of natural species has been verified by the biosensors, the biosensor network moves to the next wetland, following a circular pattern, until all wetland areas have a fully functional natural monitoring scheme. By combining species recalibration with periodic revisiting of the biosensors, the scheme progressively reaches a quasi steady-state (including seasonality), thus ensuring reliability and robustness. This framework is being pilot-tested in Voiotia, Greece, for assessing chromium levels. The system has been designed to cover short-, medium- and long-term monitoring requirements. The results to date support the use of the proposed scheme for monitoring heavy metals.

Novel Sampling Methods for Atmospheric Semi-Volatile Organic Compounds (SOCs) in a High Altitude Alpine Environment  
Offenthaler, I., G. Jakobi, A. Kaiser, M. Kirchner, N. Kraeuchi, B. Niedermoser, K.W. Schramm, I. Sedivy, M. Staudinger, G. Thanner, P. Weiss, and W. Moche.  
*Environmental Pollution*, Vol 2009 Jul 4. [Epub ahead of print]

High- and low-volume active air samplers were deployed with bulk deposition samplers to sample atmospheric SVOCs under the adverse conditions of a mountain environment. The

active samplers employed separate filters for different European source regions, and the filters were switched depending on the daily trajectory forecasts. The sampling continued on three alpine summits over five periods of four months. The prevailing trajectories varied more strongly between sampling periods than between stations. The sampling equipment (active and bulk deposition) proved dependable for operation in a mountain environment, with idle times arising mainly due to non-routine manipulations and connectivity.

#### On-Line Purge and Trap GC-MS for Monitoring 1,3-Dichloropropene in Agricultural Water and Soil Samples

Frenich, A.G., S.C. Aguado, V.J.L. Martinez, and F.J. Arrebola.

Journal of Chromatographic Science, Vol 47 No 1, p 26-30, Jan 2009

A simple and reliable method using on-line purge and trap gas chromatography mass spectrometry has been developed for the determination of the fumigant 1,3-dichloropropene (1,3-DCP) in agricultural water and soil samples. Limit of detection values of 0.05 ug/L for water and 0.005 ug/Kg for soils were obtained, while limits of quantitation were of 0.1 ug/L for water and 0.01 mg/kg for soils. Good recoveries (93 to 104%) and precision values (<6%) were obtained for the target compound in the studied matrices. This methodology has been applied successfully to the analysis of groundwater samples from an agricultural area in southern Spain, although 1,3-DCP was not detected. The method also was applied to soil samples from a greenhouse treated with a soil fumigant containing 1,3-DCP.

#### Onsite Testing for Arsenic: Field Test Kits

Feldmann, J., Univ. of Aberdeen, UK.

Reviews of Environmental Contamination and Toxicology, Vol 197, p 1-15, 2009

The performance of existing field test kits for arsenic has generally been unsatisfactory. Reports of false-negative and false-positive results exceeding 30% are not unusual, although more recent techniques appear to be more reliable; however, studies using these recent techniques had only to meet a local water standard of 50 ug/L. If the new WHO guideline (10 ug/L) is adopted as a decision-making criterion, the sensitivity of most arsenic testing kits is not sufficient, particularly in the hands of untrained operators. New developments with sophisticated electrochemical sensors might deliver the needed sensitivity but suffer from matrix effects, even with trained operators. A failing of all available commercial methods is that they do not determine organo-arsenicals, despite the fact that, in some cases, organic species may be the predominant ones present.

#### Optimal Redesign of Groundwater Quality Monitoring Networks: a Case Study

Masoumi, F. and R. Kerachian.

Environmental Monitoring and Assessment, 2009 Feb 6. [Epub ahead of print]

This paper presents a new methodology for optimal redesign of groundwater quality monitoring networks. The measure of transinformation in discrete entropy theory and the transinformation/distance (T-D) curves are used to quantify the efficiency of sampling locations and sampling frequencies in a monitoring network. The existing uncertainties in the T-D curves are taken in to account using the fuzzy set theory. The C-means clustering method is also used to



classify the study area to some homogenous zones. The fuzzy T-D curve of the zones then is used in a multi-objective hybrid genetic algorithm-based optimization model. The proposed methodology has been used for optimal redesign of the monitoring network of the Tehran aquifer in the Tehran metropolitan area, Iran.

#### Packing Procedures for High Efficiency, Short Ion-Exchange Columns for Rapid Separation of Inorganic Anions

Tyrrell, E., E.F. Hilder, R.A. Shalliker, G.W. Dicinoski, R.A. Shellie, M.C. Breadmore, C.A. Pohl, and P.R. Haddad, Univ. of Tasmania, Hobart, TAS, Australia.

Journal of Chromatography A, Vol 1208 Nos 1-2, p 95-100, 24 Oct 2008

In an optimized packing procedure for the production of high-efficiency, particle-packed, short ion-exchange columns, slurry-packing techniques were applied to a series of interconnected short columns, with the columns situated intermediate between the inlet and outlet ends of the series being used for separations. The fast separation and determination of inorganic anions was achieved using short (4 mm ID, 30 mm long) columns packed with Dionex AS20 high-capacity anion-exchange stationary phase. Seven inorganic anions (bromate, chloride, chlorate, nitrate, sulfate, chromate, and perchlorate) were separated in 2.6 min using a hydroxide gradient and a flow-rate of 1.8 mL/min. Total analysis time, including re-equilibration, was 3.5 min. Under isocratic conditions, the home-packed columns gave efficiency values of 43,000 N/m for chloride at a flow-rate of 0.3 mL/min, compared to 54,000 N/m for a commercial 250 mm AS20 column at the same flow rate; however, the short columns had a sample throughput that was roughly threefold higher. The short home-packed columns could be produced reproducibly and performed consistently over extended use.

#### The Partition Intervalometer: A Programmable Underwater Timer for Marking Accumulated Sediment Profiles Collected in Anderson Sediment Traps: Development, Operation, Testing Procedures, and Field Results

Rendigs, R.R., R.Y. Anderson, J. Xu, R.E. Davis, and E. Bergeron.

U.S. Geological Survey Open-File Report 2009-1101, 2009

This manual illustrates the development of a programmable instrument designed to deploy a series of wafer-shaped discs (partitions) into the collection tube of a sediment trap in various aquatic environments. These hydrodynamically shaped discs are deployed at discrete time intervals from the Intervalometer and provide markers that delineate time intervals within the sediments that accumulate in the collection tube. The timer and mechanical system are lodged in an air-filled, water-tight pressure housing that is vertically hung within the confines of a cone-shaped sediment trap. The instrumentation has been operationally pressure tested to an equivalent water depth of approximately 1 km. Flaws discovered during extensive laboratory and pressure testing resulted in the implementation of several mechanical modifications (such as a redesign of the rotor and the discs) that improved the operation of the rotor assembly as well as the release of discs through the end cap. These results also identified a preferred azimuth placement of the rotor disc relative to the drop hole of the end cap. In the initial field trial, five sediment traps and coupled Intervalometers were attached to moored arrays and deployed at two sites off the coast of Southern California for approximately 8 months. Each of the instruments released 18 discs at the programmed 10 day intervals, except one unit, which experienced a

malfunction after approximately 4 months. Most of the discs oriented in a near-horizontal position upon the surface of the sediment in the collection tubes. Sampling of the sediments for geochemical analyses was improved by these clearly defined markers, which indicated the changes in the flux and nature of sediments accumulated during the deployment period of each sediment trap. <http://pubs.usgs.gov/of/2009/1101/>

#### Passive Sampling and Analyses of Common Dissolved Fixed Gases in Groundwater Spalding, B.P. and D.B. Watson.

Environmental Science & Technology, Vol 42 No 10, p 3766-3772, 15 May 2008

An in situ passive sampling and gas chromatographic protocol was developed for analysis of the major and several minor fixed gases (He, Ne, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O) in groundwater. Using argon carrier gas, a HayeSep DB porous polymer phase, and sequential thermal conductivity and reductive gas detectors, the protocol achieved sufficient separation and sensitivity to measure the mixing ratio of all these gases in a single 0.5 mL gas sample collected in situ, stored, transported, and injected using a gastight syringe. Within 4 days of immersion in groundwater, the simple passive in situ sampler, whether initially filled with He or air, attained an equivalent and constant mixing ratio for 5 of the 7 detected gases.

#### Passive Sampling Combined with Ecotoxicological and Chemical Analysis of Pharmaceuticals and Biocides -- Evaluation of Three Chemcatcher Configurations

Vermeirssen, E.L., N. Bramaz, J. Hollender, H. Singer, and B.I. Escher.

Water Research, Vol 43 No 4, p 903-914, Mar 2009

The Chemcatcher is a sampler for polar organic compounds. In an investigation of the duration of integrative sampling and the effects of flow rate on performance, Chemcatchers were fitted with one of three configurations: (1) Empore styrenedivinylbenzene (SDB) XC disks (XC), (2) SDB-RPS disks (RPS), or (3) SDB-RPS disks covered with a polyethersulfone membrane (RPS-PES). Samplers were either exposed to treated sewage effluent for 5 days at various flow rates, or at a single flow rate with overlapping exposures of 3 to 24 days. Chemical analysis focused on a set of pharmaceuticals and biocides, and ecotoxicological analysis measured inhibition of photosystem II in algae. For compounds with  $\log K(OW) > 2$ , both XC and RPS disks respond dynamically to higher flow rates; uptake increased up to 5-fold when flow increased from 0.03 to 0.37 m/s. At a flow rate of 0.13 m/s, the integrative window of SDB disks approached 6 days for more hydrophobic compounds ( $\log K(OW) > 3.5$ ). The RPS-PES configuration was less affected by flow and also showed an extended integrative window (up to 24 days). The membrane causes a lag phase of up to 2.3 days, which limits interpretation of data from sampling periods of less than 10 days.

#### Perchlorate Detection at Nanomolar Concentrations by Surface-Enhanced Raman Scattering Gu, B., C. Ruan, and W. Wang.

Applied Spectroscopy, Vol 63 No 1, p 98-102, Jan 2009

A sensing technique based on surface-enhanced Raman scattering (SERS) was developed for rapid screening and monitoring of perchlorate in groundwater and surface water. The technique was found to be capable of detecting perchlorate at concentrations as low as 10<sup>-9</sup> M

(or approximately 0.1 ug/L) by using 2-dimethylaminoethanethiol (DMAE)-modified gold nanoparticles as a SERS substrate. Quantitative analysis of perchlorate was validated with good reproducibility in both simulated and actual contaminated groundwater samples. When coupled with a portable Raman spectrometer, this technique has the potential to be used as an in situ, rapid screening tool for perchlorate in the environment.

#### Performance of the Chemcatcher Passive Sampler When Used to Monitor 10 Polar and Semi-Polar Pesticides in 16 Central European Streams, and Comparison with Two Other Sampling Methods

Schaefer, R.B., A. Paschke, B. Vrana, R. Mueller, and M. Liess.

Water Research, Vol 42 Nos 10-11, p 2707-2717, May 2008

The Chemcatcher, an aquatic passive sampling device consisting of a sampler body and an Empore disk as receiving phase, was used to monitor acetochlor, alachlor, carbofuran, chlorfenvinphos, alpha-endosulfan, fenpropidin, linuron, oxadiazon, pirimicarb and tebuconazole in 16 Central European streams. Equipped with an SDB-XC Empore disk, the chemcatcher detected 7 of the studied pesticides with a total of 54 detections. The time-weighted average (TWA) concentrations reached up to 1 ug/L for acetochlor and alachlor. Toxic units derived from these concentrations explained reasonably well the observed ecological effects of pesticide stress that were measured with the SPEAR index. In a follow-up analysis, the Chemcatcher performance was compared with that of two other sampling systems. The results obtained with the Chemcatcher closely matched those of the event-driven water sampler. By contrast, the TWA concentrations were not correlated significantly with concentrations on suspended particles. The Chemcatcher appears to be suitable for the monitoring of polar organic toxicants and presents an alternative to conventional spot sampling for monitoring sporadically occurring pollutants.

#### Performance of Traditional and Molecular Methods for Detecting Biological Agents in Drinking Water

Francy, D.S., R.N. Bushon, A.M.G. Brady, E.E. Bertke, C.M. Kephart, C.A. Likirdopulos, B.E. Mailot, F.W. Schaefer III, and H.D.A. Lindquist.

U.S. Geological Survey Scientific Investigations Report 2009-5097, 17 pp, 2009

To reduce the impact from a possible bioterrorist attack on drinking-water supplies, analytical methods are needed to detect the presence of biological agents in water rapidly. Drinking-water samples were collected at 9 water-treatment plants in Ohio to assess the performance of a molecular method in comparison to traditional analytical methods that take longer to perform. Two 100-liter samples were collected at each site during each sampling event; one was seeded in the laboratory with six biological agents--*Bacillus anthracis*, *Burkholderia cepacia* (as a surrogate for *Bu. pseudomallei*), *Francisella tularensis*, *Salmonella Typhi*, *Vibrio cholerae*, and *Cryptosporidium parvum*. The seeded and unseeded samples were processed by ultrafiltration and analyzed by use of quantitative polymerase chain reaction (qPCR), a molecular method, and culture methods for bacterial agents or the immunomagnetic separation/fluorescent antibody (IMS/FA) method for *C. parvum* as traditional methods. Six replicate seeded samples also were processed and analyzed. The results indicate that the qPCR method can be used for rapid detection of *B. anthracis*, *F. tularensis*, and *V. cholerae* with some certainty in drinking-water samples, but additional work would be needed to optimize and test qPCR for *Bu. cepacia*

and *C. parvum* and establish relations to traditional methods. The specificity for the *V. cholerae* assay needs to be further investigated. Evidence is provided that ultrafiltration and qPCR are promising methods to rapidly detect biological agents in the nation's drinking-water supplies and thus reduce the impact and consequences from intentional bioterrorist events. This may be the first study to compare the use of traditional and qPCR methods to detect biological agents in large-volume drinking-water samples. <http://pubs.usgs.gov/sir/2009/5097/>

Portable SERS Instrument for Explosives Monitoring: ESTCP Cost and Performance Report  
Environmental Security Technology Certification Program (ESTCP), Project CU-9917, 41 pp,  
Jan 2008

A new method for monitoring explosives constituents has been developed based on surface-enhanced Raman spectroscopy (SERS). Raman is a vibrational spectroscopic method that produces a unique "fingerprint" spectrum for each analyte, allowing the components of a mixture to be discriminated in a single test. Normally a weak phenomenon, the Raman signal is enhanced up to  $10^6$  by adsorbing analytes onto a noble metal surface (colloidal gold, in this case), rendering it suitable for trace analysis. Project CU-9917 was designed to field and demonstrate the potential of SERS to reduce (versus lab and field methods) the time, cost, and waste generated per analysis while providing discriminate quantification of multiple analytes (even those within a chemical class) in a single measurement. The project entailed three demonstrations at two Army facilities: Alabama Army Ammunition Plant (ALAAP) and Umatilla Chemical Depot (UMCD). The objectives were to demonstrate (1) the general fieldability and ease of use of the SERS instrument, (2) capability for quantifying multiple explosives—TNT, 2,4-DNT, TNB, RDX, and HMX—in a single measurement, (3) capability for at-line remediation process monitoring using the SERS method, (4) capability for in situ and ex situ groundwater monitoring from a cone penetrometer platform, (5) improved capability for discriminating explosives versus colorimetry, and (6) the cost/benefit of the SERS technology. All six cost and performance objectives of this project were met. The demonstration illustrated some of the most important advantages of SERS: reliable quantification of important individual explosives in water samples at concentrations of regulatory relevance; faster results and lower cost than laboratory Method 8330; comparable speed, lower cost, simpler procedures, less matrix interference, and better discrimination of individual explosives compared to colorimetry; and applicability to virtually any environmental water monitoring application, such as groundwater well monitoring, expedited site characterization, and remediation process monitoring. Report at <http://www.estcp.org/Technology/upload/ER-9917-C&P.pdf>

Potential for Microbial Degradation of cis-Dichloroethene and Vinyl Chloride in Streambed Sediment at the U.S. Department of Energy, Kansas City Plant, Missouri, 2008  
Bradley, Paul M.

U.S. Geological Survey Scientific Investigations Report 2009-5137, 12 pp, 2009

Carbon-14 (C-14) radiotracer-based microcosm experiments were conducted to assess the potential for biotic and abiotic degradation of cis-DCE and vinyl chloride (VC) in streambed sediments at DOE's Kansas City Plant in Missouri. The investigation focused on the surficial and underlying hyporheic sediment from the Blue River and its tributaries, Indian Creek and Boone Creek. Substantial degradation of radiolabeled cis-DCE and VC to  $^{14}\text{CO}_2$  was observed in all

viable surficial sediment microcosms prepared under oxic conditions. No significant accumulation of reductive dechlorination products was observed under these oxic incubation conditions. The results indicate that microbial mineralization processes involving direct oxidation or co-metabolic oxidation are the primary mechanisms of cis-DCE and VC biodegradation in oxic stream sediment at the Kansas City Plant. Substantial mineralization of VC also was observed in all viable surficial sediment microcosms incubated in the absence of detectable oxygen (dissolved oxygen concentrations <25 ug/L). In general, the accumulation of mineralization products ( $^{14}\text{CO}_2$  and  $^{14}\text{CH}_4$ ) predominated with only trace-level detection of the reductive dechlorination product,  $^{14}\text{C}$ -ethene. In contrast, microbial degradation of cis-DCE by reductive dechlorination or mineralization was not significant in the absence of detectable oxygen. The potential for VC biodegradation also was significant in sediments from the deeper hyporheic zones under oxic conditions and in the absence of detectable oxygen. Microbial degradation of cis-DCE was not significant in hyporheic sediment treatments under either oxygen condition. Taken together, the results indicate that microbial mineralization processes in streambed sediments at the Kansas City Plant can be an important component of cis-DCE and VC degradation under oxic conditions and of VC degradation even in the absence of detectable oxygen. These results demonstrate that an evaluation of the efficiency of in situ cis-DCE and VC biodegradation in streambed sediments, based solely on observed accumulations of reduced daughter products, may underestimate substantially the total extent of contaminant biodegradation and thus the potential importance of the hyporheic zone and streambed sediments as barriers to the discharge of contaminated groundwater. <http://pubs.usgs.gov/sir/2009/5137/>

#### Practical Understanding and Use of Surface Enhanced Raman Scattering/Surface Enhanced Resonance Raman Scattering in Chemical and Biological Analysis

Smith, W.E., Strathclyde Univ., Glasgow, UK.

Chemical Society Reviews, Vol 37 No 5, p 955-964, May 2008

Surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS) have the unique ability to obtain molecular recognition of an analyte at very low concentrations in situ in aqueous environments. Improved understanding of the effect coupled to improvements in practical techniques make the use of SERS/SERRS much simpler than has been the case in the past. This paper is designed as a tutorial review targeted at aiding in the development of practical applications.

#### Predicting Bioavailability of PAHs in Field-Contaminated Soils by Passive Sampling with Triolein Embedded Cellulose Acetate Membranes

Tao, Y., S. Zhang, Z. Wang, and P. Christie.

Environmental Pollution, Vol 157 No 2, p 545-551, Feb 2009

Triolein-embedded cellulose acetate membrane (TECAM) was used for passive sampling of the fraction of naphthalene, phenanthrene, pyrene, and benzo(a)pyrene in 18 field-contaminated soils. The sampling of PAHs by TECAM fitted well with a first-order kinetics model, and PAHs reached 95% of equilibrium in TECAM within 20 hours. Concentrations of PAHs in TECAM ( $C(\text{TECAM})$ ) correlated well with the concentrations in soils ( $r^2=0.693-0.962$ ,  $p<0.001$ ). PAH concentrations determined in the soil solution were very close to the values estimated by  $C(\text{TECAM})$  and the partition coefficient between TECAM and water

(K(TECAM-w)). After lipid normalization, nearly 1:1 relationships were observed between PAH concentrations in TECAMs and earthworms exposed to the soils. The results suggest that TECAM can be a useful tool to predict bioavailability of PAHs in field-contaminated soils.

#### Predicting Bioremediation of Hydrocarbons: Laboratory to Field Scale

Diplock, E.E., D.P. Mardlin, K.S. Killham, and G.I. Paton.

Environmental Pollution, Vol 157 No 6, p 1831-1840, June 2009

To test laboratory-derived data and the move to the field scale, the remediation of over 30 hydrocarbon sites was studied in the laboratory using a range of analytical techniques. At elevated concentrations, the rate of degradation was best described by respiration and the total hydrocarbon concentration in soil. The number of bacterial degraders and heterotrophs as well as quantification of the bioavailable fraction allowed an estimation of how bioremediation would progress. The response of microbial biosensors proved a useful predictor of bioremediation in the absence of other microbial data. Field-scale trials on average took three times as long to reach the same endpoint as the laboratory trial. Practitioners managing remediation projects will need to justify the nature and frequency of sampling when estimations can be made using laboratory-derived data. Detailed biological, chemical, and physical characterization reduces uncertainty in predicting bioremediation.

#### Prospects for Combining Chemical and Biological Methods for Integrated Environmental Assessment

Cristina Blasco and Yolanda Picó

TrAC Trends in Analytical Chemistry, Vol 28 No 6, p 745-757, June 2009

Besides deploying a chemicals-driven strategy for ecological risk assessment of pollutants, it may be desirable to apply biological strategies, such as bioassays, biosensors, and effect-directed analysis (EDA). The authors provide a broad overview of how to assess biological monitoring of ecosystems and chemical monitoring of priority and specific substances involved in environmental contamination, with a discussion of bioanalytical tools and their integration/combination with chemical tools. The paper includes a review of the literature and generalized strategies for characterizing environmental contamination, and detecting and categorizing toxicological problems.

#### Put Together, Two-Piece Nanosensor Becomes Superdetector

R&D Daily, 7 Apr 2009

Scientists have designed tiny new sensor structures that could be used in novel security devices to detect poisons and explosives, or in highly sensitive medical sensors, according to research published in Nano Letters. The new nanosensors could be tailored to detect instantly and with high sensitivity the presence of particular molecules, such as poisons or explosives in transport screening situations, or proteins in patients' blood samples. Researchers led by physicists of Imperial College London were funded by the Engineering and Physical Sciences Research Council. The team showed that by putting together two specific nanostructures made of gold or silver, an early prototype device can be made that once optimized should exhibit a highly sensitive ability to detect particular chemicals in the immediate surroundings. The nanostructures

are each about 500 times smaller than the width of a human hair. One is shaped like a flat circular disk, while the other looks like a doughnut with a hole in the middle. When brought together, they interact with light very differently from the way they behave individually. The scientists have observed that when they are paired, they scatter some specific colors within white light much less, which leads to an increased amount of light passing through the structure undisturbed. This decrease in the interaction with light is in turn affected by the composition of molecules in close proximity to the structures. The researchers hope that this effect can be harnessed to produce sensor devices. Once bound, the target molecules change the colors that the device absorbs and scatters, alerting the sensor to their presence. The team's next step is to test whether the pair of nanostructures can detect chosen substances in lab experiments. The research was conducted by the team at Imperial College London in collaboration with IMEC and the Catholic University in Leuven, Belgium, and Rice University in Houston, Texas. See Nano Letters 9(4):1663-1667(8 Apr 2009), "Fano Resonances in Individual Coherent Plasmonic Nanocavities" by N. Verellen, et al.

Quantifying Volatile Organic Compounds in Porous Media: Effects of Sampling Method Attributes, Contaminant Characteristics and Environmental Conditions  
Oesterreich, R.C. and R.L. Siegrist, Colorado School of Mines, Golden.  
Environmental Science & Technology, Vol 43 No 8, p 2891-2898, 15 Apr 2009

The accuracy of VOC measurements was investigated using an experimental apparatus packed with sandy porous media and contaminated with known levels of VOCs, for sampling using different methods under variable but controlled conditions. Five sampling methods were examined representing different degrees of porous media disaggregation and duration of atmospheric exposure (MDE) such as can occur during sample acquisition and preservation in the field. Three VOCs (1,1,1-TCA, TCE, and PCE) were studied at low and high concentration levels. Five porous media temperatures were examined ranging from 5 to 80 degrees C to represent ambient or thermal remediation conditions, and two water saturation levels were used to mimic vadose zone and groundwater zone conditions. The results demonstrated that sampling method attributes can impact the accuracy of VOC measurements in porous media by causing negative bias in VOC concentration data ranging from near 0 to 90% or more. The magnitude of the negative bias is dependent on the attributes of the sampling method used (i.e., level of MDE) and interactions with key contaminant properties and environmental conditions (i.e., VOC KH, porous media temperature, water saturation level).

Quantification of Aromatic Oxygenase Genes to Evaluate Enhanced Bioremediation by Oxygen Releasing Materials at a Gasoline-Contaminated Site  
Nebe, J., B.R. Baldwin, R.L. Kassab, L. Nies, and C.H. Nakatsu.  
Environmental Science & Technology, Vol 43 No 6, p 2029-2034, 15 Mar 2009

Subsurface injection of oxygen-releasing materials (ORMs) is frequently performed at petroleum-contaminated sites to stimulate aerobic bioremediation of BTEX. The combination of groundwater monitoring with qPCR enumeration of aromatic oxygenase genes and PCR-DGGE profiles of bacterial 16S rRNA genes was investigated to determine the impact of ORM injection on BTEX bioremediation at a gasoline-contaminated site. Prior to injection, BTEX concentrations were >3 mg/L, DO levels were typically <2 mg/L, and butphenol hydroxylase



(PHE) and ring-hydroxylating toluene monooxygenase (RMO) genes were detected in impacted wells, indicating the potential for aerobic BTEX biodegradation. Following injection, DO increased, BTEX concentrations decreased substantially, and PHE and RMO genes copies increased by 1 to 3 orders of magnitude. Naphthalene dioxygenase and xylene monooxygenase genes were detected intermittently during periods of increased DO. Following depletion of the ORM, DO decreased, BTEX concentrations rebounded, and oxygenase genes were no longer detected. Temporal changes in PCR-DGGE microbial community profiles reflected the dynamic changes in subsurface conditions. Overall, the combination of chemical and geochemical analyses with quantification of aromatic oxygenase genes demonstrated that ORM injection stimulated BTEX biodegradation until the oxygen-releasing material was depleted.

#### Quantifying Uncontrolled Landfill Gas Emissions from Two Florida Landfills

U.S. EPA, National Risk Management and Research Laboratory, Research Triangle Park, NC.  
EPA 600-R-09-046, 128 pp, May 2009

A study was conducted to evaluate fugitive loss from two different municipal landfills. Each landfill was reported to be operating as a "wet" or bioreactor landfill and had an area regarded as a "control" cell where no additional liquid was added. Fugitive methane emissions were measured at both sites for the wet and control cells using optical remote sensing (ORS) technology. Two different instruments were used -- an open-path tunable diode laser (OPTDLAS) instrument by Boreal, Inc (the Gas-Finder 2.0) and an open-path Fourier transform infrared (OP-FTIR) instrument by IMACC, Inc. The measurements were conducted using vertical radial plume mapping (VRPM) to calculate net methane-flux emission values from the top and side slopes of each landfill cell. In addition to the ORS measurements, SUMMA canister samples were collected from the gas header pipes at the sites to obtain data on trace constituents in landfill gas, such as non-methane organic compounds, hydrogen sulfide, mercury, and other hazardous air pollutants. Using the OP-ORS data, methane emission flux rates were calculated for each cell. The methane flux results for landfill 1 indicate that fugitive methane emissions from the bioreactor cell were about twice that of the control cell (1,500 vs 3,800 kg/day). At landfill 2, methane emissions from the control cell were about 5 times higher than the bioreactor cell (~6,000 vs 1,200 kg/day), which is attributed to the fact that no liquid additions had been added to the bioreactor for several months because of heavy rainfall from a recent series of hurricanes. In addition, a fresh layer of soil had just been added to the surface of the bioreactor cell just prior to when the field measurements were conducted. Estimates of the total site emissions were calculated for Site 1 (5,300 kg/day) and site 2 (7,300 kg/day). As additional tests are conducted, data will be available the better to understand the amount of uncontrolled landfill gas and potential differences in fugitive loss between wet versus traditional landfill design and operation. <http://www.epa.gov/ORD/NRMRL/pubs/600r09046/600r09046.html>

#### Quantitative Evaluation of Perchloroethylene in Groundwater before and after its Oxidation by Helical Solid Sorbent Extraction and Gas Chromatography

Draga, M., I. Ciucanu, V. Agotici, A. Fernandez, and R. Barna.  
Chemosphere, Vol 75 No 9, p 1210-1214, May 2009

An integrated method of dynamic extraction of PCE with polydimethylsiloxane (PDMS) helical solid sorbent followed by injection into a gas chromatograph was developed for the

determination of the real concentration of PCE in groundwater before and after its degradation by oxidation with potassium permanganate (KMnO<sub>4</sub>). The main parameters (agitation, temperature, salts, pH) that affect the extraction efficiency were evaluated and optimized. The quantitative analysis of PCE was carried out with the external standard method using the calibration-curve technique. The limit of detection for PCE was found at 0.05 mg/L using a flame ionization detector. The solubility of PCE in water was studied by extraction of PCE with PDMS helical solid sorbent from standard solution with different amounts of PCE added into the same volume of water and was found to decrease with settling time, because the fine droplets created during the agitation of the mixture slowly merged into drops on the bottle walls and were not transferred into the extraction vial for GC analysis. The limit of solubility was evaluated using a graphical method and was estimated at 224.2±15.7 mg/L of PCE in water at 25 degrees C.

#### Radiello(r) Passive Sampling Method for Evaluating Vapor Intrusion

Shamory, B., DMS Environmental Services, LLC, Bellefonte, PA

The Business of Brownfields: 2009 Conference Proceedings, 15-17 April, abstract only, 2009

Vapor intrusion assessments conducted at Brownfield sites often necessitate the sampling of soil gas, and in some cases, indoor air. Samples typically are collected using Summa canisters for vapor collection and storage as required by EPA Compendium Method TO-15. The Radiello(r) passive/diffusive sampling technology presents an alternative method to active sampling that relies on unassisted molecular diffusion of the gaseous agent to migrate from the air onto the sorbent material. The technology requires very little time in the field to deploy and no expensive equipment to maintain and might eventually prove to be a significant cost-saving tool for screening level assessments of vapor intrusion in urban environments where multiple buildings need be evaluated. While this technology is most applicable to sampling indoor air, it is being tested for soil gas application in crawl spaces, sub-slab, or potentially sub-surface. Radiello(r) samplers are being deployed at various petroleum sites following active sampling (TO-15, Summa canisters and TO-17, sorbent tubes) as a means to compare their analytical performance for BTEX compounds.

#### Research Implementation and Quality Assurance Project Plan: An Evaluation of Hyperspectral Remote Sensing Technologies for the Detection of Fugitive Contamination at Selected Superfund Hazardous Waste Sites

Slonecker, E.T. and G.B. Fisher.

U.S. Geological Survey Open-File Report 2009-1048, 18 pp, 2009

This project is a research collaboration between the U.S. EPA Office of Inspector General and the U.S. Geological Survey Eastern Geographic Science Center for the purpose of evaluating the utility of hyperspectral remote sensing technology for post-closure monitoring of residual contamination at delisted and closed hazardous waste sites as defined under CERCLA and SARA. <http://pubs.usgs.gov/of/2009/1048/>

The Risk of Altering Soil and Sediment Samples upon Extract Preparation for Analytical and Bio-Analytical Investigations: A Review

Seiler, T.B., T. Schulze, and H. Hollert.

Analytical and Bioanalytical Chemistry, Vol 390 No 8, p 1975-1985, Apr 2008

Organic total extracts can be used in bio-analytical investigations to investigate a "worst-case scenario," to simulate chronic intoxication, and to provide samples for effect-directed analysis. While theoretically providing highly reliable data and good reproducibility, the whole process of sample handling and extract preparation can lead to extracts that might fail to represent a toxic potential of their corresponding sampling site accurately. This review identifies and discusses the most important possible alterations that have the potential to lead to overestimation and, more often, underestimation of the effectiveness of extracts. Incorrect data will compromise soil and sediment risk assessment as a whole; therefore, results from analytical and bioanalytical investigations of extracts demand cautious interpretation. Reliability of extract testing grows with reproducibility, so experiments should be repeated with independent extraction replicates. New or optimized extraction procedures should circumvent the issues mentioned here while being suitable for routine application.

The Role of Hydrodynamics, Matrix and Sampling Duration in Passive Sampling of Polar Compounds with Empore SDB-RPS Disks

Vermeirssen, E.L., J. Asmin, B.I. Escher, J.H. Kwon, I. Steimen, and J. Hollender.

Journal of Environmental Monitoring, Vol 10 No 1, p 119-128, 2008

To investigate the sampling properties of passive samplers using river-like flow conditions and ambient environmental matrices (i.e., river water and treated sewage effluent), Empore SDB-RPS disks in a Chemcatcher housing were selected a model sampler. The disks were exposed for 1 to 8 days at flow rates between 0.03 and 0.4 m/s. Samples were analyzed using a bioassay for estrogenic activity and by LC-MS-MS target analysis of the pharmaceuticals sulfamethoxazole, carbamazepine, and clarithromycin. To assess sampling rates of SDB disks, aqueous concentrations of the pharmaceuticals were also measured. Sampling rates increased with increasing flow rate, and this relationship was not affected by the environmental matrix. SDB disks were only sampling in the integrative mode at low flow rates <0.1 m/s and/or for short sampling times. The duration of linear uptake was particularly short for sulfamethoxazole (1 day) and longer for clarithromycin (5 days). At 0.03 m/s and 12 to 14 degrees C, the sampling rate of SDB disks was 0.09 L/day for clarithromycin, 0.14 L/day for sulfamethoxazole, and 0.25 L/day for carbamazepine. The results show that under controlled conditions, SDB disks can be used effectively as passive sampling devices.

A Rotating Disk Apparatus for Assessing the Biodegradation of Polycyclic Aromatic Hydrocarbons Transferring from a Non-Aqueous Phase Liquid to Solutions of Surfactant Brij 35

Bernardez, L.A., Univ. Federal da Bahia, Brazil.

Bioprocess and Biosystems Engineering, Vol 32 No 3, p 415-424, Apr 2009

A rotating disk apparatus was used to investigate the biodegradation of PAHs from nonaqueous-phase liquids to solutions of Brij 35. The mass transfer of PAHs in the absence of surfactant solution was not large enough to replenish the degraded PAHs. The addition of surfactant resulted in an overall enhancement of biodegradation rates compared to that observed

in pure aqueous solution. The relationship between biodegradation rate and surfactant dose and the mechanisms controlling the mass transfer of PAH from NAPLs was demonstrated. Satisfactory comparison of the experimental data with the predictions of a model, whose parameters were determined from independent solubilization and dissolution experiments and based on the main assumption that the solutes must be present in the true aqueous phase to be degraded, allows the absence of direct uptake of PAHs by bacteria to be concluded.

#### Sampling and Analysis of Nanoparticles with Cold Fibre SPME Device

Koziel, J.A., S.H. Haddadi, W. Koch, and J. Pawliszyn.

Journal of Separation Science, Vol 32 No 11, p 1975-1980, June 2009

A new approach is described to capture nano-size aerosols on the internally cooled microtubing of a solid-phase microextraction (SPME) device followed by convenient introduction of the collected analytes into an analytical instrument. Particles were generated using an aerosol formation by homogeneous nucleation of an organic vapor and subsequently grown to nano-size particles by coagulation of decanedioic acid, bis[2-ethylhexyl] ester (DEHS). The approach was validated by using carbon dioxide-cooled microtubing to collect the nanosize DEHS particles, followed by analyses on a GC-flame ionization detector. Particle size ranged from 150 to 590 nm. Temperature difference between the SPME device and DEHS particles mixture created a temperature gradient and resulted in a thermophoretic effect that determined the extraction rate. The SPME device was cooled as low as -75 degrees C, while the DEHS remained close to room temperature. Several aspects of nanoparticle sampling were tested to demonstrate the principle of the sampling approach: the effects of thermal gradient, sample flow rate, sampling time, CO<sub>2</sub> delivery mode (constant coolant delivery vs. constant temperature), and particle size. Results were normalized to measure particulate concentrations using direct sampling with PTFE filters. Nanoparticle extractions of DEHS mass were proportional to sampling time. The normalized mass of DEHS extracted increased with increase in temperature gradient and with increase of the cross-flow velocity. Preliminary results indicate that the variation of the heat transfer boundary layer caused by the variation in the cross flow velocity produces a self-compensating effect at constant coolant delivery, indicating that this approach could be used for field determinations, including the time-weighted average sampling of nanoparticles. It thus may be possible to develop a simple device based on this concept for field applications.

#### Sampling Atmospheric Pesticides with SPME: Laboratory Developments and Field Study

Wang, J., L. Tuduri, M. Mercury, M. Millet, O. Briand, and M. Montury.

Environmental Pollution, Vol 157 No 2, p 365-370, Feb 2009

To estimate the atmospheric exposure of greenhouse workers to pesticides, solid-phase microextraction (SPME) was used under non-equilibrium conditions. Using Fick's law of diffusion, the concentrations of pesticides in the greenhouse can be calculated using pre-determined sampling rates (SRs). Thus the SRs of two modes of SPME in the lab and in the field were determined and compared. The SRs for six pesticides in the lab were 20.4 to 48.3 mL/min for the exposed fiber and 0.166 to 0.929 mL/min for the retracted fiber. In field sampling, two pesticides, dichlorvos and cyprodinil, were detected with exposed SPME. SR with exposed

SPME for dichlorvos in the field (32.4 mL/min) was consistent with that in the lab (34.5 mL/min). The trends of temporal concentration and the inhalation exposure were also obtained.

#### Sampling in Freshwater Environments: Suspended Particle Traps and Variability in the Final Data

Barbizzi, S. and A. Pati, Agenzia per la Protezione dell'Ambiente e per i Servizi Tecnici (APAT), Rome, Italy.

Applied Radiation and Isotopes, Vol 66 No 11, p 1595-1598, Nov 2008

This paper reports a practical method to estimate measurement uncertainty, including sampling, derived by the approach implemented by Ramsey for soil investigations. The methodology has been applied to estimate measurements uncertainty (sampling and analyses) of Cs-137 activity concentration (Bq/kg) and total carbon content (%) in suspended particle sampling in a freshwater ecosystem. Uncertainty estimates for between locations, sampling and analysis components have been evaluated. For the considered measurands, the relative expanded measurement uncertainties are 12.3% for Cs-137 and 4.5% for total carbon. For Cs-137, the measurement (sampling+analysis) variance gives the major contribution to the total variance, while for total carbon the spatial variance is the dominant contributor to the total variance. The limitations and advantages of this basic method are discussed.

#### Sampling Strategies for Estimation of Parameters Related to Ground Water Quality

Crane, P.E. and S.E. Silliman, Univ. of Notre Dame, IN.

Ground Water. 2009 May 5. [Epub ahead of print]

Monte Carlo studies were used to assess different sampling strategies in the estimation of three parameters related to a hypothetical chemical observed in a ground water well: mean concentration (MeanC), maximum concentration (MaxC), and total mass load (TML). Five different scenarios were simulated and then subsampled using multiple simulated sampling instruments, time periods (ranging from 1 to 10 years), and sampling frequencies (ranging from weekly to semiannually to parameter dependent). Results were analyzed via the statistics of the resulting estimates, including mean square error, bias, bias squared, and precision. Results suggest that developing a sampling strategy based on what might be considered lower-quality instruments can represent a powerful field research approach for estimating select parameters when applied at high frequency. This result suggests the potential utility of using a combination of lower-quality instruments and local populations to obtain high-frequency data sets in regions where regular monitoring by technicians is not practical.

#### Selective Determination of Cyanides by Gas Diffusion-Stopped Flow-Sequential Injection Analysis and an On-Line Standard Addition Approach

Themelis, D.G., S.C. Karastogianni, and P.D. Tzanavaras.

Analytica Chimica Acta, Vol 632 No 1, p 93-100, 19 Jan 2008

A highly selective sequential injection (SI) method for the automated determination of weak acid-dissociable cyanides is based on the on-line reaction of the analyte with ninhydrin in carbonate medium to form a colored product. Cyanides are removed from sample matrix by acidification through a gas-diffusion step incorporated in the SI manifold. By adopting an on-line

standard addition protocol, the sensitivity of the proposed method was enhanced drastically, without affecting the determination range. The assay was validated in terms of linearity (up to 200 ug/L), limit of detection ( $c(L)=2.5$  ug/L), limit of quantitation ( $c(Q)=7.5$  g/L), precision ( $s(r)<2.5\%$  at 100 ug/L) and selectivity. High tolerance against critical species such as sulfides and thiocyanates was achieved. The applicability of the method was demonstrated by analyzing tap and mineral water samples at levels below the limits established by international E.U. and U.S. organizations. The percent recoveries were satisfactory in all cases, ranging between 94.2 and 103.6%.

#### A Simple Yet Highly Selective Colorimetric Sensor for Cyanide Anion in an Aqueous Environment

Niu, H.T., D. Su, X. Jiang, W. Yang, Z. Yin, J. He, and J.P. Cheng.

Organic and Biomolecular Chemistry, Vol 6 No 17, p 3038-3040, 7 Sep 2008

The nucleophilic nature of cyanide was used to create a simple, sensitive, and highly effective sensor, 2-(trifluoroacetyl-amino)anthraquinone (2-TFAQ), for easy "naked-eye" detection of very low concentrations of cyanide in an aqueous environment.

#### A Simulation Tool to Assess Contaminant Warning System Sensor Performance Characteristics

Einfeld, W., S. McKenna, and M. Wilson.

IWA Publishing, AwwaRF Report 91219, ISBN: 9781843392637, 132 pp, 2008

The purpose of this project was to develop a simulation tool to assess overall contaminant warning system (CWS) performance under various contamination event scenarios and to incorporate specific sensor performance characteristics in the tool to assess more realistically how sensor operational parameters can influence overall system performance. A sensor simulator was configured to mimic sensitivity, sampling rate, and drift using various mathematical and statistical algorithms. The spatial and temporal features of chemical contamination events were modeled using a pipe model of a real water distribution system and EPANET. The resulting contaminant pulse shapes at specific locations within the distribution system were combined with normal water quality background signals and processed through the sensor simulator. The sensor-altered signal was processed through a second event detection algorithm, and contaminant event detection statistics then were compiled and analyzed to assess overall system performance. This study has shown that simulation methods can be used successfully to evaluate contaminant warning system designs for user-specified chemical contamination events. Specific sensor performance attributes can be configured within the simulation to allow comparison of various commercial sensor options in a utility-specific contaminant warning system design. Initial testing results reveal that most commercial sensors perform equally well in chemical contamination events of moderate intensity, with sensor sampling frequency being one of the most important sensor attributes that influences overall system performance.

#### Simultaneous Quantification of Polar and Non-Polar Volatile Organic Compounds in Water Samples by Direct Aqueous Injection-Gas Chromatography/Mass Spectrometry

Aeppli, C., M. Berg, T.B. Hofstetter, R. Kipfer, and R.P. Schwarzenbach, Eawag, Swiss Federal Institute of Aquatic Science and Technology.

Journal of Chromatography A, Vol 1181 Nos 1-2, p 116-124, 15 Feb 2009

A direct aqueous injection-gas chromatography/mass spectrometry (DAI-GC/MS) method for trace analysis of 24 VOCs in water samples allows for the simultaneous quantification of BTEX, MTBE, TBA, and a variety of chlorinated methanes, ethanes, propane, ethenes, and benzenes. Applying a liquid film polyethylene glycol or a porous layer open tubular divinylbenzene GC capillary column to separate the water from the VOCs, volumes of 1 to 10 uL aqueous sample are directly injected into the GC. No enrichment or pretreatment steps are required, and sample volumes as low as 100 uL are sufficient for accurate quantification. Method detection limits determined in natural groundwater samples were between 0.07 and 2.8 ug/L, and instrument detection limits of <5 pg were achieved for 21 out of the 24 evaluated VOCs. DAI-GC/MS offers both good accuracy and precision (relative standard deviations  $\leq 10\%$ ). The versatility of the method was demonstrated for contaminant quantification in drinking water disinfection (advanced oxidation of MTBE) and for VOC concentration measurements in a polluted aquifer.

#### Simultaneous Sampling and Analysis for Vapor Mercury in Ambient Air Using Needle Trap Coupled with Gas Chromatography-Mass Spectrometry

Cai, J., G. Ouyang, Y. Gong, and J. Pawliszyn.

Journal of Chromatography A, Vol 1213 No 1, p 19-24, 5 Dec 2008

A needle trap (NT) technique developed for simultaneous sampling and analysis of vapor and particle mercury in ambient air using a gold-wire filled syringe needle relies on gold amalgamation rather than adsorption/absorption in traditional solid-phase microextraction. Hg trapped by Au-amalgamation NT is thermally desorbed in a hot-injection port of a gas chromatograph; desorbed Hg then is determined by the coupled mass spectrometer. This simultaneous sampling and analysis technique was optimized, tested, and used for the collection and accurate determination of elemental Hg in ambient air. Linear calibration curves spanning over 4 orders of magnitude were obtained for Hg sampling by NT when mass spectrometry was used for detection with excellent sensitivity and selectivity. Selected ion monitor (SIM) mode was used for the linear calibration curves. The selected quantitation ion was  $m/z$  202, since  $m/z$  202 was the strongest isotope of mercury mass spectrum. The method was verified with solution samples spiked with HgCl<sub>2</sub>. Excellent agreement was found between the results obtained for the Hg-saturated air samples and HgCl<sub>2</sub> spiked solution samples.

#### A Soil Sampling Reference Site: the Challenge in Defining Reference Material for Sampling

de Zorzi, P., S. Barbizzi, M. Belli, A. Fajgelj, R. Jacimovic, Z. Jeran, U. Sansone, and M. van der Perk, Agenzia per la Protezione dell'Ambiente e per i Servizi Tecnici (APAT), Rome.

Applied Radiation and Isotopes, Vol 66 No 11, p 1588-1591, Nov 2008

In the framework of the international SOILSAMP project, funded and coordinated by the Italian Environmental Protection Agency, an agricultural area was established as a reference site suitable for performing soil sampling inter-comparison exercises. The reference site was characterized for trace element content in soil, in terms of the spatial and temporal variability of their mass fraction. Considering that the behavior of long-lived radionuclides in soil can be expected to be similar to that of some stable trace elements and that the distribution of these trace elements in soil can simulate the distribution of radionuclides, the reference site characterized in



term of trace elements also can be used to compare the soil sampling strategies developed for radionuclide investigations.

#### Soil Sampling Strategies: Evaluation of Different Approaches

de Zorzi, P., S. Barbizzi, M. Belli, R. Mufato, G. Sartori, and G. Stocchero.

Applied Radiation and Isotopes, Vol 66 No 11, p 1691-1694, Nov 2008

The National Environmental Protection Agency of Italy (APAT) performed a soil sampling intercomparison, inviting 14 regional agencies to test their own soil sampling strategies. The intercomparison was carried out at a reference site previously characterized for metal mass fraction distribution. A wide range of sampling strategies in terms of sampling patterns, type and number of samples collected were used to assess the mean mass fraction values of some selected elements. The different strategies led in general to acceptable bias values (D) less than 2sigma, calculated according to ISO 13258. Sampling on arable land was relatively easy, with comparable results between different sampling strategies.

#### Solvent Selection for Pressurized Liquid Extraction of Polymeric Sorbents Used in Air Sampling

Primbs, T., S. Genualdi, and S.M. Simonich.

Environmental Toxicology and Chemistry, Vol 27 No 6, p 1267-1272, June 2008

Pressurized liquid extraction (PLE) was evaluated as a method for extracting SVOCs from air sampling media, including quartz fiber filter (QFF), polyurethane foam (PUF), and a polystyrene divinyl benzene copolymer (XAD-2). Hansen solubility parameter plots were used to aid in the PLE solvent selection both to reduce coextraction of polyurethane and save time in evaluating solvent compatibility during the initial steps of method development. A PLE solvent composition of 75:25% hexane/acetone was chosen for PUF. The XAD-2 copolymer was not solubilized under the PLE conditions used. The average percent PLE recoveries (and percent relative standard deviations) of 63 SVOCs, including PAHs, PCBs, and organochlorine, amide, triazine, thiocarbamate, and phosphorothioate pesticides, were 76.7 (6.2), 79.3 (8.1), and 93.4 (2.9)% for the QFF, PUF, and XAD-2, respectively.

#### SPEAR Indicates Pesticide Effects in Streams: Comparative Use of Species- and Family-Level Biomonitoring Data

Beketov, M.A., K. Foit, R.B. Schaefer, C.A. Schriever, A. Sacchi, E. Capri, J. Biggs, C. Wells, and M. Liess.

Environmental Pollution, Vol 157 No 6, p 1841-1848, June 2009

To detect effects of pesticides on non-target freshwater organisms, the Species at Risk (SPEARpesticides) bioindicator was developed and validated over different biogeographical regions of Europe using species-level biological trait data for stream invertebrates. Because many freshwater biomonitoring programs have family-level taxonomic resolution, the applicability of SPEAR[pesticides] was tested with family-level biomonitoring data to indicate pesticide effects in streams (i.e., insecticide toxicity of pesticides). The study showed that the explanatory power of the family-level SPEAR(fm)[pesticides] is not significantly lower than the species-level index. The results suggest that the family-level SPEAR(fm)pesticides is a sensitive, cost-effective, and potentially European-wide bioindicator of pesticide contamination in flowing

waters. Class boundaries for SPEARpesticides according to EU Water Framework Directive are defined to contribute to the assessment of ecological status of water bodies. Results show that SPEARpesticides can be based on family-level biomonitoring data applicable to large-scale monitoring programs to detect and quantify pesticide contamination.

#### Specialized Polymer Used to Detect Nerve Agents, Toxic Chemicals for Air Monitoring in Emergencies

Pacific Northwest National Laboratory (PNNL) News Release, 14 Apr 2009

A unique polymer that allows sensors to detect nerve agents and other toxic industrial chemicals in the air is now available to companies developing chemical detectors for emergency personnel, indoor air quality monitoring, and other uses. Researchers can access a hybrid organic/inorganic polymer known as BSP3 through Seacoast Science, Inc., thanks to a license agreement between Seacoast and Battelle, which operates DOE's Pacific Northwest National Laboratory. PNNL developed and patented the polymer and then partnered with Seacoast as part of the lab's mission to transfer technology to the marketplace. Seacoast has added BSP3 to its catalog of more than 100 polymers that are used to cover the surface of a sensor. Polymer coatings collect and concentrate the vapor molecules of airborne chemicals. Absorbing the vapor molecules creates changes in the polymer's properties, which results in sensor signal changes. Multiple sensors, each covered with a different polymer especially sensitive to a specific class of compounds, are used together as a sensor array. The collective response of a sensor array provides a "fingerprint," or characteristic pattern, that helps researchers recognize and distinguish one chemical compound from another. Sensor arrays with polymer coatings often are called "electronic noses" because they recognize response patterns from multiple sensors, just as mammalian noses recognize response patterns from several olfactory receptors. BSP3 has a strong ability to absorb toxic organophosphorus compounds like nerve agents and pesticides. Using BSP3 in sensor arrays improves sensor abilities to distinguish one compound from another. Sensors with a BSP3 coating can be used to monitor air quality in subways and buildings, and also to protect first responders at terrorist or chemical incidents. Seacoast plans to explore how BSP3 can be used to detect explosives by combining the polymer with the company's current sensor platforms. The company also wants to improve the ability of its own sensors to detect nerve agents and basic toxic industrial chemicals with BSP3. PNNL chemist Jay Grate developed the BSP3 polymer (U.S. Patent No. 6,015,869), which received an R&D 100 Award in 2004. News release at <http://www.pnl.gov/news/release.asp?id=363>

#### Specific Colorimetric Detection of Cyanide Triggered by a Conformational Switch in Vitamin B12

Zelder, F.H., Univ. of Zurich, Switzerland.

Inorganic Chemistry, Vol 47 No 4, p 1264-1266, 18 Feb 2008

"Base on"/"base off" coordination of the intramolecular bound benzimidazole nucleobase of vitamin B 12 allows for specific colorimetric detection of millimolar concentrations of cyanide in water. Experimental results showed that up to 12 different anions, as well as a 1,000-fold excess of Cl<sup>-</sup> over CN<sup>-</sup>, do not interfere with the sensor. An 8-fold increased sensitivity in the visual (naked eye) detection of CN<sup>-</sup> was observed when water was replaced by 5% MeOH/H<sub>2</sub>O as a solvent.

#### Spectral Unmixing of Airborne Hyperspectral Data for Baseline Mapping of Mine Tailings Areas

Richter, N., K. Staenz, and H. Kaufmann.

International Journal of Remote Sensing, Vol 29 No 13, p 3937-3956, July 2008

The Kam Kotia mine tailings areas near Timmins in Ontario, Canada, have been generating and discharging acidic mine drainage (AMD) into the surrounding areas for more than 35 years. In the mine's remote sensing monitoring program, hyperspectral TRW (Thompson Ramo Wooldridge Inc.) Imaging Spectrometer III data were acquired over the mine and tailings areas. This paper describes (1) the data pre-processing (noise removal, atmospheric correction, spectral smile correction, scene-based calibration) needed to radiometrically calibrate the images and (2) a novel procedure that combines constrained spectral mixture analysis and threshold-based classification. This procedure allows retrieval of fraction maps of major mine tailings-related surface materials; generation of a surface map separating green vegetation, transition zones, dead vegetation, and oxidized tailings; and calculation of the extent (surficial area) of each of the zones. The four zones are correlated with the extent and degree of vegetation cover affected by tailings material and are interpreted to span respectively from very low to medium, high, and very high AMD pollution. The procedure can be used to monitor changes in the course of the boundary between affected zones and finally to quantify the rehabilitation process in mine tailings areas with high vegetation cover.

#### Strategies for Monitoring the Emerging Polar Organic Contaminants in Water with Emphasis on Integrative Passive Sampling

Soderstrom, H., R.H. Lindberg, and J. Fick, Umea Univ., Sweden.

Journal of Chromatography A, Vol 1216 No 3, p 623-630, 16 Jan 2009

This paper contains an overview of the advantages and shortcomings of traditional and novel sampling techniques available for monitoring emerging polar organic contaminants (POCs) in water. The benefits and drawbacks of using active and biological sampling are discussed, followed by the principles of organic passive samplers (PS). A detailed overview of available types of polar organic PSs, their classes of target compounds, fields of application, and the considerations involved in using them is provided. The authors found the usefulness of biological sampling of POCs in water to be limited, whereas the use of Polar organic PS was considered to be an efficient alternative to active water sampling due to its simplicity, low cost, freedom from power supply or maintenance, and the ability to collect time-integrative samples with one sample collection. The polar organic PSs need to be further developed, however, before they can be used as standard in water quality monitoring programs.

#### Stream Thermometry as an Effective Tool for Revealing Communication Areas between Mine Water and Surface Streams: Uranium Mine Rozna Case Study (Czech Republic)

Ricka, A., T. Kuchovsky, and J. Zeman.

10th International Mine Water Association Congress, Technical University of Ostrava, Karlsbad, Czech Republic 2008. International Mine Water Association, Paper 59, 4 pp, 2008

The Rozna mine is the last active uranium mine in Europe. When the mine is closed and flooded, the original groundwater circulation will be restored. The goal of using thermometry was to identify the groundwater effluent positions at possible preferential drainage areas and to characterize potentially endangered parts of the mining district and its surroundings. Measured values show that the aquifer is strongly non-homogenous. The majority of groundwater inflows to streams were identified in the environment of amphibolite and brittle rocks such as migmatite, orthogneiss and granite and in the vicinity of structural features, particularly diagonal faults in the direction of 55 to 70 degrees. The temperature and electrical conductivity values show obvious correlation of drainage zones to geological position, as was expected. Thermometry allows identification of places endangered by enhanced potential for formation of contaminated groundwater effluents. Supported by measurement of electrical conductivity, this demonstration of thermometry proved that it can be a very useful tool for regional investigation of zones where surface water and groundwater communicate in fractured rock areas.

[http://www.imwa.info/docs/imwa\\_2008/IMWA2008\\_059\\_Ricka.pdf](http://www.imwa.info/docs/imwa_2008/IMWA2008_059_Ricka.pdf)

#### System Design of Open-Path Natural Gas Leakage Detection Based on Fresnel Lens

Xia, H., W.Q. Liu, Y.J. Zhang, R.F. Kan, Y.B. Cui, M. Wang, Y. He, X.J. Cui, J. Ruan, and H. Geng.

Guang Pu Xue Yu Guang Pu Fen Xi, Vol 29 No 3, p 844-847, Mar 2009 [Article in Chinese]

Based on tunable diode laser absorption spectroscopy (TDLAS) technology in conjunction with second harmonic wave detection, a long open-path TDLAS system using a 1.65  $\mu\text{m}$  InGaAsP distributed feedback laser was developed for detecting pipeline leakage. In this system, a high-cost performance Fresnel lens is used as the receiving optical system for a laser beam reflected by a solid corner cube reflector. The lens focuses the receiving laser-beam to the InGaAs detector. At the same time, the influences of the concentration to the fluctuation of light intensity were taken into account in the process of measurement, and were eliminated by the method of normalized light intensity. As a result, the measurement error caused by the fluctuation of light intensity was less than 1%. During the simulation of the detection of natural gas leakage, the detection sensitivity was  $0.1 \times 10^{-6}$  (ratio by volume) with a total path of 320 m. According to the receiving light efficiency of the optical system and the detectable minimum light intensity of the detector, the detectable maximal optical path of the system was 2,000 m. The results indicate that use the Fresnel lens as a receiving optical system is a feasible design that can satisfy the need for natural gas leak detection.

#### Technology Performance Summary for Chemical Detection Instruments

U.S. EPA, National Homeland Security Research Center.

EPA 600-S-09-015, 8 pp, 2009

Sixteen commercially available detection devices were tested to determine their capability to screen samples submitted to all hazards receipt facilities (AHRFs). AHRFs were developed to prescreen for chemical, radiochemical, and explosive hazards in samples collected during suspected terrorist attacks. The technologies (i.e., instruments) used in AHRFs are intended to screen samples prior to a full analysis, helping to protect responders, laboratory workers, and others from potential injury. Evaluations of these technologies are summarized in two technology evaluation reports: (1) Testing of Screening Technologies for Detection of

Chemical Warfare Agents in All Hazards Receipt Facilities (CWAs), and (2) Testing of Screening Technologies for Detection of Toxic Industrial Chemicals in All Hazards Receipt Facilities (TICs). The chemicals listed in the reports were chosen because they might be used during, or develop as a byproduct from, a terrorist attack. The screening technologies are intended to be rapid and qualitative, be simple to use and of relatively low cost, and indicate if samples contain hazardous chemicals of concern. Not all of the technologies evaluated were deemed suitable for the AHRF, although they might be useful for on-scene responders. For more information about the technologies evaluated for use in AHRFs or by first responders, visit the NHSRC Web site at [www.epa.gov/nhsrc](http://www.epa.gov/nhsrc), or view the full reports, "Testing of Screening Technologies for Detection of Chemical Warfare Agents in All Hazards Receipt Facilities" and "Testing of Screening Technologies for Detection of Toxic Industrial Chemicals in All Hazards Receipt Facilities" in the publications section of the NHSRC site.

Temporal Geophysical Signatures from Contaminant-Mass Remediation  
Che-Alota, W., E.A. Atekwana, E.A. Atekwana, W.A. Sauck, and D.D. Werkema, Jr.  
Geophysics, Vol 74 No 4, p B113-, 2009

Changes in bulk electrical conductivity, self-potential (SP), and ground-penetrating-radar (GPR) reflections in a field setting caused by biogeochemical transformations of hydrocarbon-contaminated media have been documented. These transformations are associated with hydrocarbon biodegradation. The results of surface geophysical surveys acquired in 1996, 2003, and 2007 document changes in geophysical signatures associated with removing hydrocarbon mass in the contaminated zone. Initial investigations in 1996 showed that relative to background, the contaminated area was characterized by higher bulk electrical conductivity, positive SP anomaly, and attenuated GPR reflections. Repeated surveys in 2003 and 2007 over the contaminated area showed that in 2007, the bulk electrical conductivity had reverted to near-background conditions, the positive SP anomaly became more negative, and the zone of attenuated GPR reflections showed increased signal strength. Removal of hydrocarbon mass in the vadose zone over the plume by an SVE system installed in 2001 was primarily responsible for the changing geophysical responses. Although chemical data from groundwater showed a 3-m-thick conductive plume in 2007, the plume was not imaged by electrical resistivity. Forward modeling indicates that apparent bulk electrical conductivity of the saturated zone plume has to be three to five times higher than background values to be imaged by electrical resistivity. The authors suggest that hydrocarbon contaminant-mass reduction by natural or engineered bioremediation can be imaged effectively by temporal geophysical surveys.

Tests of Concepts for Streamflow Sampler Design  
Replogle, J.A., ARS-USDA, Maricopa, AZ.  
Journal of Hydrologic Engineering, Vol 13 No 1, p 65-74, Jan/Feb 2009

Total-load sampling usually involves a combination of bed-load sampling devices, suspended load suction samplers, and some kind of flume for total flow rate. This paper proposes total-load, sediment-sampler design concepts that can perform all three of these functions. The resulting designs would require installation at sites that can provide a step-overfall height about equal to the maximum channel flow depth. The concepts are simple, but appear to have been overlooked or ignored for the past many decades. The concepts are based on a moving conveyor

belt that is long and wide, with many slots, all of the same size, onto which the stream to be sampled discharges. All flow drops through the slots, and with equal-sized slots, each must catch a similar proportion of the total flow, which means only one slot needs to be collected. As a practical extension, the conveyor belt could be replaced with a rack having several slots that represent a short section of the total conveyor belt that is large enough such that the flow does not notice the missing belt parts. This rack then is traversed back and forth on a track through the falling nappe. Laboratory tests of this proposed sampling-assembly rack indicated that the number of the required slots is related to the channel depth and the sum of the slot openings. When the rack is composed of sufficient slots such that the slot-width sum is more than half the channel overfall depth, the system under-sampled from 0 to 2%, but with insufficient slots whose sum represents less than one-third of the overfall depth, the system under-sampled by over 8%. The concepts are extended to the condition with a stopped belt where several sampling-slot groups are equally spaced beneath the overfall. In the performance of a test-of-concept sampler assembly, the sample catch across the stream was within about 4% of expected, offering a total load sampling system where motorized equipment is difficult to install, or electric power is not available.

Three-Dimensional Seismic-Reflection Imaging of a Shallow Buried Paleochannel  
Fradelizio, G.L., A. Levander, and C.A. Zelt.  
Geophysics, Vol 73 No 5, p B85-, 2008

A suite of reflection seismology investigations of the shallow subsurface was conducted at Hill Air Force Base, Ogden, UT, at a groundwater contamination site with very large subsurface mechanical heterogeneity. The investigations were designed to expand and improve understanding of the subsurface environment developed from well data and previous seismic investigations. The goal of the investigations was to image the sides and bottom of a paleochannel eroded in a clay layer 10 to 15 m below the surface. The paleochannel is filled with a mix of sands, clays, and gravels of different compaction and water saturation. The paleochannel acts as a contaminant trap for DNAPLs; hence, a detailed map of its geometry, lateral boundaries, and depth is crucial to remediation efforts. The results of processing a 3D reflection data set over the channel showed that it is possible to image and delineate the geometry and depth of a very shallow structure. Seismic results agreed well with the available well data in the deepest part of the buried paleochannel. The map of the channel derived from seismic data replaces the need for many wells.

Time Integrative Passive Sampling: How Well Do Chemcatchers Integrate Fluctuating Pollutant Concentrations?

Shaw, M. and J.F. Mueller.

Environmental Science & Technology, Vol 43 No 5, p 1443-1448, 1 Mar 2009

This paper describes a study in which Chemcatchers using SDB-RPS Empore disks as the sorbent phase were exposed to herbicides for 28 days in a calibration chamber. A pulsed event of 10-fold greater concentrations was introduced on day 5 and returned to background concentrations over a period of 3 days. Observed uptake was compared with that predicted by a first-order uptake model and by the reduced form of this model describing a strictly integrative response for samplers deployed with two surfaces exposed, with one surface exposed, and

surfaces covered with a polyethersulfone membrane. The membrane-covered samplers predicted time-weighted average water concentrations within a factor 0.7 to 1.2 after 28 days exposure, while the one- and two-sided naked samplers under-predicted the average by a factor 1.9 to 2.2 and 2.4 to 3.2, respectively. First-order modeling predicted uptake in membrane-covered and one-sided naked samplers and was therefore applied to predict sampler response to several fluctuating concentration event scenarios.

#### Time-Lapse ERT Monitoring and Measures of Model Reliability for an Injection/Withdrawal Experiment in a Near-Surface Aquifer

Oldenborger, G.A., P.S. Routh, and M.D. Knoll.

SEG Expanded Abstracts, Vol 27, p 3709-3713, 2008

To quantify performance of 3D time-lapse electrical resistivity tomography (ERT), a sequential injection/withdrawal experiment was designed for geophysical monitoring of the pump-and-capture remediation of a conductive solute in an unconfined alluvial aquifer. Borehole ERT data were collected over several days and inverted for 3D electrical conductivity using both independent and time-lapse regularization techniques. The ERT-estimated electrical conductivity can be used to predict solute concentration and solute mass in the aquifer over time via post-inversion parameter differencing. At any experimental stage, the total solute mass in the aquifer can be predicted with a maximum accuracy of 60 to 85% depending on regularization protocol and survey geometry. Sequential ERT models can also be used to estimate the withdrawn solute mass for every experimental stage (the change in mass between experimental stages). Withdrawn mass estimates are more reliable than total mass estimates, do not require background data, and do not exhibit systematic under-prediction or dependence on the regularization protocol. Withdrawn mass predictions are accurate provided that changes in mass are not too large--how large is too large is data and model dependent. Measures of model reliability, including prediction accuracy, the volume of investigation, and the pointspread function, can provide valuable insight into the performance of ERT and the applicability of time-lapse differencing.

#### Tiny "Lab-on-a-Chip" Can Detect Pollutants, Disease and Biological Weapons

American Friends of Tel Aviv University News Release, 17 Feb 2009

Tel Aviv University researchers have made a great leap forward in the detection of pollutants. A team led by Prof. Yosi Shacham-Diamand, vice-dean of TAU's Faculty of Engineering, has developed a nano-sized laboratory, complete with a microscopic workbench, to measure water quality in real time. The "lab on a chip" is a breakthrough in the effort to keep water safe from pollution and bioterrorist threats, pairing biology with the cutting-edge capabilities of nanotechnology. Essentially a micro-sized, quarter-inch square 'lab'--the platform employs genetically engineered bacteria that light up when presented with a stressor in water. Equipment on the chip can detect the tiny light levels the bacteria produce. Based on a plastic chip, the system is faster, more sensitive, and much cheaper than using aquatic animals to help detect threats to a water supply. The nano-scale platform is designed to get information out of biological events, and it can be used to evaluate a variety of biological processes with practical applications, e.g., microbes in water, stem cells, or breast cancer development. Funded by a \$3 million grant from DoD's Defense Projects Agency (DARPA), the new lab on a chip can be modified to become a defensive weapon that protects America from biological warfare by



reacting to chemical threats and pollution. With some tweaking, the platform can be updated as new threats are detected.

Today's Environmental Technologies--Innovative Solutions for Regional Issues: U.S. EPA ETV and SBIR Programs Regional Workshop, October 7-8, 2008, U.S. EPA Region 2, New York City, New York: Meeting Summary Report

U.S. EPA, National Risk Management Research Laboratory, Cincinnati, OH.

EPA 600-R-09-043, 62 pp, Apr 2009

The workshop was conducted to provide information about new innovative technologies to help solve important regional environmental issues; learn about the specific technology priorities and needs of the regional and local participants; and identify opportunities for collaboration among ETV, SBIR, and regional and local organizations on technology development and verification activities for high-priority areas. The technologies discussed covered a wide range of applications: (1) an improved rapid detector for viable waterborne pathogens, (2) a remote-sensing instrument for on-road heavy-duty diesel nitrogen oxides and particulate matter, (3) a sensitive and affordable compact ammonia monitor, (4) a continuous real-time fine particulate matter chemical speciation monitor for ambient aerosols, (5) an inexpensive drinking water chlorination unit for small communities, (6) a handheld laser-based sensor for remote detection of gas leaks, (7) membranes for air venting and retaining volatile organic compounds in gasoline storage tanks, (8) a spot-test kit for lead in paint and dust, and (9) a field screening detector for metals in soil. A total of 137 participants attended the workshop.

<http://www.epa.gov/etv/pubs/600r09043.pdf>

Trace Gas Detection in Hyperspectral Imagery Using the Wavelet Packet Subspace

Salvador, Mark A.Z., Ph.D. dissertation, George Mason Univ., Fairfax, VA. 228 pp, 2008

This dissertation describes research into a new remote sensing method to detect trace gases in hyperspectral and ultra-spectral data. The new method is based on the wavelet packet transform. It attempts to improve both the computational tractability and the detection of trace gases in airborne and spaceborne spectral imagery. Atmospheric trace gas research supports various disciplines, including pollution monitoring, natural disasters, and intelligence and military applications. Hyperspectral and ultra-spectral data significantly increases the data glut of existing Earth science data sets. Spaceborne spectral data in particular significantly increase spectral resolution while performing daily global collections of the earth. Application of the wavelet packet transform to the spectral space of hyperspectral and ultra-spectral imagery data potentially improves remote sensing detection algorithms and facilitates the parallelization of these methods for high performance computing. This research seeks to develop a new spectral imagery detection algorithm and facilitate the parallelization of trace gas detection in spectral imagery data. <http://mars.gmu.edu:8080/dspace/handle/1920/3067>

Tracer Test for the Measurement of Gas Diffusion and Non-Aqueous Phase Liquid (NAPL) Saturation in Soil

Van De Steene, J. and P. Hoehener.

Chemosphere, Vol 74 No 2, p 224-231, Jan 2009

Work was conducted to develop a gas tracer test that yields information on both gas diffusion and residual saturation with NAPLs in unsaturated soil heaps. One conservative tracer (methane) and 4 partitioning gas tracers (diethylether, MTBE, chloroform, and n-heptane) were injected as vapors into laboratory columns filled with unsaturated sand with increasing NAPL saturation. Breakthrough curves of gaseous compounds were measured at two points and compared to analytical solutions of an analytical diffusive/reactive transport equation. NAPL saturation was most accurately measured by the moderately water soluble tracers (ethers and chloroform). The hydrophobic tracer n-heptane did not partition into water-immersed NAPL. The authors describe an easy and accurate way to assess air/NAPL partitioning constants from gas chromatography retention times, concluding that gas tracer tests have the potential for measuring two important properties in soil bioremediation systems easily and quickly.

#### Turn-On Fluorescent Cyanide Sensor Based on Copper Ion-Modified CdTe Quantum Dots Shang, L., L. Zhang, and S. Dong.

Analyst, Vol 134 No 1, p 107-113, Jan 2009

A new fluorescent sensor for the sensitive and selective detection of cyanide in aqueous media is based on cyanide-modulated quenching behavior of Cu(2+) toward the photoluminescence (PL) of CdTe quantum dots (QDs). In the presence of cyanide, the PL of QDs that have been quenched by Cu(2+) was recovered efficiently, which then allows cyanide detection in a very simple approach. Experimental results showed that the pH of the buffer solution, concentration of copper ions, and size of CdTe QDs all influenced the response of the sensor to cyanide. Under optimal conditions, a good linear relationship between the PL intensity and the concentration of cyanide can be obtained in the range of  $3.0 \times 10^{-7}$  to  $1.2 \times 10^{-5}$  M, with a detection limit as low as  $1.5 \times 10^{-7}$  M. The fluorescent sensor possesses remarkable selectivity for cyanide over other anions, and negligible influences were observed on cyanide detection by the coexistence of other anions or biological species such as albumin and typical blood constituents.

#### Turn-On Fluorescent Detection of Cyanide Based on the Inner Filter Effect of Silver Nanoparticles

Shang, L., C. Qin, L. Jin, L. Wang, and S. Dong.

Analyst, Vol 134 No 7, p 1477-1482, July 2009

A simple, sensitive, fluorescent method for detecting cyanide has been developed based on the inner filter effect (IFE) of silver nanoparticles (Ag NPs). The turn-on fluorescent assay for cyanide is based on the strong absorption of Ag NPs to both excitation and emission light of an isolated fluorescence indicator. In the presence of cyanide, the absorber Ag NPs will dissolve gradually, which then leads to recovery of the IFE-decreased emission of the fluorophore. The concentration of Ag NPs in the detection system was found to affect the fluorescence response toward cyanide significantly. Under optimum conditions, the IFE-based approach can detect cyanide ranging from  $5.0 \times 10^{-7}$  to  $6.0 \times 10^{-4}$  M with a detection limit of  $2.5 \times 10^{-7}$  M, which is much lower than the corresponding absorbance-based approach and compares favorably with other reported fluorescent methods. In addition, the method possesses a good selectivity for cyanide over other common anions and further application in cyanide-spiked water samples suggested a recovery between 98.2 and 101.4%.

#### Ultraviolet Absorbance as a Proxy for Total Dissolved Mercury in Streams

Dittman, J.A., J.B. Shanley, C.T. Driscoll, G.R. Aiken, A.T. Chalmers, and J.E. Towse.  
Environmental Pollution, Vol 157 No 6, p 1953-1956, June 2009

Stream water samples were collected over a range of hydrologic and seasonal conditions at three forested watersheds in the northeastern United States. Samples were analyzed for dissolved total mercury (THgd), DOC concentration and DOC composition, and UV254 absorbance across the three sites over different seasons and flow conditions. Pooling data from all sites, a strong positive correlation of THgd to DOC ( $r^2 = 0.87$ ) was observed, but with progressively stronger correlations of THgd with the hydrophobic acid fraction of DOC ( $r^2 = 0.91$ ) and with UV254 absorbance ( $r^2 = 0.92$ ). The strength of the UV254 absorbance/THgd relationship suggests that optical properties associated with dissolved organic matter might be excellent proxies for THgd concentration in these streams. Ease of sample collection and analysis, the potential application of in situ optical sensors, and the possibility for intensive monitoring over the hydrograph make this an effective, inexpensive approach to estimate THgd flux in drainage waters. UV absorbance measurements are a cost-effective proxy to estimate dissolved mercury concentration in stream water.

#### Uptake and Release of Polar Compounds in SDB-RPS Empore Disks: Implications for Their Use as Passive Samplers

Shaw, M., G. Eaglesham, and J.F. Mueller.  
Chemosphere, Vol 75 No 1, p 1-7, Mar 2009

Laboratory-based calibration experiments were conducted to compare the uptake kinetics of several key pesticides with the release of three pre-loaded performance reference compound (PRCs) in Chemcatchers using styrenedivinylbenzene/reverse-phase sulfonated (SDB-RPS) Empore disks deployed either with or without a membrane. For compounds with log  $K_{OW}$  values ranging from 1.8 to 4.0, uptake into samplers with or without a membrane was linear over 30d and 10d, respectively. While uptake was linear and reproducible, PRC loss was not linear, meaning that the dissipation rates of these PRCs cannot be used to estimate field exposure conditions on uptake rates. An alternative in situ calibration technique using PRC loaded polydimethylsiloxane (PDMS) disks deployed alongside the Empore disk samplers as a surrogate calibration phase has been tested in the current study and shows promise for future applications.

#### Use of Depuration Compounds in Passive Air Samplers: Results from Active Sampling-supported Field Deployment, Potential Uses, and Recommendations

Moeckel, C., T. Harner, L. Nizzetto, B. Strandberg, A. Lindroth, and K.C. Jones.  
Environmental Science & Technology, Vol 43 No 9, p 3227-3232, 1 May 2009

Depuration compounds (DCs) are added to passive air samplers (PASs) prior to deployment to account for the wind-dependency of the sampling rate for gas-phase compounds. This correction is particularly useful for providing comparable data for samplers that are deployed in different environments and subject to different meteorological conditions, such as wind speeds. Two types of PAS--the polyurethane foam (PUF) disk sampler and semipermeable membrane devices (SPMDs)--were deployed at eight heights on a 100-m tower to test whether

the DC approach could yield air concentrations profiles for PCBs and organochlorine pesticides and account for the wind-speed gradient with height. Average wind speeds ranged from 0.3 to 4.5 m/s over the 40-day deployment, increasing with height. Two low-volume active air samples (AAS), one collected at 25 m and one at 73 m over the 40-day deployment, showed no significant concentration differences for target compounds. As expected, the target compounds taken up by PAS reflected the wind profile with height. The wind-dependency of the PAS was also reflected in the results of the DCs. A correction based on the DC approach successfully accounted for the effect of wind on PAS sampling rates, yielding a profile consistent with the AAS. In terms of absolute air concentrations, differences noted between the AAS and PAS-derived values for some target compounds were attributed to different sampling characteristics of the two approaches that may have resulted in slightly different air masses being sampled. Based on the study results, guidelines are presented for the use of DCs and for the calibration of PAS using AAS.

#### Use of Gene Probes to Assess the Impact and Effectiveness of Aerobic In Situ Bioremediation of TCE

Hazen, T.C., R. Chakraborty, J.M. Fleming, I.R. Gregory, J.P. Bowman, L. Jimenez, D. Zhang, S.M. Pfiffner, F.J. Brockman, and G.S. Saylor.

Archives of Microbiology, Vol 191 No 3, p 221-232, Mar 2009

Gene probe hybridization was used to determine distribution and expression of cometabolic genes at a contaminated site undergoing in situ methanotrophic bioremediation of TCE. The bioremediation strategies tested included a series of air, air/methane, and air/methane/nutrient pulses of the test plot using horizontal injection wells. During the test period, the levels of TCE decreased drastically in almost all test samples. Sediment core samples (n=367) taken from 0 m (surface) to 43 m depth were probed for gene coding for methanotrophic soluble methane monooxygenase (sMMO) and heterotrophic toluene dioxygenase (TOD), which are known to co-metabolize TCE. The same sediment samples also were probed for genes coding for methanol dehydrogenase (MDH) (catalyzing the oxidation of methanol to formaldehyde) to assess specifically changes in methylotrophic bacterial populations in the site. Gene hybridization results showed that the frequency of detection of sMMO genes was stimulated ~250% following 1% methane:air (v/v) injection. Subsequent injection of 4% methane/air (v/v) resulted in an 85% decline, likely due to nutrient limitations, since addition of nutrients (gaseous nitrogen and phosphorus) thereafter caused an increase in the frequency of detection of sMMO genes. Detection of TOD genes declined during the process, and they were non-detectable by the final treatment, suggesting that methanotrophs displaced the TOD gene containing heterotrophs. Active transcription of sMMO and TOD was evidenced by hybridization to mRNA. These analyses combined with results showing the concomitant decline in TCE concentrations, increases in chloride concentration and increases in methanotroph viable counts, provide multiple lines of evidence that TCE remediation was caused specifically by methanotrophs. The results suggest that sMMO genes are responsible for most, if not all, of the observed biodegradation of TCE. The use of nucleic acid analytical methods provided a gene-specific assessment of the effects of in situ bioremediation of TCE.

Use of High Resolution Soil Core and Aqueous-phase Monitoring to Investigate TCE Biodegradation Heterogeneity within a DNAPL Source Zone Area

White, R.A., N. At, M.O. Rivett, G.P. Wealthall, & M.R. Lelliott.

Groundwater Quality: Securing Groundwater Quality in Urban and Industrial Environments (Proc. 6th International Groundwater Quality Conference, Fremantle, Western Australia). IAHS Publ. 324, p 287-294, 2008

High resolution monitoring has been used to investigate spatial variability in biodegradation activity occurring within the area of a DNAPL source zone. Preliminary analysis of data obtained from the SABRE research site is presented where a 30 x 4 x 6-m sheet-pile cell partially isolates a TCE source zone at a UK industrial site. The DNAPL source is spatially heterogeneous and its architecture is in part determined. Aqueous-phase plumes of TCE and biotic dechlorination products have exhibited significant spatial heterogeneity, showing concentration and daughter/parent molar ratios that vary rapidly over four orders of magnitude. Biotic dechlorination activity appeared most prevalent in the areas immediately surrounding and downgradient of the DNAPL source zone. The parent/daughter product heterogeneity observed is likely to be typical, but unresolved, at many DNAPL-contaminated sites.

Use of Hydrogeological and Geochemical Methods to Investigate the Origin and Fate of Vinyl Chloride in Groundwater in an Urban Environment, Ferrara, Italy

Pasini, M. and A. Gargini (Univ. of Ferrara, Italy); R. Aravena (Univ. of Waterloo, ON, Canada); D. Hunkeler (Univ. of Neuchatel, Switzerland).

Groundwater Quality: Securing Groundwater Quality in Urban and Industrial Environments (Proc. 6th International Groundwater Quality Conference, Fremantle, Western Australia). IAHS Publ. 324, p 102-109, 2008

The authors discuss recent data derived from a geochemical and isotopic fingerprinting study carried out at the Pandora site (Ferrara, Italy), which is characterized by the existence of a long vinyl chloride (VC) plume, and at the Caretti site, where high concentrations of chlorinated compounds, including VC, occur. Data also were collected at an unconfined aquifer beneath a major petrochemical plant. The isotopes data show that the unusual negative  $\delta^{13}\text{C}$  values observed in the VC at both sites could not be attributed to reductive dechlorination of manufactured primary PCE or TCE. Unusual negative  $\delta^{13}\text{C}$  values for PCE and TCE also characterize the impacted aquifer beneath the petrochemical plant and the Caretti site. Based on the industrial history of the region, which includes production of PVC and chloromethanes, contamination in the Ferrara region might be linked to wastes originating from the production of chloromethanes. The primary organic compound used in chloromethane production is methane, which is strongly depleted in  $\text{C-13}$ , similar to the values observed in VC, PCE, and TCE at the investigated sites. The authors also hypothesize that the contamination is linked to dumping of industrial waste in the abandoned lagoons used by the sugar industry and in clay pits associated with the clay industry.

The Use of MIMS-MS-MS in Field Locations as an On-Line Quantitative Environmental Monitoring Technique for Trace Contaminants in Air and Water

Etzkorn, J.M. N.G. Davey, A.J. Thompson, A.S. Creba, C.W. LeBlanc, C.D. Simpson, E.T. Krogh, and C.G. Gill.

Journal of Chromatographic Science, Vol 47 No 1, p 57-66, Jan 2009

Because membrane introduction mass spectrometry (MIMS) interfaces are simple and robust, they are ideally suited for operation in MS instrumentation used for in-field applications. An on-line permeation tube was used for continuous infusion of an isotopically labeled internal standard for continuous quantitative determinations in atmospheric and aqueous samples without the need for off-line calibration. This approach provided important information on the operational performance of the analytical system during multi-day deployments. Measured signal stability during on-line deployments in air and water was 7% based on variation of the internal standard response. This technique was used to quantify BTEX, pinenes, naphthalene and 2-methoxyphenol (guaiacol) in urban air plumes at parts per billion by volume levels. The authors present several recent applications (laboratory, remote, and mobile deployments) of MIMS-MS/MS for on-line environmental monitoring in atmospheric and aqueous environmental samples; the use of a thermally assisted MIMS interface for direct measurement of PAHs, alkylphenols, and other SVOCs in the low ppb range in aqueous environmental samples; and discussion of improvements in both the sensitivity and response times for selected SVOCs. The significant improvements in field-deployable mass spectrometric techniques enable direct on-site analytical measurements of VOC and SVOCs in environmental samples.

#### Using Helicopter Electromagnetic Surveys to Identify Potential Hazards at Mine Waste Impoundments

Hammack, R.

GeoCongress 2008: Geosustainability and Geohazard Mitigation, Proceedings of GeoCongress 2008. ASCE/GEO Institute, Reston, VA, Geotechnical Special Publication No 178, ISBN 978-0-7844-0971-8, p 199-206, 2008

In July 2003, helicopter electromagnetic surveys were conducted at 14 coal waste impoundments in southern West Virginia to detect conditions that could lead to impoundment failure either by structural failure of the embankment or by the flooding of adjacent or underlying mine works. Specifically, the surveys attempted to 1) identify saturated zones within the mine waste, 2) delineate filtrate flow paths through the embankment or into adjacent strata and receiving streams, and 3) identify flooded mine workings underlying or adjacent to the waste impoundment. Data from the helicopter surveys were processed to generate conductivity/depth images. Conductivity/depth images were then spatially linked to georeferenced air photos or topographic maps for interpretation. Conductivity/depth images were found to provide a snapshot of the hydrologic conditions that exist within the impoundment. This information can be used to predict potential areas of failure within the embankment because of its ability to image the phreatic zone. Also, the electromagnetic survey can identify areas of unconsolidated slurry in the decant basin and beneath the embankment. Although the survey identified shallow flooded mineworks beneath the impoundment, it cannot be assumed that electromagnetic surveys can detect all underlying mines. A preliminary evaluation of the data implies that helicopter electromagnetic surveys can provide a better understanding of the phreatic zone than the piezometer arrays that typically are used.

Using Reversed Polarity Airborne Transient Electromagnetic Data to Map Tailings Around Mine Sites

Smith, R.S., L.Z. Cheng, and M. Chouteau

The Leading Edge, Vol 27 No 11, p 1470-1478, Nov 2008

The response measured by transient electromagnetic (TEM) systems normally is of a predictable sign, particularly for coincident-loop ground TEM systems, where the response in theory always should be positive when the ground conductivity is a constant function of frequency and the quasi-static assumption is satisfied. In most cases, these are good assumptions, but, occasionally, coincident-loop negative transients are observed. These negatives can be explained if material in the ground has a conductivity that changes with frequency, or equivalently, has non-zero polarizability.

## **SBIR AND OTHER GRANT AWARDS**

### **Environmental Security Technology Certification Program (ESTCP)**

Demonstration of an In-Situ Friction-Sound Probe for Mapping Particle Size at Contaminated Sediment Sites (ESTCP 2009 Grant)

Project ER-0919, 2009 to 2012

Dr. Bart Chadwick, PI, SPAWAR Systems Center, San Diego, 619-553-5333,

[bart.chadwick@navy.mil](mailto:bart.chadwick@navy.mil)

The project goal is to demonstrate a sediment friction-sound probe (SED-FSP) for direct, in situ measurement of grain size at contaminated sediment and groundwater/surface water interaction (GSI) sites. Specific objectives include development of a commercial prototype friction-sound probe, verification of sensor performance in the laboratory, and field demonstration and verification at three DoD sites.

<http://www.estcp.org/Technology/ER-0919-FS.cfm>

Demonstration of the Gore Module for Passive Ground Water Sampling (ESTCP 2009 Grant)

Project ER-0921, 2009-2011

Louise Parker, PI, U.S. Army Corps of Engineers, ERDC-CRREL

Long-term groundwater sampling programs, which are required to assess contaminant trends in groundwater and risk to human health, are costly. The Gore Module developed by W.L. Gore & Associates, Inc. can be used to sample a wide variety of volatile and semi-volatile organic compounds. The project objective is to demonstrate the utility, sensitivity, comparability, and potential cost savings of passive groundwater sampling using the Gore Module at DoD and DOE sites. <http://www.estcp.org/Technology/ER-New-Starts.cfm#ER-0921>

Field Portable GC-MS Unit for Semi-Volatile Compound Analysis in Groundwater (ESTCP 2009 Grant)

Project ER-0922, 2009-2011

Dr. Anthony Bednar, U.S. Army Corps of Engineers, Engineer Research and Development Center, Vicksburg, MS, 601-634-3652, [Anthony.J.Bednar@usace.army.mil](mailto:Anthony.J.Bednar@usace.army.mil)

The concentration of munitions constituents in groundwater at military ranges is an ongoing concern that requires periodic monitoring. The traditional monitoring scenario requires that large amounts of sample (2 to 4 liters) be shipped overnight, under chain-of-custody control, to a fixed laboratory for analysis by regulatory-approved methods. Additionally, the samples must be packed on ice and shielded from light to prevent any degradation of the samples during transport and storage. Once in the laboratory, the typical analysis and data reporting time is 30 to 45 days. This process results in data being unavailable to the customer, concentration data to be at least one month old, and expenses incurred for sample collection and shipping. The objective of this project is to demonstrate a field-portable gas chromatograph-mass spectrometer (GC-MS) for analysis of the explosives on site. This methodology provides near real time (within 1.5 hours of sampling) data of the concentration of munitions constituents in a groundwater sample. The use of the mass spectrometer as a detection technique provides absolute confirmation of the munitions constituents and a means to identify unknown compounds present in the sample that might otherwise provide false positive detections.

<http://www.estcp.org/Technology/ER-0922-FS.cfm>

Demonstration of the Attributes of Multi-Increment Sampling and Proper Sample Processing Protocols for the Characterization of Metals on DoD Facilities (ESTCP 2009 Grant)

Project ER-0918, 2009 to 2012

Alan Hewitt, PI, U.S. Army Corps of Engineers, ERDC-CRREL, Hanover, NH. 603-646-4388, [Alan.D.Hewitt@ERDC.usace.army.mil](mailto:Alan.D.Hewitt@ERDC.usace.army.mil)

Environmental studies of military training ranges have shown that energetic residues are distributed heterogeneously, and as such, multi-increment sampling methods have been recommended for site characterization. This project will employ a multi-increment sampling technique, coupled with adequate sample processing, to demonstrate superior data quality and address the data gap that exists with the characterization of metals on training ranges. This technique will be similar to EPA Method 8330B for the characterization of energetic residues.

<http://www.estcp.org/Technology/ER-0918-FS.cfm>

Parallel In Situ Screening of Remediation Strategies for Improved Decision Making, Remedial Design, and Cost Savings (ESTCP 2009 Grant)

Project ER-0914, 2009 to 2011

Dr. Rolf Halden, PI, Arizona State University, Tempe, 480-727-0893, [rhalden@asu.edu](mailto:rhalden@asu.edu) ; DoD Liaison: Dr. Nancy Ruiz, NFESC, Port Hueneme, CA, 805-982-1155, [nancy.ruiz@navy.mil](mailto:nancy.ruiz@navy.mil)

The project aims to demonstrate the in situ microcosm array (ISMA) technology for remedial design of chloroethene remediation and to develop a guidance document and workshop, both based on real-world experience gained and data collected. The ISMA technology answers key questions frequently posed by remediation regulators and decision makers: (1) Are contaminants being attenuated naturally, and if so, at what rate? (2) Can this rate of contaminant removal be accelerated? (3) Among the available active remediation approaches, which one will perform most favorably at the site and what is the ideal dosage regime for any given chemical or biological supplement? (4) Is active remediation economically attractive when compared to natural attenuation? And, finally (5) will the manipulation of environmental conditions at the site lead to unwanted effects, such as sediment clogging or solubilization of toxic metals?

<http://www.estcp.org/Technology/ER-0914-FS.cfm>



Passive Polyethylene Sampling in Support of In Situ Remediation of Contaminated Sediments (ESTCP 2009 Grant)

Project ER-0915, 2009 to 2012

Dr. Philip Gschwend, PI, Massachusetts Inst. of Technology, Cambridge, 617-253-1638, [pmgschwe@mit.edu](mailto:pmgschwe@mit.edu); DoD Liaison: Amy Hawkins, NFESC, Port Hueneme, CA, 805-982-4890, [amy.hawkins@navy.mil](mailto:amy.hawkins@navy.mil)

The overall project objective is to demonstrate that the polyethylene (PE) passive sampling methodology is a commercially viable technology for determining horizontal and vertical distributions of hydrophobic organic compounds (HOC) in sediments while assessing in situ remediation and/or pursuing long-term monitoring (LTM). Specific objectives include (1) demonstrating the accuracy of the PE passive sampling method for use in situ, (2) demonstrating the advantages of using PE passive sampling for defining the horizontal and vertical extent of contamination, (3) showing that PE passive sampling is well suited to LTM programs, and (4) establishing the performance capabilities (limits of detection, accuracy, precision) and the cost benefits of this passive sampling approach while making this a commercially viable tool.

<http://www.estcp.org/Technology/ER-0915-FS.cfm>

Validation of an In Vitro Bioaccessibility Test Method for Estimation of Bioavailability of Arsenic from Soil and Sediment (ESTCP 2009 Grant)

Project ER-0916, 2009-2011

Dr. Susan Griffin, U.S. EPA, Denver, CO, 303-312-6651, [griffin.susan@epa.gov](mailto:griffin.susan@epa.gov)

The objective of this project is to develop an in vitro bioaccessibility assay for arsenic in soils and sediments and validate it against 41 different arsenic-containing test materials from mining, smelting, herbicide, pesticide, chromated copper arsenate (CCA), and chemical-plant sites across the United States that have been tested previously for bioavailability in an in vivo cynomolgus monkey or juvenile swine study. This information will then be presented to the U.S. Environmental Protection Agency (EPA) as part of an integrated effort to generate formal agency guidance and training of regional staff regarding in vitro methods for assessing the relative oral bioavailability (RBA) of arsenic on a site-specific basis.

<http://www.estcp.org/Technology/ER-0916-FS.cfm>

## National Science Foundation

Aptamer-Based Colorimetric Test Kit for Biological Contamination Detection (NSF 2009 SBIR Phase 1)

NSF Award 0912131

Anastasia Bogomolova, PI, 727-595-6175. [abogomol@hotmail.com](mailto:abogomol@hotmail.com)

Smart Polymers Research Corporation, Belleair Beach, FL

July 1, 2009 - December 31, 2009

\$99,999

This Phase I project is dedicated to the development of rapid aptamer-based dipstick sensor, a colorimetric test strip sensor based on a known DNA aptamer. The initial target organism is *B. thuringiensis* (anthrax simulant in spore form), to demonstrate its performance

and to characterize its sensitivity, specificity, detection time, and stability. Using the developed prototype, the team will substitute the aptamer by the one specific to B. anthracis spores and demonstrate detection of anthrax spores in spiked water samples. Phase II will expand the approach to Shiga toxin, cholera toxin, staphylococcal enterotoxin B, botulinum toxin A, ricin toxin, and tularemia bacteria to create test-strip sensors for these agents and perform additional sensitivity and performance optimization and stability testing. Individual testing strips can be assembled on a single laminating support card to result in a multi-specific single-dip colorimetric sensing card, ready for field use. Since the innovative technology is universal, it will find use in a variety of applications. A team of scientists and commercial partners has been assembled to ensure success of the program all the way through commercialization of the technology. The sensor will have immediate applications for environmental monitoring, providing rapid specific detection and identification of multiple biological agents without extensive sample preparation or expensive detection equipment. In addition to biowarfare agents, the developed technology will be suitable for environmental monitoring of air and water, including drinking water.

Automated Identification and Rapid Detection of Explosives Using Piezoresistive Micro- and Nano-Cantilever Arrays (NSF 2009 SBIR Phase 1)

NSF Award 0912423

Weibin Zhu, PI, 734-972-9348, [zhuwb@picocal.com](mailto:zhuwb@picocal.com)

PICOCAL, Inc., Ann Arbor, MI

July 1, 2009 - December 31, 2009

\$99776

This project proposed to develop an inexpensive, rugged piezo-resistive micro-cantilever sensor array for explosives and toxins detection with the ability for wireless data transmission. The sensor can identify analytes by changes in the electronic properties of the sensor material due to analyte absorption or binding. The sensitivities and detection limits are significantly improved by using ultra-compliant coated polymers that show a high degree of sensitivity and selectivity to different explosives. Ultrathin metallic piezo-resistive sensors are embedded into the cantilevers to enable both static and dynamic measurements. Compared to micro GC systems and film-based sensor arrays for detection of explosives, the sensor proposed has several advantages including a low-cost fabrication process, higher sensitivity for lower detection limits, and highly selective coating materials for absorption of chemical vapors from improvised explosive devices. This proposed sensor potentially can enable low-cost and reliable handheld systems for remote detection of analytes and wireless sensing networks in buildings.

Chemical Sensors for In situ Monitoring of Collector Chemicals in Complex Copper Mine Effluents (NSF 2009 STTR Phase 1)

NSF Award 0930087

Jon Thompson, PI, 651-213-6185, [jthompson@unitedsciencecorp.com](mailto:jthompson@unitedsciencecorp.com) and Philippe Buhlmann, Co-PI

United Science LLC, Center City, MN partnered with the University of Minnesota

July 1, 2009 - June 30, 2010

\$150,000

The goal of Phase I is the preparation of sensors that permit the measurement of collector chemicals used in flotation suspensions. The proposed sensors are not affected by turbidity, have a collector selectivity that can be tuned with specific receptors, and require no off-stream sample handling. The project will take advantage of the highly selective and fouling-resistant fluoropolymer membranes introduced by the academic partner Phil Buhlmann (UMN). This research aims to reduce significantly the amount of toxic chemical waste associated with froth flotation and its inevitable environmental impact, thus improving mining sustainability by eliminating an estimated 891,000 kg of unnecessary chemical discharges.

Eliminating 'Nonpoint': Using Nanotechnology to Identify Pollution Sources in the Landscape (NSF 2009 Standard Grant)

M. Walter, PI, 607-255-5014, [mtw5@cornell.edu](mailto:mtw5@cornell.edu), and Dan Luo, Co-PI

Cornell University, Ithaca, NY

Award 0853809

July 1, 2009 - June 30, 2012

\$494,805

The principal objective of this project is to develop an itracer system for identifying and characterizing different flowpaths at field and watershed scales by labeling or coding itracers with unique DNA-based nanobarcodes so that many flowpaths can be identified simultaneously. The goal is to have the capacity of introducing itracers at different points in a watershed and collecting them elsewhere in the watershed; using a portable nanobarcode reader, the hydrological linkages and transport times between the collection point(s) and the points of itracer-introduction could then be determined. The itracers used are nanobarcodes encapsulated in safe, degradable microspheres. A nanobarcode is an engineered, tree-like network of non-coding DNA with a fluorescent marker attached to the end of each branch. The barcodes are distinguished by their unique combinations of fluorescent colors and can be 'read' by flow cytometry. One advantage of this technology is that the detection limit is one itracer, whereas traditionally used tracers require substantially higher quantities for reliable detection. Also, the itracer size is similar to that of microorganisms and thus serves as a good proxy for many microbial pathogens. This project builds on recent research at Cornell, which has successfully manufactured itracers, fabricated and successfully read nanobarcodes, and experimented with itracers in a variety of small-scale laboratory experiments. The proposed project will move this novel technology to the field.

Fiber Optic Surface Enhanced Raman Sensor for High Sensitivity and Automatic Molecule Identification (NSF 2008 Standard Grant)

NSF Award 0823921

Claire Gu, PI, 831-459-5278, [claire@ee.ucsc.edu](mailto:claire@ee.ucsc.edu) and Jin Zhang, Co-PI

University of California-Santa Cruz

October 1, 2008 - September 30, 2011

\$330,000

The objective of this research is to develop and demonstrate a novel fiber sensor based on surface enhanced Raman scattering (SERS) using metal nanostructures for chemical, biological, and environmental detection. The approach is to integrate 1) novel nanoparticle substrates that

provide the high sensitivity and consistency, molecular specificity, and applicability to a wide range of compounds; 2) a unique hollow core optical fiber probe with double SERS substrate structure that provides the compactness, reliability, low cost, and ease of sampling; and 3) an innovative matched spectral filter set that provides automatic preliminary molecule identification.

Low Cost, Robust Multi-Gas Sensors for Environmental Sensing Applications (NSF 2009 SBIR Phase 1)

NSF Award 0912463

Jon James, 803-429-9966, [jonjames1@hotmail.com](mailto:jonjames1@hotmail.com)

SENS4, Aiken, SC

July 1, 2009 - December 31, 2009

\$100,000

This project will develop an integrated high-performance, low-cost, and compact gas sensor device for environmental monitoring, with emphasis placed on the early and reliable detection of a variety of prevalent environmental and industrial airborne contaminants. The sensor system will be fast (i.e., having a response time <100 milliseconds) while demonstrating a minimum number of false positives. This detection requires sensors that are prevalent, sensitive, robust, and inexpensive. Furthermore, the response to targeted gases will be orthogonal to interfering species while also displaying fast recovery times. Many types of current gas sensors reveal large interfering sensitivities to molecules other than those of interest, typically resulting in false positive signals for the targeted gases. A micro-cantilever-based gas sensor technology that provides high sensitivity and low cross-sensitivity will be developed. The proposal will concentrate its efforts on detecting 5 gases of commercial and environmental importance: carbon monoxide, nitrogen dioxide, hydrogen sulfide, ammonia, and benzene.

Nanoselenium for Simultaneous Detection and Capture of Mercury Vapor in Fluorescent Lighting Technology (NSF 2009 STTR Phase 1)

Love Sarin, PI, 512-795-5835, [love.sarin@gmail.com](mailto:love.sarin@gmail.com) and Robert Hurt, Co-PI

Aspen Sciences, Inc., Austin, TX partnered with Brown University

NSF Award 0930303

July 1, 2009 - June 30, 2010

\$150,000

This project is focused on the development of a new technology for reducing the human health risks associated with mercury over the life-cycle of fluorescent lamps. Fluorescent lamps can break and release their internal inventory of mercury, which is a known neurotoxicant, environmental pollutant, and developmental toxicant of special concern for children and women of child-bearing age. Aspen Sciences is teaming with Brown University and ARCH Venture Partners to develop nano-selenium-based products to react with and capture mercury vapor during fluorescent lamp shipping, use, collection, and recycling. The research focuses on cost-effective nano-selenium synthesis; study of reaction rates and sorbent color change for mercury detection; design and testing of reactive barriers as box or bag safety liners; and sorbent stability during storage use and disposal.

Novel Nanostructured ZnO Gas Sensors on (100) Si Wafers (NSF 2008 Standard Grant)

Agis Iliadis, PI, 301-405-6269, [agis@eng.umd.edu](mailto:agis@eng.umd.edu)

University of Maryland, College Park

NSF Award 823996

August 1, 2008 - July 31, 2011

\$329,967

The objective of this research is to develop nanostructured ZnO on Si multi-gas sensors capable of room temperature operation with high sensitivity, responsivity, and specificity compatible with CMOS technology. The approach is to substantially increase the performance capabilities of the sensor (a) by increasing sensor surface through nanostructures and thin catalytic metal contacts, (b) by introducing a field-assisted sensing process through nanojunctions, and (c) by conditioning the field-assisted process. The broader impact will be in environmental safety, quality, and security, in particular in unstable explosive, toxic, and hazardous environments, where rapid, sensitive detection is needed.

Planar Array Infrared (PA-IR): A Compact Rugged Double Beam Infrared Spectrometer for Laboratory and Field Analysis (NSF 2008 STTR Phase 2)

Daniel Frost, PI, 302-695-4434, [dwf62@comcast.net](mailto:dwf62@comcast.net) and John Rabolt, Co-PI

PAIR Technologies, LLC, Wilmington, DE partnered w/ University of Delaware

NSF Award 0848096

February 1, 2009 - January 31, 2011

\$499,844

This project will demonstrate the utility of infrared planar array technology to study water pollutants, such as industrial contaminants and biological impurities. It proposes to optimize the design and construction of a compact, high-sensitivity, double-beam infrared instrument based on focal plane array detection that meets or exceeds performance standards of commercially available Fourier transform infrared spectroscopy (FT-IR) solutions and is able to operate in ambient environments to provide measurements of dilute concentrations of organic and biological contaminants. If successful the outcome of this project will enable real-time effluent detection from, for example, a manufacturing site. A portable Planar Array Infrared (PA-IR) spectrograph could be used to measure contaminants in rivers, streams, and ponds, thereby providing real-time feedback on changes in the environment. The world laboratory analytical instrument market is estimated to be \$9.36B in 2008. IR spectroscopy is estimated to be \$738M.

Rapid Identification of Environmental Contaminants Using an Electrospray Ionization - Ion Mobility Spectrometer / Chiral Ion Mobility Spectrometer (NSF 2009 SBIR Phase 1)

Ching Wu, 978-264-1980, [ching.wu@excellims.com](mailto:ching.wu@excellims.com)

Excellims Corporation, Acton, MA

NSF Award 0912422

July 1, 2009 - December 31, 2009

\$100,000

This project is focused on the development of a stand-alone electrospray ionization-ion mobility spectrometer/chiral ion mobility spectrometer (ESI-IMS/CIMS) for on-site separation,

detection and identification of environmental contaminants with the unique capability of separating chiral molecules. Many pesticides are applied as a mixture of chiral forms despite the fact that each chiral form may differ in its impact on environmental and biological processes. Efficient methods for chiral analysis will facilitate the study of stereoisomer-dependent toxicity and biodegradation, as well as permit evaluation of pollutant potential and agricultural pesticide loading. The ESI-IMS/CIMS system will be used in place of slow, expensive, lab-based chiral separation methods and will be able to detect both volatile and non-volatile non-chiral species concurrently. In Phase I, the focus is on the development of a commercial ESI-IMS system and identification and validation of chiral modifiers for use in CIMS.

## **Strategic Environmental Research and Development Program (SERDP)**

An Assessment of Aquifer/Well Flow Dynamics: Identification of Parameters Key to Passive Sampling and Application of Downhole Sensor Technologies (SERDP 2009 Grant)

Project ER-1704, 2009 to 2012

Sanford Britt, PI, ProHydro, Inc., Fairport, NY. 585-385-0023, [sandy.britt@prohydroinc.com](mailto:sandy.britt@prohydroinc.com)

This project aims to develop a comprehensive understanding and description of how contaminant concentrations measured in a well using either passive sampling devices or in situ sensors relate to contaminant concentrations in the surrounding formation. The research will elucidate the relationship between solute concentrations in wells and in the surrounding formation, thus providing the understanding and documentation necessary for efficient and cost-effective application of alternative sampling and monitoring strategies.

<http://www.serdp.org/Research/ER-1704-FS.cfm>

Improved Understanding of Sources of Variability in Groundwater Sampling for Long-Term Monitoring Programs (SERDP 2009 Grant)

Project ER-1705, 2009 to 2012

Dr. Charles Newell, PI, GSI Environmental, Inc., Houston, TX. 713-522-6300, [cjnewell@gsi-net.com](mailto:cjnewell@gsi-net.com)

The objective of this project is to identify key sources of variability that influence VOC concentration measurements in water samples collected from groundwater monitoring wells using current sampling and analysis techniques. The hypotheses are that (1) in addition to sample collection and analytical methods, other specific sources of monitoring variability such as aquifer and well dynamics can be identified and quantified and (2) the variability attributable to many of the specific sources can be reduced through the use of new tools or the modification of common well sampling methods.

<http://www.serdp.org/Research/ER-1705-FS.cfm>

Lab-on-a-Chip Sensor for Monitoring Perchlorate in Ground and Surface Water (SERDP 2009 Grant)

Project ER-1706, 2009 to 2010

Dr. Donald Cropek, PI, U.S. Army Corps of Engineers, ERDC-CERL, Champaign, IL. 217-373-6737, [donald.m.cropek@usace.army.mil](mailto:donald.m.cropek@usace.army.mil)

The objective is to study zwitterionic surfactant chemistry to create a miniaturized sorption zone that selectively and controllably binds and releases perchlorate in the presence of excess common environmental anions such as nitrate and chloride. This novel concentration zone will be embedded onto a microfluidic sensor platform to test its ability for perchlorate extraction and concentration to provide rapid (<10 min/sample), sub-ppb analysis of perchlorate in surface water and groundwater samples. In this limited-scope effort, the underlying chemical basis for the extraction technique will be studied with an aim towards developing a fieldable sensor in a follow-on effort.

<http://www.serdp.org/Research/ER-1706-FS.cfm>

Quantifying the Presence and Activity of Aerobic, Vinyl Chloride-Degrading Microorganisms in Dilute Groundwater Plumes by Using Real-Time PCR (SERDP 2009 Grant)

Project ER-1683, 2009 to 2012

Dr. Timothy Mattes, PI, University of Iowa, Iowa City, 319-335-5065, [tim-mattes@uiowa.edu](mailto:tim-mattes@uiowa.edu)

The project objective is to develop and validate real-time polymerase chain reaction (PCR) techniques that can quantify both the presence and functionality of aerobic VC-degrading bacteria in groundwater samples from dilute VC plumes. After the PCR-based techniques are developed, researchers will determine if the aerobic VC degradation rate in groundwater samples can be correlated with aerobic VC degradation functional gene and mRNA transcript abundance. The proposed molecular biological tools represent significant potential cost savings to DoD by improving bioremediation assessment and design in the field and reducing uncertainty where remediation of VC is involved.

<http://www.serdp.org/Research/ER-1683-FS.cfm>