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JOURNAL OF HAZARDOUS MATERIALS

Special Issue

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JOURNAL OF HAZARDOUS MATERIALS

Management — Handling — Disposal — Risk Assessment

Review papers, normal papers, project reports and short communications are published dealing with all aspects of hazardous materials arising from their inherent chemical or physical properties. The scope of the journal is wide, ranging from basic aspects of preparation and handling to risk assessment and the presentation of case histories of incidents involving real hazards to employees or the public.

The following list, though not exhaustive, gives a general outline of the scope:

Properties: toxicity, corrosiveness, flammability, explosiveness, radioactivity, information data banks, dose–response relationships

Safety and health hazards: manufacturing, processing, transport, storage, disposal, major hazards and hazardous installations

Legislation: international, national and local codes of practice, threshold values, standards

Incidents: prevention, control, clean-up, communication, labelling, sources of information and assistance, case histories

Assessment: economic and general risk assessment, insurance, test methods, technical aspects of risk assessment of industrial hazards, reliability and consequence modelling, decision-making in risk management

Special Issue

Ground Water — The Problem and Some Solutions

Proceedings of the Gulf Coast Hazardous Substance Research
Center Fourth Annual Symposium:
Ground Water — The Problem and Some Solutions
Lamar University, Beaumont, TX, U.S.A., April 2–3, 1992

Guest Editors

William A. Cawley
Gulf Coast Hazardous Substance Research Center
P.O. Box 10613
Lamar University
Beaumont, TX 77710

Raymond C. Loehr
University of Texas at Austin
Department of Civil Engineering
Cockrell Hall
Austin, TX 78712

and

Herb Ward
Rice University
Department of Environmental Science and Engineering
P.O. Box 1892
Houston, TX 77251

Notice

Preface

The *Gulf Coast Hazardous Substance Research Center* (GCHSRC) was created by Section 118(I) SARA for the purpose of "conducting research to aid in more effective hazardous substance response and waste management throughout the Gulf Coast". For each of FY89 and FY90, $1.5 million was appropriated, and in FY91 and FY92, $2.5 million was appropriated for GCHSRC as part of the EPA funding bill. Texas Senate Bill 39 (70th Session) created a parallel state organization for the four Texas universities in the consortium. For the 1988–89 and the 1990–91 biennium, a total of $2.4 million ($600,000 per year) was appropriated for the Texas Center by the Texas legislature. Funding for 1992–93 biennium is slightly less – $1.16 million.

The consortium universities are Louisiana State University, Mississippi State University, Texas A&M University/TEES, The University of Alabama, University of Central Florida, University of Houston, University of Texas–Austin, and Lamar University.

The Center's effort is concentrated in the areas of waste minimization and alternate technology development. This activity includes, in the broadest definition, process modifications, process engineering, and recycle reuse approaches. The technology program includes a number of projects on various aspects of biological treatment bioremediation. other physical and chemical methods as well as a multiuniversity, interdisciplinary effort on understanding the mechanisms of solidification/stabilization. A small portion of the program is devoted to an effort to support and enhance the application of technology. This activity is presently in the areas of biology, sociology, and microbiology.

The research is done by the faculties of the member universities on their campus. Proposals for research projects within the framework of the Center's program are submitted by faculty members for review by the Science and Industry Advisory Committees. These committees advise the Center Director on the technical and scientific quality of the proposals and assist him in selecting the projects which will make up the program.

At this time, the Center has some 70 projects in progress in a joint federal, state, industry effort at the Texas Universities and a federal, industry supported research activity outside the state.

Each year during April as a part of its technology transfer program, GCHSRC hosts a symposium on a subject which is of major importance in the hazardous waste management field and which is within the research mandate of the Center. The 1989 subject was incineration with particular emphasis on trial burns, instrumentation and operations, while the 1990 meeting discussed Solidification/Stabilization — Mechanisms and Applications. In 1991, bioremediation was the subject which focused, as is the pattern for these meetings, on fundamentals and applications. Included as a major part of the Symposium is a poster session presenting all the research in progress within GCHSRC.

These Proceedings are the papers and summaries of the posters that have been presented at the Gulf Coast Hazardous Substance Research Center's 1992 Symposium on Ground Water — The Problem and Some Solutions.

WILLIAM A CAWLEY
Gulf Coast Hazardous
Substance Research Center
Beaumont, TX. USA

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Review

Journal of Hazardous Materials, 32 (1992) 129-136
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Factors limiting the success of groundwater remediations *

Bob Hockman

Amoco Corporation, Environmental Affairs and Safety Department, Groundwater Management Section, P.O. Box 3385, Tulsa, OK 74 102 (USA)

Abstract

Non-optimal treatment technologies such as excavation and disposal of petroleum hydrocarbon contaminated soil may result when remediation decisions are driven by political agendas, economic gains, and/or public perception as opposed to a sound, site specific technical analysis. Resultant misdirection of financial and technical resources could prevent remedial action at another contaminated site that poses a greater risk to public welfare. This paper discusses these problems and presents ideas to improve the situation. Technical considerations include (1) project management can take advantage of the asymptotic behavior of remediation technologies to reevaluate and possibly modify components of the existing technology, and (2) most successful remediations result from additive affects of multiple, complementary technologies that have been customized for the site conditions.

Introduction

As of April, 1991, the U.S. Environmental Protection Agency (EPA) Office of Underground Storage Tanks had identified approximately 128,000 "confirmed releases" of petroleum hydrocarbons from underground storage tanks to the environment. Approximately 21,000 of these were considered "completed remediations". Most of the "completed remediations" were actually excavation of contaminated soils and disposal in a landfill [1]. Even though it is included in the U.S. EPA statistics as remediation, excavation and disposal may actually cause additional groundwater contamination.

Excavation and disposal simply moves the contaminated soils to another location. If the contamination from these soils reaches groundwater below the

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Correspondence to: B. Hockman, Amoco Corporation, Environmental Affairs and Safety Department, Groundwater Management Section, P.O. Box 3385, Tulsa, OK 74 102 (USA). Fax: (918) 660-4443.

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disposal location, a second remediation may result. Excavation and disposal may have actually caused more groundwater contamination than it prevented.

Few of the completed remediations factored into the U.S. EPA statistics include shutdown of groundwater pump-and-treat systems that had reached contaminant levels mandated by regulatory programs [1]. Groundwater remediations that have successfully reduced contaminants to permissible levels are rare even though pump-and-treat systems have been active for 5–10 years. Why? The following text discusses reasons for frequent use of excavation and disposal as a remediation method and the lack of pump-and-treat successes.

Forgetting the basics

When asked, most professionals conclude that the laws controlling groundwater remediations include RCRA, CERCLA, Clean Water Act, Safe Drinking Water Act, andthe state and/or local regulatory programs based on them. This assertion is only partly true. Three other laws actually have a more important role in controlling groundwater remediations.

The first, and most important technically, was written in 1856 and is known as Darcy's Law [2]. Darcy's Law states that the rate at which fluids will move through a porous media is limited by characteristics of the media, characteristics of the fluids, and the hydraulic gradient of the fluids within the media.

Darcy's Law, coupled with partitioning [2] of the contaminant present, will determine how the remediation should be performed, the rate it will progress, and if it will be successful in meeting the permissible contaminant levels. Professionals managing groundwater remediations often fail to consider Darcy's law limitations and engineer remediation systems that are inadequate for the physical conditions or fluids present. These flawed systems often result from attempting to satisfy regulatory requirements and/or lack of experience performing groundwater remediations.

The second, and most important practically, is "Murphy's Law". Anyone who has managed or even worked on a groundwater remediation knows that any possible complication that can cause difficulties will occur. These complications can include geologic surprises, technology malfunction, contractor malpractice, permit delays or combinations of all of these. As a result, remediation projects are infamous for being slow and/or over budget. The experienced remediation professional has usually learned this the hard way and factors the effects of Murphy's Law into projects accordingly.

The third, and most important pragmatically, is the "Law of the Squeaky Wheel". That is, the groundwater resource often is not the driving factor in a groundwater remediation. Groundwater remediations are often driven and prioritized by political agendas, economic gains, and/or related public perception. The resource and the effects of the contaminant(s) on it are often not the dominant consideration in developing groundwater remediations. Both regulatory officials and responsible parties may be forced to focus limited resources at locations more significant from a public perception standpoint than from a groundwater standpoint.

Technical decisions are often based on non-technical considerations thus limiting the potential success of a remediation. As a result, excavation and disposal of contaminated materials in landfills often result from the Law of the Squeaky Wheel. The professional managing and the regulatory official overseeing a groundwater remediation project may be forced, by non-technical factors, to use excavation and disposal even though there is no threat to groundwater on site. This may also prevent the professional from using better remediation techniques or simply monitoring the site for natural degradation and/or dispersion of the contaminants. A remediation technique is used, not because it is the best technically, but because it can be initiated rapidly to quell negative public perception.

Travis and Doty [3] in their evaluation of Superfund remediations concluded that "remediation decisions appear to be driven more by cost, EPA policy, compliance with state and federal environmental regulations and professional judgement rather than by current or future risk levels." Groundwater remediation requirements should be based on the risks posed by the contaminants present combined with the potential for the contaminants to reach groundwater.

Requiring remediation simply because a site has been contaminated limits the potential for groundwater protection in general due to misdirection of financial resources. Attempting to remediate all sites and the resultant workload precludes prioritization based on risk. Sites where groundwater is most at risk often are not addressed properly because regulatory officials, consultants, and responsible parties are "fighting fires".

Delays in remediation system start-up

Zhu et al. [4] evaluated the affects of delaying free-phase hydrocarbon recovery after a release. As shown in Fig. 1, delaying recovery significantly decreases the ratio of hydrocarbons recovered as free-phase vs. the quantity spilled.

As a result, significantly more of the hydrocarbon release migrates from the spill origin and is trapped in the geologic matrix as residual phase contamination (Fig. 2). Remediating residual phase hydrocarbons is significantly more difficult than recovering free-phase hydrocarbons. Thus, delaying free-phase recovery can limit the potential to successfully remediate the release to permissible levels.

In practice, groundwater remediations are often delayed due to the regulatory process and related public mistrust. The regulatory system often seems to work against the regulatory official and the responsible party attempting to

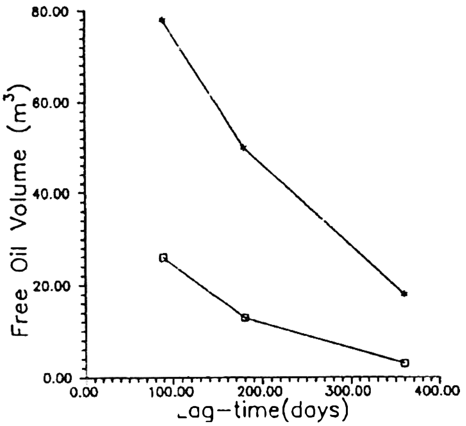

Fig. 1. Effects of delayed starting on free-phase hydrocarbon recovery (From Zhu et al., 1991). (*) Free oil before pumping, and (□) recovered hydrocarbon.

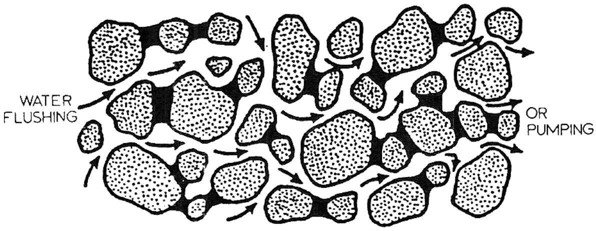

Fig. 2. Trapped oil at residual saturation (from API, 1989). Flushing will not remove all of the trapped product because of capillary attraction.

begin a remediation. Even when groundwater and/or people are threatened, the process is slowed by the number of approvals and/or permits required to install and operate a remediation system.

Nationwide, millions of dollars worth of remediation equipment is sitting idle or recovering contamination passively while awaiting air or water discharge permits. This is not a reflection of the lack of dedication or efforts by the responsible party or regulatory officials involved. It reflects the fact that the permitting processes were not designed or staffed to handle the number of permits resulting from groundwater remediations.

A single disgruntled neighbor, unaffected by the remediation, can delay a project resulting in increased exposure to others. This delay usually arises from the lack of trust by the general public in the regulatory process and/or the responsible party.

Groundwater remediation and asymptotic performance

While initially successful in rapidly decreasing contaminant concentrations in groundwater, remediation technologies respond asymptotically, as shown in

Fig. 3 [5], resulting in ineffective contaminant removal rates. During remediation, contaminant concentrations usually decline rapidly (Zone 1 on Fig. 3) and then level off, reaching the asymptotic phase (Zone 2 on Fig. 3). Asymptotic response is most often associated with pump-and-treat groundwater remediations (7-9) but it is also observed with aquifer venting [10] and can be expected with bioremediation.

Decreased effectiveness can result in increased time of remediation, increased costs relative to mass of contaminants removed, or loss of control of migration of the plume. Asymptotic performance often goes undetected or is misunderstood because of inadequate project management of ongoing remediations. Project management is usually focused on designing and installing remediation technology at the "new" site rather than operating existing sites.

Asymptotic performance can occur soon after system start-up. Figure 4 shows actual data from a remediation system that showed asymptotic performance

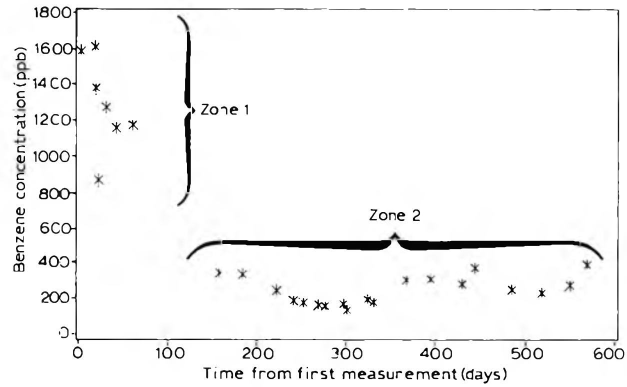

Fig. 3. Site 1 Data set - benzene concentration in a recovery well (from API, 1991).

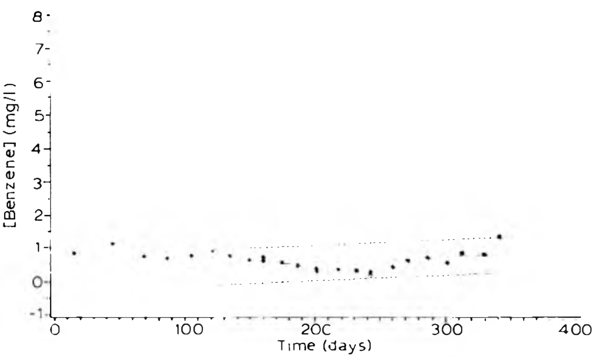

Fig. 4. Benzene concentration from a recovery well showing asymptotic response immediately after startup.

immediately after start-up. As shown in Fig. 5, a system also may operate for several years before showing asymptotic performance.

For materials less dense than water, such as petroleum hydrocarbons, Zone 1 reflects the removal of free-phase hydrocarbons and/or existing dissolved phase hydrocarbons. For inorganic contaminants, Zone 1 reflects removal of dissolved compounds. Zone 2 reflects residual soil contamination (Fig. 2) releasing contaminants at a rate nearly equal to that of removal by the remediation technique and entry of uncontaminated water into the zone of influence [5,6].

It is important to note that, even though a groundwater remediation has reached the asymptotic phase, contaminants are still removed and plume migration can be controlled. Continuing the existing remediation technology is acceptable at sites where there are no time constraints and/or risk due to exposure is controlled. Even if the existing technology is continued, the remediation can be optimized. The project manager should use the onset of Zone 2 as a benchmark to re-evaluate the components of the existing technology. For example, fluids pumped during Zone 1 may be treated most effectively and cheaply using air stripping with off-gas treatment. During Zone 2, the contaminant concentrations may decrease to levels that fluids are treated more effectively and cheaper using liquid phase carbon.

If time allocated is limited or exposure cannot be controlled, then the existing remediation technique may be modified to address residual soils contamination. The project manager can add aquifer venting, air sparging, or other technologies. An existing air sparging system can be modified to inject steam, nutrients, or oxygen to more effectively remove residual contamination. Re-

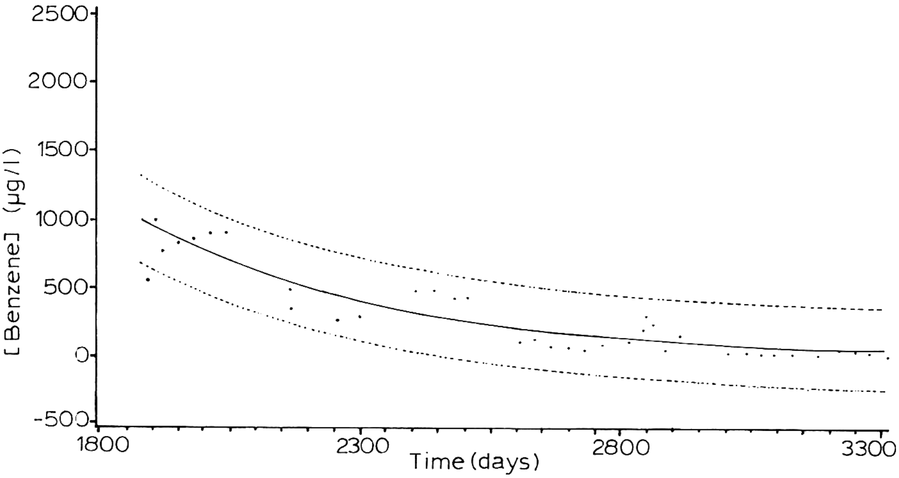

Fig. 5. Benzene concentration from a recovery well showing asymptotic response 3000 days after start-up.

mediation technologies are complementary and most successful remediations will results from the additive affects of multiple technologies customized for the contaminants present and the geological matrix underlying the site.

Technology modification may not always be the best alternative. In some situations, simply shutting the technology off and monitoring groundwater is the appropriate action. This approach is most applicable in locations where groundwater is not usable or where natural processes will render concentrations below permissible levels.

The average remediation system is not managed to assure optimum performance and effectiveness because asymptotic performance goes undetected. Due to workload, the effort expended during design cannot be maintained during operation. The system is monitored by a technician to assure that it is still operating. The professional who designed the remediation system is usually re-assigned to develop another and is not able to track the performance and adequacy of systems previously installed.

Conclusions

Groundwater remediation is an emerging science. Most ongoing remediations have only been operating for less than three years. More groundwater remediations will be designed and implemented within the next five years than the total installed to date. Professionals developing these groundwater remediation systems will not have the benefit of evaluating long term performance because of the lack of projects that have successfully reduced contaminants to permissible levels.

Ideally, the rate of installation of groundwater remediation systems should be slowed down to allow an assessment of the overall approach to groundwater remediation by both academics and field practitioners. This would allow intensive evaluation of both successful and unsuccessful remediations to develop both analytical and physical models to better manage and optimize.

Cooperation and communication are the most important components of any groundwater remediation. Each project must be viewed as a partnership between the responsible party, regulatory official, and affected neighbor. Each member of the partnership must be educated to fully understand just what can and cannot be accomplished with science of groundwater remediation. Without communication, groundwater remediation projects will not succeed.

Acknowledgments

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Factors influencing the transport and fate of contaminants in the subsurface *

M.L. Brusseau

Soil and Water Science Department, University of Arizona, 429 Shantz, Tucson, AZ 85721 (USA)

Abstract

The present status of research on the transport and fate of contaminants in the subsurface will be briefly reviewed. The discussion will center on solution-phase processes; other equally important processes (e.g., transformation reactions, vapor-phase processes, immiscible liquid-phase processes) are discussed in other papers presented in this issue.

Introduction

Hazardous waste sites, pesticide use, and the potential impact of human activities on drinking water quality have become prominent issues for the public. This concern has driven increased interest in and funding for research on the transport and fate of contaminants in the subsurface. As a result, many advances in this area have been made recently. However, there is still much left to discover and understand. This paper will briefly review the present status of the field, with a focus on the factors and processes that influence the transport and fate of contaminants in the subsurface. The discussion will center on solution-phase processes; other equally important processes (e.g., transformation reactions, vapor-phase processes, immiscible liquid-phase processes) are discussed elsewhere in this issue.

The outdated paradigm for solute transport

The transport of solute in porous media has been under investigation for quite some time. The paradigm that had been developed for solute transport and used as a basis for the development of mathematical models describing

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Correspondence to: M.L. Brusseau, Soil and Water Science Department, University of Arizona, 429 Shantz, Tucson, AZ 85721 (USA). Fax: (602) 621-1647.

solute transport included several fundamental assumptions. Among these assumptions were those of porous-media homogeneity and linear, instantaneous sorption. Research over the past 10 to 15 years has shown that these assumptions may often be invalid. Solute transport that does not conform to that predicted by the paradigm-based model can be considered as non-ideal. There are many factors that may cause non-ideal transport; these are presented in the next section.

Non-ideal solute transport

The various factors that may cause transport to be non-ideal are enumerated below; detailed discussions of these factors are provided in several recent reviews [1-3]. The focus is on solution and solid phases, given that other factors will be covered elsewhere.

Non-linear sorption

The distribution of the solute between sorbed and solution phases is characterized by the sorption isotherm. Several models have been proposed to describe isotherms, the appropriate one being a function of the particular application. Many solute transport models have been developed with the assumption that the sorption isotherm is linear. For many solutes this assumption will be invalid under certain conditions (cf. [4]).

Irreversible sorption

The sorption process is most often assumed to be reversible. However, this may not be the case under certain conditions. A review of many supposed instances of sorption hysteresis for organic compounds revealed that such observations may often be an artifact related to experimental conditions [3]. True irreversibility may, however, be exhibited for some systems.

Non-equilibrium sorption

The distribution of solute between the solution and solid phases has most often been assumed to be instantaneous in the development of transport models. A growing body of research has shown, however, that sorption of many solutes (especially organic compounds) is not instantaneous. The mechanism responsible for non-equilibrium is dependent on the system; for low-polarity organic compounds, the mechanism appears to involve an intrasorbent diffusion process (cf. [3,5-8]).

Sorption-capacity variability

Sorption capacity is all most always assumed to be spatially homogeneous when developing models, although it may often be spatially (and temporally) variable. There has been relatively little work done on characterizing the variability of sorption capacity at the field scale, but what has been done demonstrates the existence of variability (cf. [9,10]).

Facilitated transport

There are several factors or processes that can reduce the affinity of a solute for the solid phase, thereby reducing retardation. This reduction in retardation leads to enhanced or facilitated transport. Organic solvents and colloidal matter are two components that can greatly enhance transport under certain conditions.

Hydraulic-conductivity variability

Hydraulic-conductivity homogeneity was one of the first assumptions that was relaxed in the development of solute transport models. There are several ways that have been proposed for representing hydraulic-conductivity heterogeneity, including stochastic, stratification, and two-domain approaches. Each approach has its advantages and disadvantages, and each has been proven successful for specific applications.

Other factors

Other factors, such as vapor-phase processes, immiscible liquid-phase processes, and transformation reactions, can cause transport to deviate from that expected based on models that do not account for the effects of these processes.

Field observations of non-ideal transport

Several field experiments have been performed to evaluate the transport of sorbing solutes under natural and induced hydraulic gradients. These experiments have yielded results that are inconsistent with the simplifying assumptions of porous-media homogeneity and instantaneous sorption that were described above. Personnel from the U.S. Department of Agriculture and the R.S. Kerr research center were involved in one of the first attempts to evaluate the field-scale transport of sorbing organic solutes in an aquifer. In two separate experiments, solutions containing DDT [11] and three herbicides (picloram, atrazine, trifluralin) [12] were first injected into and then extracted from a portion of the Ogallala aquifer. Non-ideal transport of the herbicides was manifest in a delayed approach to relative concentrations of one (i.e., "tailing"), whereas non-ideal transport of DDT was indicated by incomplete removal.

An experiment conducted to evaluate the behavior of organic solutes during groundwater recharge was reported by Roberts et al. [13]. Breakthrough curves for the tracers and the organic solutes, obtained at a monitoring well, exhibited tailing.

The dispersive and adsorptive properties of a sandy aquifer were evaluated by Pickens et al. [14], who performed a radial injection experiment with ^{131}I

as the non-reactive tracer and ^{85}Sr as the reactive tracer. Non-ideal transport of ^{85}Sr, which was manifest as tailed breakthrough curves, was attributed to rate-limited sorption.

The sorptive behavior of several organic solutes under induced-gradient conditions was evaluated in an experiment that was performed to assess the efficacy of flushing as a means to remediate a contaminated aquifer [15]. Contaminant profiles obtained from the experiment, which was performed using an injection–extraction well couplet, exhibited extended tails. This non-ideal behavior was attributed to rate-limited desorption.

An extensive field experiment designed to investigate solute transport in a sand aquifer under natural-gradient conditions was undertaken by personnel from Stanford University and the University of Waterloo [16–20]. Significant non-ideal transport was observed for the organic solutes, wherein the plumes decelerated with time. This temporal increase in retardation factors was postulated to result from rate-limited sorption, involving diffusion within microporous particles [16,19].

A natural-gradient tracer experiment reported by Garabedien et al. [21] was conducted to examine the transport of bromide and lithium in a sand and gravel aquifer. The enhanced longitudinal dispersion observed for lithium was attributed to physical and geochemical heterogeneity, specifically a negative correlation of hydraulic conductivity and sorption capacity. However, the potential of rate-limited sorption contributing to the non-ideal transport was not ruled out.

The results of a series of induced-gradient experiments performed as part of an effort to evaluate *in situ* biorestoration were recently reported [22]. Breakthrough curves for the organic solutes exhibited tailing, which was suggested to result from rate-limited sorption or hydraulic-conductivity heterogeneity. It is noteworthy that breakthrough curves for the non-reactive tracer also exhibited tailing.

The results of the experiments discussed above demonstrate that the transport of sorbing solutes at the field scale is characteristically non-ideal. The non-ideal behavior has been attributed to rate-limited sorption, hydraulic-conductivity heterogeneity, or sorption-capacity heterogeneity. In addition to these controlled experiments, there have been many anecdotal observations of non-ideal transport associated with aquifer restoration. For example, a typical observation for "pump-and-treat" systems is that the time and volume of water required to remove the contaminants is much greater than had been estimated in the planning stage. This type of phenomenon has been attributed to the effect of various non-ideality factors on transport.

Multi-factor non-ideality

We have seen evidence of non-ideal transport and have reviewed several factors that may cause such transport. It is possible, and often likely, that more than a single factor may contribute to the observed non-ideal behavior, especially at the field scale. In response to this possibility, transport models are being developed that account for more than one source of non-ideality (i.e., multi-factor non-ideality models). Models that account for hydraulic-conductivity heterogeneity and sorption-capacity heterogeneity have been presented by Smith and Schwartz [23], Van der Zee and Van Riemsdijk [24], Garabedien et al. [21], Cvetkovic and Shapiro [25], and Kabala and Sposito [26]. Models that account for hydraulic-conductivity heterogeneity and rate-limited sorption have been presented by Bahr [27], Valocchi et al. [28], and Cvetkovic and Shapiro [25]. Models that account for hydraulic-conductivity heterogeneity, sorption-capacity heterogeneity, and rate-limited sorption have been presented by Bahr [27], Brusseau et al. [5,29], Sudicky et al. [30], and Destouni and Cvetkovic [31].

These multi-factor non-ideality models will hopefully provide a more accurate description of solute transport under non-ideal conditions. The performance of these models, however, has yet to be evaluated, to any great extent, by using them to attempt to predict the results of field-scale experiments involving transport of sorbing solute. Until this has been done, the accuracy of these models will remain untested.

One model that has been evaluated for the ability to simulate field data is the one-dimensional model presented by Brusseau et al. [5]. This model accounts for the effects of porous media heterogeneity, which is represented by the two-domain approach, and for rate-limited sorption, which is represented as being a combination of instantaneous and rate-limited interactions. Brusseau [32] evaluated the performance of the model by attempting to predict data obtained from four field experiments performed under natural or induced gradients. The predictions produced with the multi-factor non-ideality model provided very good descriptions of breakthrough curves obtained from the experiments. The results of the analyses indicated that, while several factors appeared to have contributed in varying degrees to the non-ideal transport observed during the experiments, the impact of hydraulic-conductivity heterogeneity was important for all cases. For example, the effect of rate-limited sorption, which was postulated by Roberts et al. [19] to have caused the non-ideal transport for the Borden experiment, appears to have been a minor contributor in comparison to the effect of heterogeneity for the Borden experiment.

Considering that all parameter values were obtained independently for the predictions, it appears that the model may be used to simulate non-ideal transport of sorbing solutes at the field scale. Although the approach used to represent heterogeneity is simple in comparison to other approaches (e.g., stochastic), this model should be useful for situations where the extensive field data required to use more complex models are not available. Application of this one-dimensional model is obviously limited to systems that can be represented as one dimensional, such as breakthrough curves measured at monitoring wells.

Summary

Many of the assumptions inherent to the paradigm that has been the basis for the development and use of many solute transport models have been shown to be invalid. A new generation of models are being developed to address factors such as heterogeneity of porous media properties and non-equilibrium sorption. A complete description of solute transport will require models that account for multiple sources of "non-ideality".

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Pilot scale field studies of *in situ* bioremediation of chlorinated solvents *

Lewis Semprini, Gary D. Hopkins, Paul V. Roberts and Perry L. McCarty
Western Region Hazardous Substance Research Center, Stanford University, Stanford, CA 94305-4020 (USA)

Abstract

This paper discusses results from pilot scale field studies that evaluated enhanced *in situ* bioremediation of chlorinated solvents. A stimulus-response methodology for performing controlled field experiments is exemplified. The cometabolic transformation of chlorinated aliphatic compounds by methanotrophic bacteria is of primary focus.

Introduction

There is much interest in applying *in situ* biological processes for remediating aquifers contaminated with organic compounds. *In situ* bioremediation may serve as a means of (1) decreasing the time required for restoring contaminated aquifers; (2) degrading the compounds completely to circumvent the risk of transferring the contaminants elsewhere; and (3) using the subsurface as a bioreactor to eliminate the need for surface treatment processes. Controlled field studies are the most direct and convincing means of assessing different *in situ* biological treatment processes. Methods are being developed for performing studies that permit scientific evaluation of the treatment process. Questions that need to be addressed in these studies include the following:

- Are biological transformations actually observed?
- What are the extents of transformation?
- What are the transformation products?
- What are the transformation rates?
- Which factors limit the transformation rates?

Obtaining this information in the complex subsurface environment is a major challenge. Transport, physical, and chemical processes as well as biological

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Correspondence to: L. Semprini, Western Region Hazardous Substance Research Center, Stanford University, Stanford, CA, 94305-4020 (USA). Fax: (415) 725-8662.

processes must be considered. Thus, when designing field experiments, and determining the experimental protocol, it is important to consider whether the above questions can be answered given the complexity of the subsurface environment and the many processes that are occurring.

The *in situ* bioremediation of aquifers contaminated with organic compounds has been thoroughly reviewed by Lee et al. [1], McCarty [2] and Wilson et al. [3]. The *in situ* bioremediation of contaminated aquifers was first attempted systematically by Raymond et al. [4], who pioneered *in situ* reclamation of aquifers contaminated by petroleum products. Raymond's work showed that promoting the proper conditions in the subsurface (i.e., by adding oxygen and nutrients), stimulated a native population of microorganisms that degraded the hydrocarbon contaminants, whereby the bacteria used the hydrocarbons as primary substrates for growth.

Enhancing biological transformations in the subsurface will usually require the addition of nutrients. The addition may include growth substrates, electron acceptors such as oxygen, and minor nutrients such as nitrogen and phosphorus. Understanding transport and mixing processes is critical in determining how to effectively add the nutrients to enhance biological transformations. When nutrient addition and mixing are performed, it is often difficult to determine whether the observed decrease in contaminant concentration results from biological transformations or dilution. Experimental methodologies must therefore consider how advective and dispersive transport processes affect the spatial and temporal distribution of contaminants, nutrients, and microbial population in the subsurface. Thus obtaining information on transport in the treatment zone is critical.

Contaminant sorption onto the aquifer solids is a process that must also be considered. Sorption will determine the contaminant mass associated with the aquifer solids and the mass in solution. For strongly sorbed compounds, most of the contaminant mass will be associated with the aquifer solids. In order for biotransformation to proceed, desorption to the aqueous phase must occur. Slow desorption from the aquifer solids provides a continued source of contamination, and may bias estimates of the extents and the rates of transformation. Slow desorption may also limit the overall rates of clean-up. Thus, obtaining information on the sorption process through laboratory and field studies is needed in designing and evaluating *in situ* bioremediation tests.

Mathematical models that represent the key physical, transport, chemical and biological processes are powerful tools for evaluating field tests results, since they provide a means of simulating the combined processes. Models can also be used to compare results of laboratory studies with those obtained under different conditions in the field. Models that are validated through field studies might also be used as a tool in designing field scale *in situ* treatment.

This paper presents the results from pilot scale field studies that evaluated the enhanced *in situ* bioremediation of chlorinated solvents. Examples will be presented to illustrate a stimulus–response methodology for performing controlled field experiments that has proven to be very useful. Model simulations will also be presented for simulating the concentration response to the experimental stimulus.

Background

In situ biorestoration of aquifers contaminated by halogenated aliphatic compounds (HACs) requires a different approach than that used for petroleum contamination, since in most cases HACs cannot be utilized by native microorganisms as primary substrates for growth. However, they can be degraded by cometabolism, a process in which microorganisms growing on one compound (primary substrate) produce an enzyme which fortuitously transforms another compound, from which they cannot obtain energy for growth [5].

In 1985, Wilson and Wilson [6] showed for the first time that trichloroethylene (TCE) may be susceptible to aerobic degradation (by soil microbial communities fed natural gas). Methanotrophs that grow on methane under aerobic conditions possess an enzyme, methane monooxygenase (MMO), that initiates the oxidation of TCE [7]. Scientific research aimed at exploiting this phenomenon has included numerous laboratory investigations [7–13] as well as directed field experiments [14,15].

Based on the findings with methanotrophs [7,17], it can be concluded that TCE is most likely oxygenated to TCE-epoxide, an unstable compound which is quickly rearranged nonenzymatically in aqueous solution to yield various products including carbon monoxide, formic acid, glyoxylic acid, and a range of chlorinated acids [18]. In nature, where cooperation between the TCE oxidizers and other bacteria (most prominently heterotrophs) occurs, TCE can be completely mineralized to carbon dioxide, water, and chloride [8–10].

Pilot scale field studies were performed that assessed, under field conditions, the capacity of native microorganisms, i.e., bacteria indigenous to the groundwater zone, to degrade HACs when proper conditions are provided to enhance bacterial growth. Specifically, the growth of methanotrophic bacteria was stimulated in a field situation by providing ample supplies of dissolved methane and oxygen. Under biostimulation conditions, the transformation of representative HACs, including *cis*- and *trans*-1,2-dichloroethylene (c-DCE and *t*-DCE), and vinyl chloride (VC), was assessed by means of controlled addition, frequent sampling, quantitative analysis, and mass balance comparisons.

The experimental approach taken was similar to that proposed for bioremediation in the field (Fig. 1). Extracted groundwater from the treatment zone is amended with methane and oxygen and reinjected to stimulate methanotrophic growth. HACs in the extracted groundwater are reinjected into the biostimulated zone. Bioremediation conducted in this manner will promote

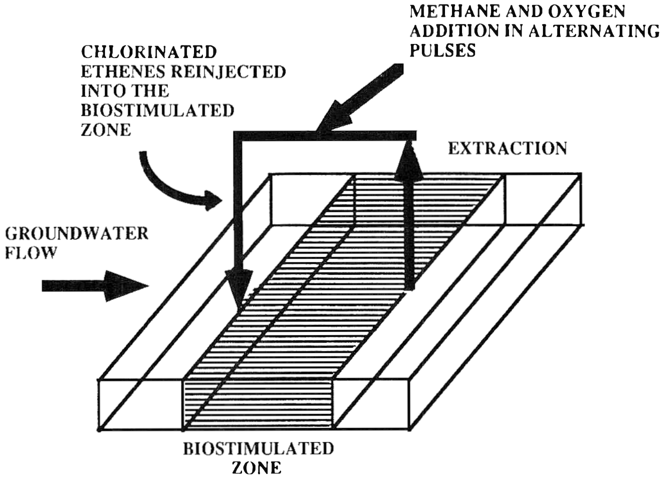

Fig. 1. Conceptual model for *in situ* bioremediation by methanotrophic bacteria (from McCarty et al. [31].

degradation of inplace contaminants as well as contaminants that are extracted and reinjected, thus obviating above ground treatment.

Site characterization

The test methodology was developed after detailed information on the pilot scale test zone was obtained through thorough site characterization. The site chosen for the field demonstration, at Moffett Naval Air Station, offered a near-ideal combination of characteristics [14]. The test drilling identified a shallow confined aquifer which is known as the "A" Aquifer, the shallowest of several in the region. Drilling logs revealed that the aquifer at the test site consisted of a layer of silt, sand, and gravel, approximately 1.2 m thick, at shallow depth (approximately 5 m below the ground surface), well confined above and below by a silty clay layer of low permeability (Fig. 2). The aquifer, consisting of fine-to-coarse grained sand and gravels, appears poorly sorted in most cores. The site is representative of a typical situation of groundwater contamination in the San Francisco Bay area and elsewhere, in which a shallow sand-and-gravel aquifer is contaminated by chlorinated aliphatic compounds widely used as solvents.

The formation groundwater was also of appropriate composition for the field experiments. The water was moderately saline (TDS of 1500 mg/L) and was substantially contaminated by chlorinated organic compounds, mainly 1,1,1-trichloroethane, but was devoid of the chlorinated alkenes – TCE, 1,2-DCE

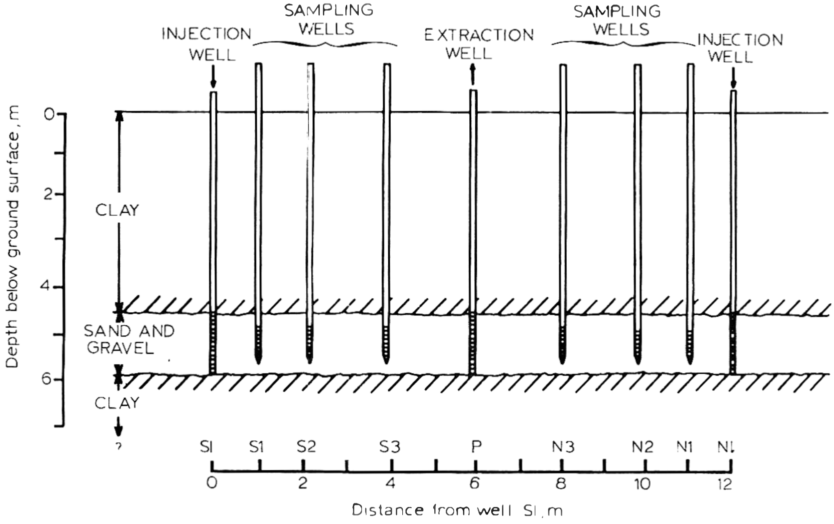

Fig. 2. Cross section of the test zone and the wellfield used in the experiments (from Roberts et al. [14]).

isomers, and VC – chosen as target compounds for this study. Thus, these compounds would have to be added in a controlled manner in the study.

There were no appreciable amounts of toxic metals [19]. Nitrate was present in adequate amounts in the native groundwater (25 mg/L) as a source of nitrogen. Phosphorus concentrations were low (<0.1 mg/L) but near solubility limits of common phosphorus minerals, which were probably the source of phosphorus .

Sustained pump tests showed that the transmissivity was sufficiently high (approximately 100 m^2/day) to permit extracting water at the design rate (approximately 10 L/min) without excessive drawdown at the extraction well. Detailed analysis of the pump tests showed the aquifer behaved as a leaky aquifer, with a water-table aquitard model best fitting the pump test observations [20].

Bromide tracer tests under natural gradient conditions showed that the local groundwater velocity was approximately 2 m/day. Mathematical modeling of the flow field with RESSQ, [21], imposing a forced gradient on the natural flow field to simulate injection/extraction operations, showed that injection and extraction rates of approximately 1 L/min and 10 L/min, respectively, would be sufficient to satisfy the two main requisites for the field experiment from the hydraulic point of view: (1) complete permeation by injected fluid of the aquifer in the observation zone between the injection and extraction points (i.e., minimum dilution by native groundwater in that zone); and (2) complete recovery of the injected fluid at the extraction well (to assure accurate mass balances).

Microbiological studies

Microbial studies included mixed and pure culture studies on TCE transformation, and soil microcosm studies. These studies determined whether methane-utilizing populations were present and were capable of transforming TCE. Mixed and pure culture studies were performed in the laboratory using microbes enriched and isolated from the aquifer solids samples and from the formation groundwater. Details of these studies are provided by Henry and Grbić-Galić [9,17,22], and Henry [23]. These studies showed different types of methanotrophs were present in the test zone. They all had the ability to degrade TCE, but at different rates. The mixed cultures completely degraded the TCE to CO_2 and chloride. The rates of TCE transformation were also shown to depend on growth conditions, such as the mineral growth media used.

Details of the soil microcosm studies are presented by Mayer et al. [13] and Lanzarone and McCarty [11]. These studies also confirmed that methane-utilizing bacteria could be easily stimulated through methane and oxygen addition. Approximately 20% of the TCE added was degraded to CO_2 at TCE concentrations ranging from 20 to 40 μg/L.

Sorption studies

The sorption of the organic solutes by aquifer core samples from the Moffett site was studied in batch laboratory experiments. Details of these studies and the methods used are given by [14,24]. Figure 3 shows TCE sorption isotherms with Moffett core solids. The studies confirmed that sorption equilibrium was

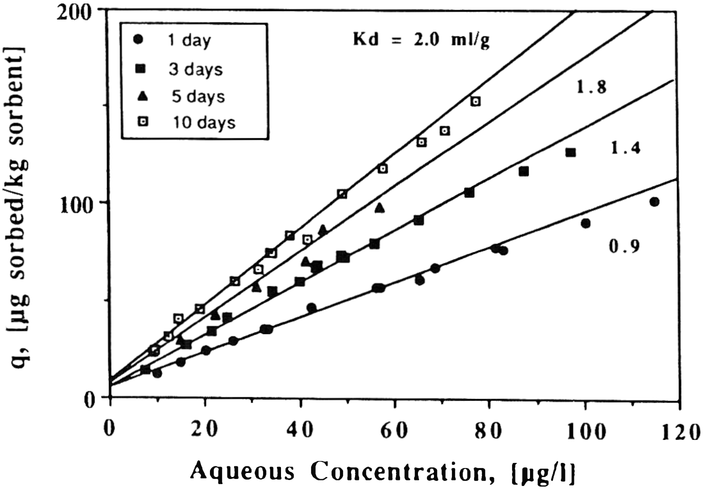

Fig. 3. Sorption isotherm at increasing times for Moffett bulk solids and TCE (from Roberts et al. [14]).

approximately linear, justifying the use of a distribution coefficient for interpreting and reporting the sorption equilibrium data. The studies also showed the apparent K_d increasing with the time of equilibration due to slow diffusion of TCE into the porous aquifer solids [24]. This finding points out that deviations from sorption equilibrium owing to rate limitations may be an important factor influencing bioremediation, since desorption from the solids to the aqueous phase would be required for transformation to occur. The studies also found that sorption was strongest for TCE and weakest for VC, among the compounds studied.

Mathematical modeling

A non-steady-state model [16,25] developed for simulating the results of the field experiments proved extraordinarily useful in interpreting the results and comparing with the laboratory data. The model incorporated advection, dispersion, sorption with and without rate limitation, and the microbial processes of substrate utilization, growth, and cometabolic transformation of the halogenated aliphatics using a competitive inhibition model. The transport was simplified by assuming one-dimensional, uniform flow, as a computational compromise to permit more rigorous representation of the biological processes. Input parameters were estimated based on the results of the laboratory research, or on values from the literature. The initial population of methane-utilizing bacteria was allowed to vary as an unconstrained fitting parameter. Transformation rate coefficients for the HACs were also fitted to the field observations, and compared with laboratory derived rates. Both the response to biostimulation (methane and dissolved oxygen (DO) uptake), and the biotransformation of the chlorinated aliphatics were simulated.

Experimental methodology

The detailed characterization of the test zone and early bromide tracer tests indicated several important factors had to be included in the experimental design. The absence of several of the HACs in the test zone required their continuous controlled addition to the test zone. The strong component of regional flow required the experiments to be conducted under induced gradient conditions created by pumping from a downgradient extraction well (P), while introducing solutes in known amounts at an injection well (SI) six meters upgradient, and measuring concentrations regularly at the injection, extraction, and intermediate observation points (Fig. 2). Interpretation of biotransformation behavior could then be made by quantitative examination of the solutes' concentration histories at the several monitoring points, comparing results under biostimulation conditions with results obtained under similar conditions in the absence of biostimulation measures.

A specially designed, automated data acquisition and control system constructed for this purpose, proved capable of providing continuous records of high-accuracy data over sustained periods that enabled the computation mass balances with relative errors of only a few percent. Details of the system design and operation are presented by Hopkins et al. [26]. The monitoring setup was capable of measuring key chemical components: bromide as a conservative tracer, the halogenated aliphatics (TCE, c-DCE, *t*-DCE, and VC), methane, and DO, with one sample processed hourly.

The frequency of analysis realized by the automated data acquisition system permitted stimulus–response experiments with rapid dynamic forcing functions. The stimulus is the injection of chemicals of interest, and the response being the measured concentration histories of the chemicals at observation locations. A systematic sequence of stimulus-response experiments was performed to (1) determine transport characteristics of the test zone; (2) demonstrate convincingly enhanced *in situ* biodegradation by methanotrophic bacteria; and (3) gain an understanding of complex processes effecting biodegradation, such as competitive inhibition. The series of experiments are outlined in Table 1.

Bromide was used as a conservative tracer during all phases of the experiments. Initially bromide was used to quantify advection and dispersion transport. During the latter stages of the experiments it was used to quantify the degree of breakthrough of the injected fluid at observation locations, thus helping to insure that contaminant concentration decreases were associated with transformation processes rather than changes in hydraulic conditions.

The experimental sequence provided strong evidence that biotransformation was occurring in response to biostimulation of methane-utilizing bacteria. The sequence included the following phases (Table 1): a pseudo-control (Phase 2) during which the contaminants were added in the absence of biostimulation;

TABLE 1

Sequence of field experiments

Phase	Injected chemicals	Phenomena investigated
1	Br^-	Advection/dispersion
2	$Br^- + \text{Organic} + O_2$	Retardation/transformation
3	$CH_4 + 2$	Biostimulation/biotransformation
4	(2) + Transient tests	
	a) Dynamic pulsing CH_4	Biotansformation competitive/inhibition
	b) CH_4 Stopped	Biotransformation
	c) Formate/methane	Competitive/inhibition biotransformation

an active biostimulation (Phase 3) with methane addition, where evidence of biotransformation in response to biostimulation was obtained; and a series of transient tests (phase 4) to provide additional evidence for biostimulation and to study complex process such a competitive inhibition. Examples will be presented that illustrate some of the stimulus–response tests that were performed in the different phases.

Results from the field experiments

Example of a bromide and organic transport experiment

Bromide tracer and organic transport experiments were undertaken to quantify transport velocities and residence times in the test zone, to determine how strongly the chlorinated organics were retarded due to sorption processes, as to serve as a pseudo control prior to active biostimulation. Figure 4 shows the normalized concentration breakthrough of bromide and TCE at the S1 observation well during an induced flow test. The arrival of TCE was retarded compared to that of bromide tracer due to TCE sorption onto the aquifer solids. Detailed modeling studies of Harmon et al. [24] simulated this breakthrough response using a transport model that included rate-limited diffusional sorption with input parameters derived from laboratory sorption studies (Fig. 3).

The bromide tracer tests confirmed that the aquifer was virtually completely permeated by the injected fluid in the observation zone, and the injected fluid was essentially completely recovered by the extraction well. The hydraulic residence times between the injection well and the two nearest observation wells (S1 and S2), ranged from 8 to 23 h, and 25 to 40 h to the extraction well (Table 2). The retardation factors for the organic solutes, evaluated from relative mobility data obtained in the field, were in the range of two to ten (Table 2). Retardation estimates were in the range of those based on the laboratory sorp-

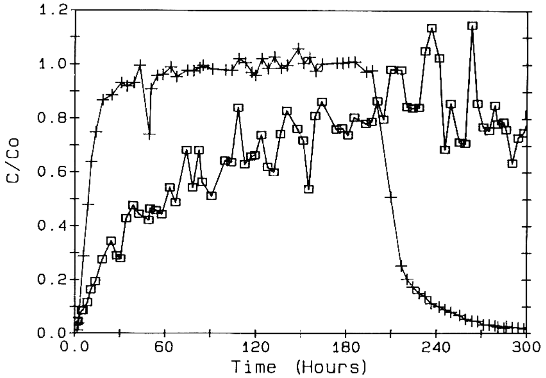

Fig. 4. Normalized breakthrough of bromide (+) and TCE (□) at the S1 observation well in an induce flow tracer test.

TABLE 2

Resident times ($t_{50\%}$ breakthrough) and retardation factors for the chlorinated organic compounds (from [14])

Experiment	Compound	Well S1 $^{t}50\%$ (h)	Well S2 $^{t}50\%$ (h)	R (S1)	R (S2)
Tracer 4	Br^-	8	20		
	1,1,1-TCA	10	30	1.3	1.5
Tracer 5	Br^-	9	17		
	TCE	40	160	5	9
	Br^-	7.5	16		
Tracer 8	TCE	60	150	8	9
	t-DCE	50	150	7	9
	c-DCE	30	70	4	4
	Br^-	9	23		
Tracer 11	TCE	50	175	6	8
	t-DCE	120	280	13	12
	c-DCE	45	90	5	4
Tracer 12	Br^-	8	21		
	VC	13	42	1.6	2.0

tion studies, with TCE being the most strongly sorbed and VC the most weakly sorbed. Breakthrough of the chlorinated organics to 90 to 95% of the injected concentration at the S1 and S2 observation wells indicated minimal losses before biostimulating the test zone. Details of the results of the tracer tests and modeling the tracer breakthroughs are given by Roberts et al. [14], and Chrysikopoulos et al. [27].

Example of biostimulation experiments

The experimental methodology used in the biostimulation and biotransformation experiments is discussed by Roberts et al. [14] and Semprini et al. [15,28]. Groundwater was saturated with methane or oxygen using two countercurrent gas sorption columns, one for oxygen and the other for methane. The columns achieved effluent concentrations ranging from 16 to 20 mg/L methane and 33 to 38 mg/L oxygen, approximately 80 percent of the saturation values at 20°C and atmospheric pressure. The injection solenoids and a pulse timer permitted the alternated injection of groundwater containing either methane or oxygen, with varying pulse lengths.

The *in situ* biostimulation of a native population of methane-oxidizing bacteria was achieved in three successive field seasons through the introduction of methane and oxygen dissolved in groundwater, without any other supplementary nutrients (N and P). Figure 5 shows the concentration history of methane and DO at the S2 observation well during the initial biostimulation experiment along with model simulations. At early time, methane and DO behaved like the conservative bromide tracer, indicating no retardation and minimal consumption. During the period of 200 to 430 h methane and DO concentrations rapidly decreased, indicating the growth of methane-utilizers. The model simulations represented by the solid line matched the field observations using a reasonable set of biological input parameters. The model supports the conclusions that methanotrophic bacteria were stimulated in the test zone and that the processes can be well simulated when appropriate rate equations are used [16].

In order to control the clogging of the injection well and borehole interface, the alternate pulse injection of methane and oxygen containing groundwater was initiated at 430, with a pulse cycle time of 4 and 8 h, respectively. The arrival of methane and DO pulses at the S2 well was observed at later time. Model simulations reproduced well the dynamic response due to pulsing and predicted a more distributed biomass [16]. Biofouling of the near well-bore region was thus limited by the pulsing methodology, as anticipated in the experimental design.

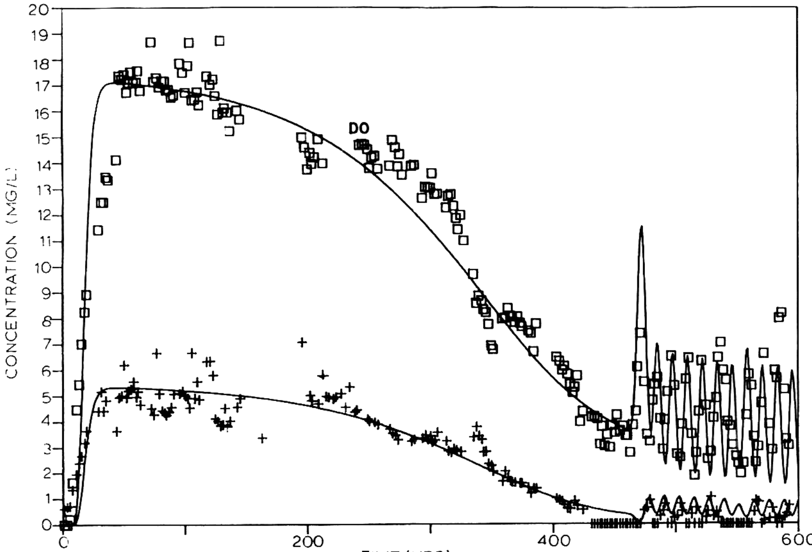

Fig. 5. Methane (+) and DO (□) response at the S2 well due to biostimulation of the test zonew during the first season of field testing. The solid lines are model simulations of Semprini and McCarty [16].

Example of biotransformation experiments

In order to evaluate biotransformation, the chlorinated compounds were added to the injected water at concentrations ranging from 50 to 100 µg/L, in the absence of methane, until the soil was saturated, as evidenced by complete breakthrough at the monitoring wells. The feed was then supplemented with dissolved oxygen and methane. Figure 6 shows the response at the S1 well of the target compounds in the third season and corresponding model simulations. Transformation of the organic target compounds ensued immediately following the introduction of methane at time zero, increasing with time as the bacterial population grew. Rapid transformations of VC and *t*-DCE were observed, followed by c-DCE and TCE (not shown). Competitive inhibition of VC and *t*-DCE transformation by methane was indicated in response to the dynamic pulsing of methane and oxygen that was initiated at 20 h. Model simulations [25] matched well the response observed in the field, with the effects of competitive inhibition more pronounced at the S1 well compared to the S2 well as indicated by greater oscillations in concentration at the S1 well. Both competitive inhibition kinetics and rate limited sorption were required to reproduce the field observations.

The effects of rate-limited sorption are illustrated by Fig. 7, where the response of VC at the S2 observation well is shown along with model simulations. The rate-limited sorption model provides a better match to the field observa-

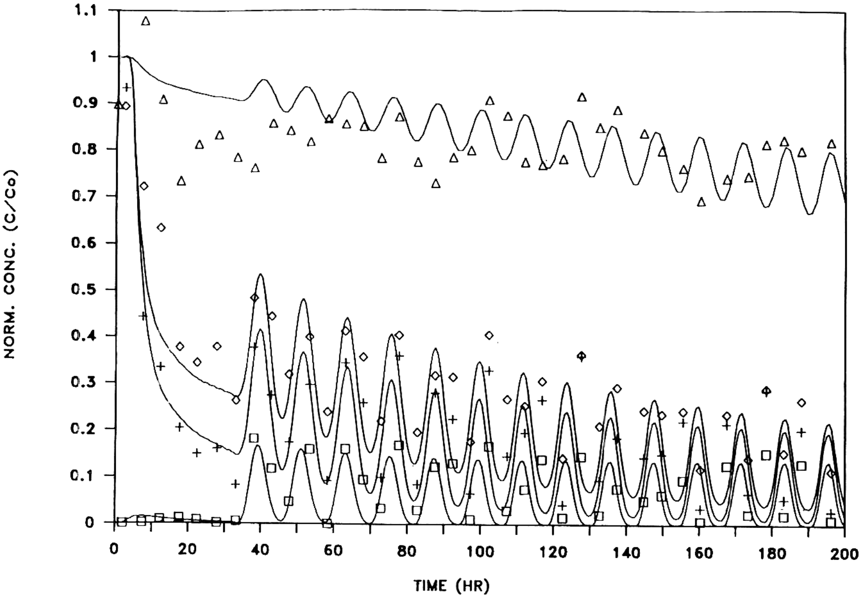

Fig. 6. Response of methane (□), VC (+), *trans*-DCE (◇), and *cis*-DCE (△) at the S1 well due to biostimulation in the third season of field testing and model stimulations (from Semprini and McCarty, [25].

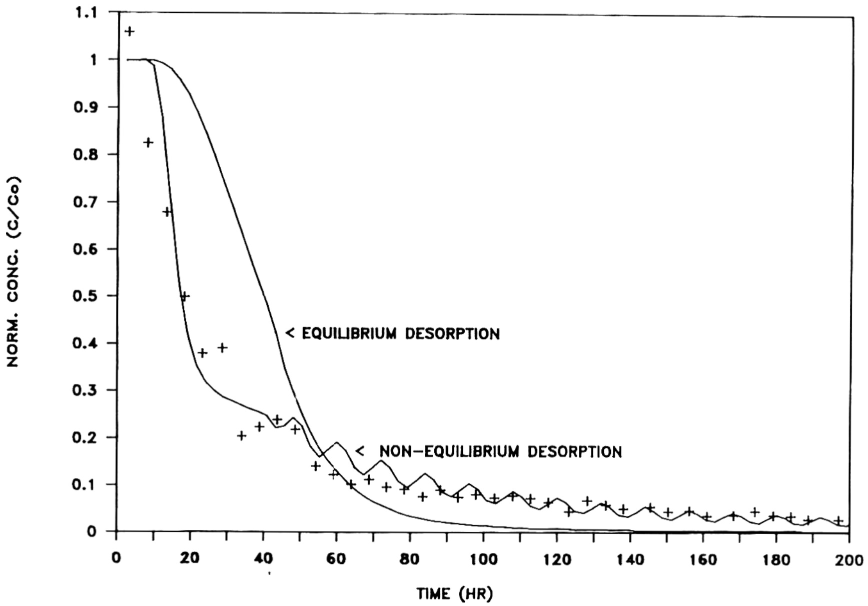

Fig. 7. Response of VC (+) at the S2 well and simulations based on rate-limited sorption and equilibrium sorption.

TABLE 3

Model parameters for sumulation of cometabolic transformations (from Semprini and McCarty [25])[a]

Compound	K_d (1/mg)	α (d^{-1})	k (d^{-1})	K_s (mg/L)	k/K_s (L/mg-d)
Methane	0.0	0.00	2.0	1.0	2.0
VC	0.40	0.5	1.0	1.0	1.0
t-DCE	1.60	0.3	1.0	1.0	1.0
c-DCE	1.60	0.3	0.05	1.0	0.05
TCE	2.25	0.2	0.01	1.0	0.01

[a] K_d = sorption distribution coefficient, α = rate coefficient for sorption, k = maximum transformation rate, K_S = half-saturation coefficient.

tions than the equilibrium sorption model. The simulations indicate that the overall rate of decrease in VC concentration may have been limited by the rate of its desorption from the aquifer solids. The simulations indicated that physical processes such as desorption can limit times of clean-up of an enhanced microbial process.

The comparison of the rate parameters (Table 3) shows VC and *t*-DCE were transformed at rates similar to that of methane the substrate for growth, while *c*-DCE and TCE were transformed at rates one to two orders of magnitude slower than methane. The simulations indicate that *t*-DCE concentrations decrease more slowly than VC, since it is more strongly sorbed (higher K_d) and thus a greater contaminant mass must be degraded. The difference in rates for *c*-DCE and *t*-DCE illustrates the effect that a small change of structure can exert on the cometabolic transformation rates.

Example of a transient to confirm biotransformation

Gas chromatographic analysis of water samples during active biotransformation of *t*-DCE provided evidence of an intermediate transformation product identified in laboratory studies to be the epoxide of *t*-DCE [29], which was present in amounts equivalent to a few percent of the parent compound. No other intermediate products were identified. The presence of the epoxide supported the biotransformation of *t*-DCE by methane-utilizing bacteria.

Figure 8 shows results of a transient test in which methane addition was terminated after active biostimulation. Details of this test are presented by Semprini et al. [15]. Termination of the methane feed at approximately 275 h was followed by cessation of transformation activity, as indicated by the increase in *t*-DCE concentration and the decrease in concentration of the epoxide transformation product. The increase occurs at approximately the same time scale as that of organic transport (i.e, one to ten days). Upon reintroduction of methane at 475 h, the *t*-DCE concentration decreased and the epoxide reappeared. Model simulations (not shown) indicate that the microbial population remained active in the absence of methane for only a short time before ceasing to transform the target organic compounds. The transient test confirmed that the transformation was strongly tied to methane-utilization.

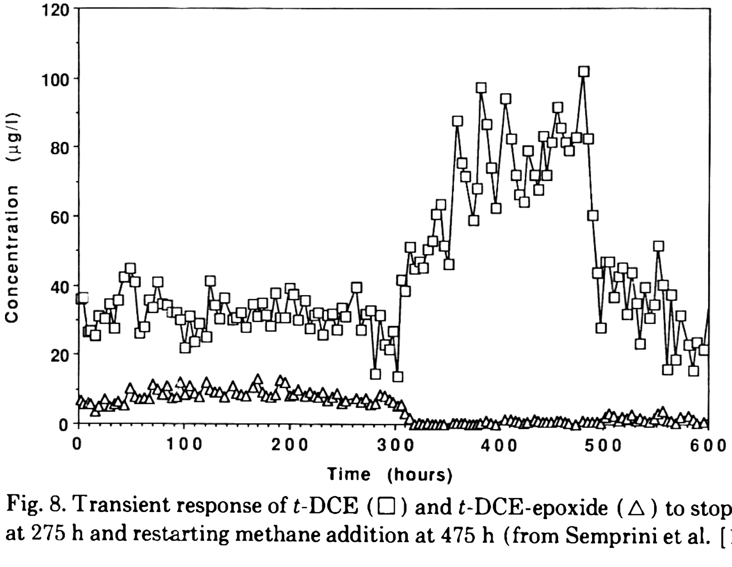

Fig. 8. Transient response of *t*-DCE (□) and *t*-DCE-epoxide (△) to stopping methane addition at 275 h and restarting methane addition at 475 h (from Semprini et al. [15]).

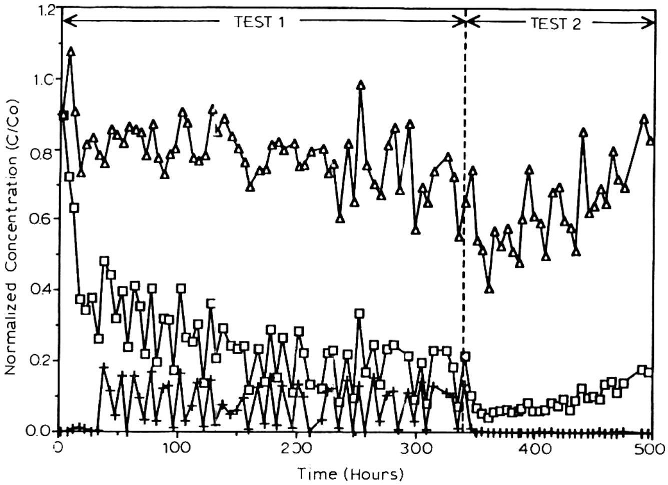

Fig. 9. Transient response of methane (+), c-DCE (△), and t-DCE (□) at the S2 well during the transition from methane (Test 1) to formate addition (Test 2) (from Semprini et al. [28]).

Example of a transient test to confirm competitive inhibition

A transient test was performed where formate was substituted for methane to confirm competitive inhibition of contaminant transformation by methane, and to determine whether enhanced transformation rates resulted. Details of this test are provided by Semprini et al. [28]. Formate provides an energy source for methanotrophs but does require the MMO enzyme to be assimilated [30]. Thus, formate should not inhibit the transformation, and may enhance it. The results of the transient test with formate are shown in Fig. 9. Upon switching to formate the concentration oscillations of t-DCE essentially stopped, indicating competitive inhibition by methane. Transformation was temporarily enhanced with formate addition, demonstrating the need of an energy source to drive the transformation.

Discussion

The examples presented illustrate that carefully planned stimulus-response tests constitute a powerful means of studying *in situ* bioremediation processes. The examples presented here focus on the cometabolic transformation of HACs by methanotrophic bacteria. A similar stimulus-response methodology, however, can be used to study other types of *in situ* treatment processes. While helping to demonstrate that transformations were occurring, they also provided a means of investigating more complex processes such as the competitive inhibition of cometabolic transformation, and the effects of rate limited desorption from the aquifer solids.

Careful monitoring is required for such studies. This study was aided by an automated data acquisition system that provided frequent and reproducible analyses. Also of key importance is the ability to control transport in the subsurface and to apply a controlled stimulus which in these tests was the constant or pulsed controlled addition of chemicals. Design of stimulus–response tests also required adequate understanding of the key microbial and transport processes.

Mathematical modeling is a powerful tool for simulating the results of transient-response experiments. Modeling helps the study of complex kinetic and transport processes that are indicated by the stimulus-response tests. In developing appropriate models, it is essential to strike a judicious compromise between the competing goals of accurate process representation and computational feasibility. The mathematical model chosen for the present application stressed relatively complete representation of the relevant biological processes, and compensated with a highly simplified, one dimensional model for advective/dispersive transport.

The mathematical modeling supported the experimental evidence that a methanotrophic population was stimulated in the aquifer, using rate parameters expected for methanotrophic bacteria. The simulations also indicated that the chlorinated organics were transformed at different rates. The cometabolic transformation modeling required a competitive inhibition kinetic model, while sorption was best modeled as a rate-limited process. The simulation indicated that slow descrption probably limited the removal of the more rapidly transformed contaminants, and influenced the response due to competitive inhibition.

The results support incorporating experimental controls and quantitative mass balances to the fullest possible extent as an absolute prerequisite for meaningful experimentation, in the field as in the laboratory. Strong dynamic forcing is helpful in stimulating positive characteristic responses that aid in identifying mechanisms and in testing hypotheses and mathematical models. Only field experimentation of this kind can provide a reliable engineering scientific basis for evaluating and designing *in situ* biorestoration measures.

Acknowledgments

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In situ bioremediation of aquifers containing polyaromatic hydrocarbons*

Gaylen R. Brubaker[a] and Hans F. Stroo[b]

[a]*Remediation Technologies, Inc., 127 Kingston Drive, Suite 105, Chapel Hill, NC 27514 (USA).*
[b]*Remediation Technologies, Inc., Seattle, WA (USA).*

Abstract

In situ bioremediation has increasingly been proposed as a remediation option for a broad range of sites. A comparison of pump-and-treat processes to *in situ* bioremediation for a hypothetical polyaromatic hydrocarbon (PAH) contaminated aquifer is discussed with support from laboratory analyses. Influence of micro-processes such as desorption, dissolution, and diffusion on pollutant bioavailability and subsequent effectiveness of biodegradation at complex PAH-contaminated sites is considered. Low solubilities of four and five-ringed PAHs render them essentially impossible to remediate through pump-and-treat processes. Analyses indicate that following removal of more soluble PAHs in an *in situ* biodegradation process, the rate of degradation will be limited by the rate of dissolution such that oxygen transport requirements will decrease as the process continues.

Introduction

One of the dominant themes in the aquifer remediation literature of the past two years has been that the performance of pump-and-treat processes is limited by certain inherent factors associated with the dissolution, desorption and diffusion of contaminants [1-3]. During this same period, *in situ* bioremediation has increasingly been proposed as a remediation option for a broad range of sites, including those with soil permeabilities and contaminants which have not generally been considered amenable to this process [4].

In situ bioremediation treats both soils and groundwater contaminated with organic constituents by enhancing the natural biodegradation of the contaminants within the saturated zone. The process typically relies on indigenous bacteria which use the contaminants as a source of carbon and energy, converting the contaminants to carbon dioxide and water [5]. *In situ* bioremedia-

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Correspondence to: Dr. G.R. Brubaker, Remediation Technologies, Inc., 127 Kingston Drive, Suite 105, Chapel Hill, NC 27514 (USA). Fax: (919) 967-3754.

tion involves installing a groundwater injection and extraction system to transport dissolved oxygen and water-soluble nutrients through the contaminated area. Selection of the best injection/recovery design depends upon the distribution of contaminants, the location of groundwater, the hydraulic conductivity of the soil and physical limitations of the site.

The vast majority of *in situ* bioremediation field experience has been associated with sites containing motor fuels (gasoline, diesel, jet fuel) where volatile aromatic hydrocarbons are the primary constituents of concern. However, *in situ* bioremediation is increasingly being considered for sites containing coal tars, heavy petroleum distillates, or residues from manufactured gas, petrochemical and refining operations where polyaromatic hydrocarbons (PAHs) are the primary constituents of concern. This paper will examine the rationale for considering an *in situ* bioremediation process at sites containing these constituents. It will then explore potential differences between remediation of volatile aromatic hydrocarbons and remediation of PAHs that may be significant when evaluating and/or designing clean-up processes. Finally, a series of laboratory biodegradation studies that evaluate the accessibility of PAHs to *in situ* treatment will be discussed.

Physical, chemical and microbial properties of PAHs

By definition, polyaromatic hydrocarbons are chemicals containing only hydrogen and carbon atoms, with two or more aromatic rings. They are, in a sense, the semi-volatile cousins of the volatile aromatic compounds (benzene, toluene, ethylbenzene and xylene) and, like the BTEX compounds, they are

TABLE 1

Important properties[a] of representative aromatic hydrocarbons

Compound	Number of rings	Molecular formula	Solubility (mg/L)	K_{OC}	Log K_{OW}	R	Biodegradation half-life (days)
Benzene	1	C_6H_6	1780	85	2.1	5.25	5-10
Naphthalene	2	$C_{10}H_8$	30	2300	3.25	57	9-13
Anthracene	3	$C_{14}H_{10}$	0.045	1.8×10^4	4.45	886	<9-50
Phenanthrene	3	$C_{14}H_{10}$	1.0	1.8×10^4	4.46	908	<6-43
Benz[a]anthracene	4	$C_{18}H_{12}$	0.0057	1.38×10^6	5.6	6.9×10^4	63-231
Pyrene	4	$C_{16}H_{10}$	0.132	3.8×10^4	4.88	2.4×10^3	
Chrysene	4	$C_{18}H_{12}$	0.0018	2×10^5	5.61	1.3×10^4	41-116
Benzo[a]pyrene	5	$C_{20}H_{12}$	0.0012	5.5×10^6	6.06	2.7×10^5	

[a] R is estimated for a soil with 35% porosity and an organic carbon content of 1%.
Solubilities and partitioning coefficients taken from Verschueren [15].
Biodegradation half-lives from API [16].

of significant environmental concern. The solubilities of PAHs in water decrease as their molecular weight increases. They are all considered to be biodegradable, but their rates of biodegradation appear to be limited by the rates of dissolution, which are related to their aqueous solubilities. Two and three-ring PAHs are generally considered to be readily biodegradable, while the biodegradation half-lives of four and five-ring PAHs can be on the order of months to years, depending upon both the treatment conditions and the contaminant matrix [6,7].

Table 1 summarizes the molecular formulae, solubilities, organic carbon partitioning coefficients (K_{oc}), the octanol–water partitioning coefficients (K_{ow}), retardation factors (R), and biodegradation half-lives for benzene and seven representative PAH compounds. The larger PAH compounds have very low solubilities in water; they are tightly bound to the organic constituents in soil; they biodegrade slowly, and they are also of sufficient potential environmental risk that targeted cleanup goals can be as low as 0.2 ppb in groundwater.

Analyzing pump-and-treat for a PAH-contaminated aquifer

A first approximation of the performance of a pump-and-treat process for organic constituents can be developed based on partitioning coefficients and the organic carbon content of the aquifer. The distribution of each of these compounds between the sorbed and the dissolved phases can be estimated from the octanol-water partitioning coefficient and organic carbon content of the soil. (This analysis does not distinguish between PAHs which are sorbed on soils and those present within occluded droplets within the soil matrix.) This distribution coefficient, K_d, is the ratio of the concentrations of the sorbed phase to the concentrations of the dissolved phase compound, and K_d can be multiplied by the density of soil and divided by the porosity of the aquifer to determine the relative mass of sorbed contaminant to dissolved contaminant per unit volume. This ratio will be referred to as K_a, the aquifer partitioning coefficient.

By combining the compound-specific information provided in Table 1 with the estimated values for the porosity and bulk density of the aquifer, the efficiency of a simple pump-and-treat system can be estimated. If we envision that all of the "contaminated" water from a particular volume of an aquifer is replaced by clean water, then the mass of PAH removed is equal to

$$1/(K_a+1)$$

and the amount remaining is

$$1-1/(K_a+1)$$

The fraction remaining after "N" pore volumes of flushing is equal to

$$[1-1/(K_a+1)]^N$$

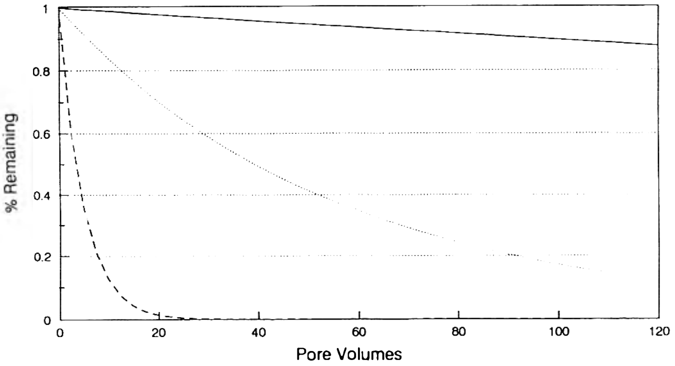


Fig. 1. Removal of aromatic hydrocarbons during pump-and-treat. (—) phenanthrene, (...) naphthalene, and (- - -) benzene. $F_{(oc)} = 1\%$ (organic carbon fraction).

The results of these calculations are summarized in Table 2.

Table 2 shows the fraction of each of the eight constituents remaining after an extended period of flushing at a site. As a point of reference, one pore volume of flushing is likely to require between one month and several years, depending upon the size of the treatment area and the rate of groundwater removal. The values calculated for benzene, naphthalene and phenanthrene are also displayed graphically in Fig. 1.

This analysis is obviously, overly simplistic. It ignores heterogeneities of the site, effective versus total porosity, flushing efficiencies, rates of dissolution

TABLE 2

Flushing efficiency of representative aromatic hydrocarbons

Compound	Fraction of contamination remaining after N pore volumes of flushing						
	1	10	20	40	60	90	120
Benzene	0.810	0.121	0.015	0.000	0.000	0.000	0.000
Naphthalene	0.982	0.838	0.702	0.493	0.346	0.203	0.120
Anthracene	0.999	0.989	0.978	0.956	0.934	0.903	0.873
Phenanthrene	0.999	0.989	0.978	0.957	0.936	0.906	0.876
Benz[a]anthracene	1.000	0.999	0.998	0.997	0.995	0.993	0.990
Pyrene	1.000	0.996	0.992	0.983	0.975	0.963	0.951
Chrysene	1.000	0.999	0.998	0.997	0.995	0.993	0.991
Benzo[a]pyrene	1.000	1.000	0.999	0.999	0.998	0.998	0.997
Average	0.974	0.866	0.833	0.798	0.773	0.745	0.725

[a] These calculations assume 35% porosity and an organic content of 1%.

and multiple other factors. But, it still provides a general analysis of the relative rates of extraction that can be expected for various constituents of a contaminated site. And for PAHs, the conclusion of this analysis is clear: pump-and-treat systems are very inefficient at removing PAHs from contaminated aquifers.

Analyzing *in situ* bioremediation for a PAH-contaminated aquifer

Oxygen transport has been identified as the rate limiting parameter for the *in situ* biodegradation of compounds at sites containing readily biodegradable compounds, including naphthalene and benzene [5,8]. The kinetics of microbial degradation in these systems are so much faster than the rate at which dissolved oxygen can be transported through a site, that rates of desorption, temperature effects and other factors which are significant in oxygen-rich environments, have proven to be of minor importance in designing *in situ* bioremediation projects. As a result, a first approximation of the rate of biodegradation achievable can by made by estimating the oxygen demand of the site and comparing this value with the rate at which oxygen can be supplied. This rate is, in turn, controlled by the rate of water movement through the site and the concentration of dissolved oxygen within the water.

The relative rate of *in situ* bioremediation under these conditions can now be compared with that of pump-and-treat by comparing the rate of oxygen supply to the rates of extraction. Table 3 presents a comparison of the two processes for a series of hypothetical aquifers containing various concentrations of PAHs. In each instance, the initial PAH concentration (1000, 250 or 100 mg/kg) is assumed to consist of equal amounts of each of the eight PAHs listed in Table 2. The performance estimates for *in situ* bioremediation are provided for three levels of dissolved oxygen; 10 ppm (water saturated with air), 40 ppm (water saturated with oxygen) and 150 ppm (water containing 300 ppm of hydrogen peroxide as an oxygen carrier). The calculations assume that three pounds of oxygen must be delivered to biodegrade one pound of PAH and that no other sources of oxygen demand are significant. The top portion of the table illustrates performance of the two processes expressed as mass removed per pore volume of treatment, while the bottom portion illustrates the percent of PAH that would remain after 10, 40 and 120 pore volumes of treatment. In Table 3A, the incremental performance of each process is shown, while in Table 3B the removal rates for *in situ* bioremediation are added to those estimated for pump-and-treat alone.

The implications of the type of analyses presented in Tables 2 and 3 are consistent with the results of more detailed analyses performed at actual sites.

- *In situ* bioremediation is most cost-effective when treating contaminants which have retardation factors greater that ten, where pump-and-treat is not very efficient.

- At sites containing contaminants with a wide range of solubilities, pump-and-treat may be the more efficient process initially and *in situ* bioremediation the more cost-effective at later stages of the project.
- A pump-and-treat process is often cost-effective (relative to *in situ* bioremediation), as long as the concentration of contaminants in the extracted water is greater than the concentration of contaminants that could be degraded by dissolved oxygen injected during an *in situ* bioremediation process.

Thus far, this paper has focused on the potential benefits associated with using *in situ* bioremediation for PAHs and has assumed that PAHs will respond to treatment in a manner similar to that in which volatile aromatic hydrocarbons respond. The next section of this paper explores the possibility

TABLE 3

A. Performance comparison of pump-and-treat versus *in situ* bioremediation[a]

Initial PAH concentration (mg/kg)	Pump-and-treat PAH removed (in mg/kg) during various flushes				*In situ* bioremediation PAH removed (in mg/kg) based on the D.O. content of the injected water (ppm)		
	PV-1	PV-10	PV-20	PV-50	10	40	150
1000	26	5.8	2.3	1.3	0.8	3.2	12
250	6.5	1.45	0.58	0.33	0.8	3.2	12
100	2.6	0.58	0.23	0.13	0.8	3.2	12

B. Percent PAH remaining after various pore volumes of treatment[b]

Initial PAH concentration (mg/Kg)	No. of PV	Pump-and-treat only	Concentration of D.O. in groundwater (ppm)		
			10	40	150
1000	10	86.6	85.8	83.4	74.6
	40	79.8	76.6	67.0	31.8
	120	72.5	62.9	34.1	0
250	10	86.6	83.4	73.8	38.6
	40	79.8	67.0	28.6	0
	120	72.5	34.1	21.3	0
100	10	86.6	78.6	54.6	0
	40	79.8	47.8	0	0
	120	72.5	0	0	0

[a] Calculations assume that PAHs are comprised of equal quantities of the eight PAHs listed in Table 2 and no other source of oxygen demand is present. PV means pore volumes.

[b] Calculations assume that PAH biodegradation is limited only by the transport of dissolved oxygen.

that PAH desorption/biodegradation, and not oxygen transport, becomes the rate limiting factor as the *in situ* bioremediation process progresses.

Total versus instantaneous oxygen demand

One fundamental assumption in the design of *in situ* bioremediation processes is that oxygen transport is the rate limiting step for the overall process. This model is used in designing the oxygen transport strategy including the injection and recovery system, the concentration of dissolved oxygen to be delivered, the type and frequency of monitoring and the predicted time frame of remediation. However, the rates of biological degradation within soil systems for the four and five ring PAHs, summarized in Table 1, are ten to twenty times slower than those for BTEX compounds and lighter PAHs. Similar results have been reported in slurry systems [7,9]. Biodegradation studies in Remediation Technologies, Inc.'s (RETEC's) laboratories and those of several academic institutions have also noted that these degradation rates vary widely and in some instances, compounds which are generally readily biodegradable are simply not "bioavailable" [9,10]. Collectively, the available information on PAH diffusion, dissolution and biodegradation suggest that dissolution and diffusion will control biodegradation and that biodegradation will control remediation at many PAH sites.

Recent research on the biodegradation of PAHs in soils from former manufactured gas facilities suggests that the soil matrix may control the extent of biodegradation achievable as well as the rate [11]. Four soils, designated B, F, G and J were selected for a series of biodegradationexperiments.

These four soils were selected because their organic carbon contents ranged from less than 1% to over 50% (because of the presence of lampblack and other materials) and because the percentage of fine grained material ranged from 3% to 26%. Earlier studies had suggested that these two parameters might have a significant effect of the biodegradation process. Each soil was treated in two systems. The first was a simulated land treatment process, where the soils were amended with nutrients, kept moist and were mixed regularly to provide aeration and general mixing. The extent and rates of removal of PAH constituents during this "unsaturated" treatment for these four soils are summarized in Table 4. For comparison, a second set of biodegradation experiments were performed with the same soils, using a slurry phase treatment. This experiment was designated as "saturated" treatment. The rate and extent of PAH removal of these studies also appear in Table 4. As expected, the slurry treatment provided more rapid treatment than did the unsaturated treatment, but the ultimate concentrations of PAH achieved using the two methods is essentially the same for three of the four soils. However, Soil F, which contained 26% fines and 6.5% organic material, demonstrated 84% PAH removal in the slurry phase but no significant reduction in the less aggressive unsaturated treatment. The

TABLE 4

Summary of soil characteristics and modified first-order coefficients

Soil	Initial PAH concentration (mg/kg)	Fines content (%)	Carbon fraction (%)	First-order decay rate (day^{-1})		Reduction of PAHs (%)	
				Unsaturated	Saturated	Unsaturated	Saturated
B	160	3	0.6	0.054	0.24	93	96
F	190	26	6.5	-[b]	0.57	<20	84
G	20,000	7	16	0.024	0.19	78	74
J	29,000	27[a]	58	0.041	0.24	42	46

[a] Includes lampblack fines.

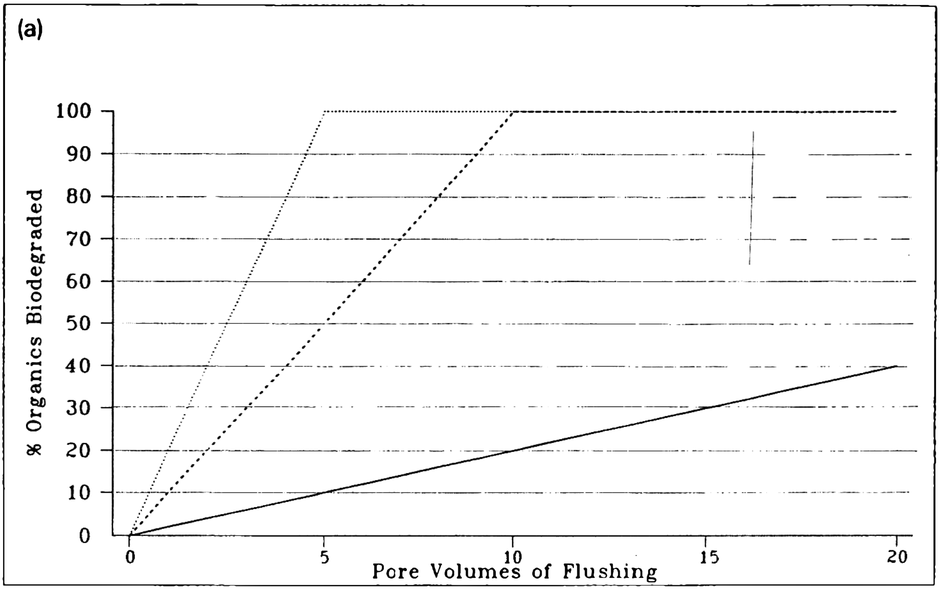
[b] Data was not fit to the mathematical model.

authors suggest that the presence of these fines allows the formation of aggregates which can retain significant quantities of organic constituents. Since these pores are smaller than bacteria, and many PAHs are very insoluble, these constituents remain unavailable for biodegradation in the absence of sufficient water (and perhaps mechanical energy) to disperse the aggregates.

If we extend the results of this study to an *in situ* bioremediation process where minimal mixing exists, it seems likely that the rate of PAH removal may be very low at sites containing lenses of fine grained soils. In these environments, the rate and extent of remediation will be limited by the rate of dissolution and diffusion of low soluble constituents from low permeability zones into those portions of the site where groundwater movement, oxygen exchange and microbial activity are occurring.

The distinction between an oxygen transport-limited and a diffusion-limited process is illustrated in Fig. 2. Scenario I represents the traditional assumption that oxygen transport is the rate limiting factor for *in situ* biodegradation. The plots shown in Scenario I demonstrate the effect of increasing the concentration of dissolved oxygen on the rate of *in situ* bioremediation. The three lines show the rates of remediation when a pore volume of water contains 2%, 10% or 20% of the total biological oxygen demand (BOD) of the area being treated. Under these conditions, the optimum design will deliver as much oxygen per unit volume of water as can be delivered without other detrimental effects (such as oxygen loss due to instability or degassing). Under these conditions, increasing the density of injection and recovery wells will result in increased oxygen transport and, subsequently, increased rates of remediation.

The Scenario II plot illustrates the rate of *in situ* bioremediation, if 20% of the contamination is "instantly degradable" and the remaining portion of the contamination desorbs at the rate of 1% per pore volume. Under these conditions, as soon as the instantaneous demand is satisfied (the readily degraded-constituents have been depleted) there is no advantage to supplying more dis-



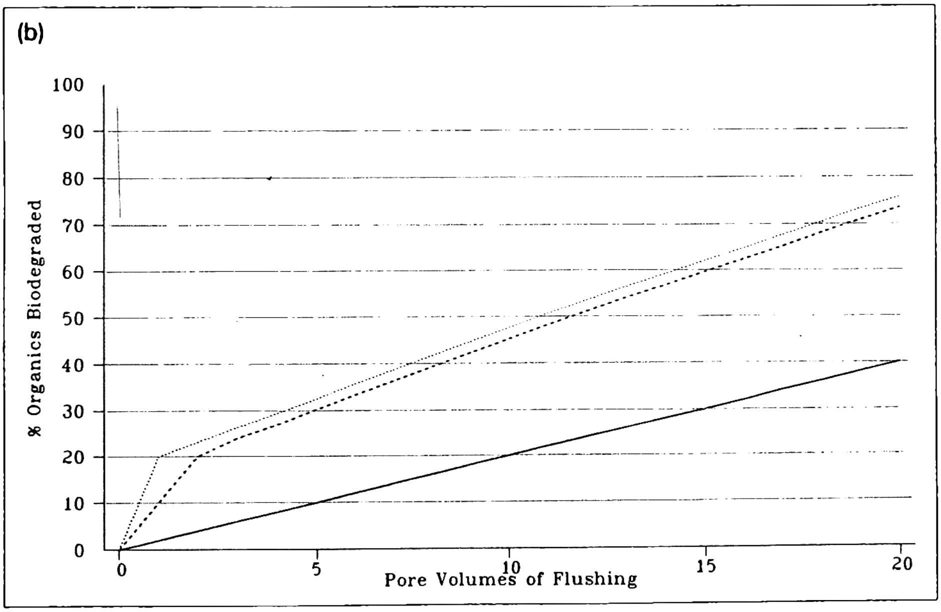


Fig. 2. Rate of bioremediation as a function of oxygen supply. (% BOD per PV). (a) Scenario I - All organics readily available, (b) Scenario II - 20% of organics readily available. (...) 2%, (- - -) 10%, and (—) 20% BOD per PV.

solved oxygen than is required to satisfy the continued oxygen demand created by freshly desorbed constituents.

Under the Scenario II conditions, after five pore volumes of flushing at the 10% level, continued oxygen delivery at the 5% level (meaning a concentration which delivers 5% of the total BOD of the site in one pore volume) provides the same level of remediation as the addition of four times that level.

Utilization of a "Scenario I" process for a "Scenario II" site can lead to serious design errors, including unrealistic predictions of remediation rates; addition of greater quantities of oxygen than can be used efficiently; possible termination of the process, when original oxygen breakthrough occurs while 80% of the total oxygen demand remains in the aquifer; and/or design of an aggressive injection/recovery system, when a system designed for a slower rate of oxygen delivery would produce comparable results.

In situ biodegradation under desorption-controlled kinetics

In a pump-and-treat process, a PAH molecule which dissolves from the contaminant matrix is then likely to resorb and desorb multiple times before it is finally extracted to the surface. The relative time spent in the soluble and insoluble forms is reflected by the partitioning coefficient for that compound. In an *in situ* bioremediation process, the aquifer contains a viable population of PAH-degrading bacteria, plus the necessary oxygen and nutrients for microbial activity. Under this scenario, the PAH, once dissolved, may be biologically degraded, thus providing continued depletion of PAH constituents throughout the aquifer.

As the total mass of readily degradable contaminant is depleted and the rates of desorption of slowly desorbable constituents decrease, less and less oxygen will be needed in the treatment area to maintain an oxygen surplus. In many instances, hydraulic containment may not be warranted, as long as this oxygen surplus condition is maintained. Eventually, the dissolved oxygen supplied by the natural groundwater moving into the site will be adequate to maintain an oxygen surplus; and, continued oxygen delivery will no longer be beneficial, as the kinetics of remediation are independent of externally controlled forces.

Many micro-processes contribute to the effectiveness of biodegradation at complex PAH-contaminated sites. In particular, the time required to achieve targeted concentration goals is contingent upon the mechanisms of desorption, dissolution and diffusion. These same factors, along with the presence of other degradable constituents, are also likely to control the level of remediation that can be achieved. Soils containing two- and three-ring PAHs, which are soluble in the parts per million range, can be treated to very low levels because the rate and extent of desorption is sufficient to maintain viable bacterial activity. However, given the minimal solubility and strong sorption of higher molecular weight PAHs, whose maximum solubilities are only a few parts per trillion and whose cleanup standards are very low, biological activity may not be great enough to support a viable microbial population, depending upon the availability of other carbon sources in the aquifer. After the more soluble PAHs have been removed, the rate of degradation will be limited to the rate of dissolution. At extremely slow rates of dissolution, the total mass of degradable carbon will below and could drop below the critical level of carbon needed to maintain a viable population of PAH-degrading bacteria. However, there is no general agreement on what the effectiveness of *in situ* bioremediation will be.

Laboratory and field studies with groundwater from a wood treating site in Conroe, Texas suggested that biodegradation of PAHs could not reduce concentrations below 5–30 ppb for individual PAHs [8]. By contrast, dozens of treatability studies using slurries and trickling filters have shown soluble concentrations of PAH and volatile aromatic compounds can be reduced to below detection levels (1 ppb). Several carefully documented studies have also indicated biodegradation of various organic constituents to very low levels, though most of these compounds are more soluble than four-ringed PAHs [12,13]. More experimentation is required to understand those factors which control biodegradation at very low organic concentrations and to understand whether *in situ* bioremediation can achieve the extremely low concentrations being set for some remediation designs [14].

Laboratory studies

Ultimately, many of the questions raised in this paper can only be resolved after a combination of carefully controlled laboratory-scale experiments and field-scale experience. As a initial step in this process, RETEC has recently completed a series of studies using soils from a former wood treating facility .

Soil samples were collected from two different areas of the site. The first soil sample, designated "A", was collected near a former lagoon, which had received runoff from a wood treating operation for many years. The soils generally consisted of a mixture of silt, clay and fine sand. The in-place permeabilities of soils in this portion of the site are in the range of 10^{-3} cm/s. The soils obtained for the treatability study contained 11,706 ppm of PAHs prior to treatment.

The second soil sample, designated "B", was collected near a former pond located some distance from the lagoon. When the facility was in operation, heavy rainfall would cause the lagoon to overflow, thus contaminating the pond. Soils from the pond area were found to be clayey silts and silty clay, though in-place hydraulic conductivity was estimated at 2×10^{-4} cm/s, probably due to secondary permeability. The soils collected from this area contained 813 ppm total PAHs prior to treatment. A third soil, designated "C", was collected downgradient of the lagoon. This sample, though containing only 19 ppm of PAHs, was still sufficiently contaminated such that groundwater in contact with this soil was considered a potential threat to the environment.

Soils from all three areas were treated in a slurry reactor for 12 weeks to determine the maximum extent of remediation that could be achieved. Soils were analyzed for total and carcinogenic PAHs at the beginning and end of the treatment. In addition TCLP extractions were performed on the soils to determine how the mass of "extractable" PAHs (meaning extractable to leachate or groundwater) compared to the "total" PAHs detected (those extractable with an organic solvent). The results of these studies are summarized in the top portion of Table 5.

The concentration of total PAHs decreased by over 90% in reactors A and B and by about 60% in reactor C. Perhaps more significantly, the TCLP extractable fraction of the contamination was reduced by greater than 99.5% in the soils that were highly and moderately contaminated and TCLP extractable constituent levels were reduced to below detection limits in the slightly contaminated soil. This suggests that those constituents which are off the greatest risk to the environment, because of their migration potential, were almost completely removed during biological treatment.

Two of the soils, B and C were then placed into glass columns, through which water was transported at a rate of four pore volumes per day for 22 weeks. (A pore volume is the volume of water contained within the column). This water was amended with 40 ppm of dissolved oxygen as well as microbial nutrients. These results appear in the lower half of Table 5.

TABLE 5

Laboratory treatability studies with PAH-contaminated soils

Slurry study (12 weeks)	Soil A		Soil B		Soil C	
(12 weeks)	Soil (mg/kg)	TCLP extract (mg/L)	Soil (mg/kg)	TCLP extract (mg/L)	Soil (mg/kg)	TCLP extract (mg/L)
Initial total PAHs	11,706	5.473	813	2.683	18.93	0.00327
Initial carcinogenic PAH	665	<0.04	<50	<0.01	12.56	0.00008
Final total PAHs	707	0.028	4.59	0.00097	7.11	0.00047
Final carcinogenic PAHs	273	0.002	1.73	0.00004	3.35	ND
Reduction of total PAHs (%)	94	99.5	99.4	99.9	62	85
Reduction of carcinogenic PAHs (%)	59				73	
Soil column			Soil (mg/kg)	Effluent (mg/L)	Soil (mg/kg)	Effluent (mg/L)
Initial total PAHs			1174	0.0037	19	0.0083
Initial carcinogenic PAH			40			
Final total PAHs			350	0.000065	21	0.00048
Final carcinogenic PAHs			46			
Reduction of total PAHs (%)			70	98	0	94
Reduction of carcinogenic PAHs (%)			0			

For soil B, the PAH concentration in soil decreased from 1174 to 350 ppm (70%) while the level of contamination in the effluent decreased by 98%. In the column containing the slightly contaminated soil, C, there was no discernable change in soil concentration but the effluent concentrations decreased by 94%. A plot of effluent concentration versus time (Fig. 3) for these two column studies suggests a first-order decrease in concentration, both achieving concentrations of less than 1 μg/L total PAHs after extensive treatment (300–700 pore volumes).

Although no microbial inhibited controls were included in these studies, the

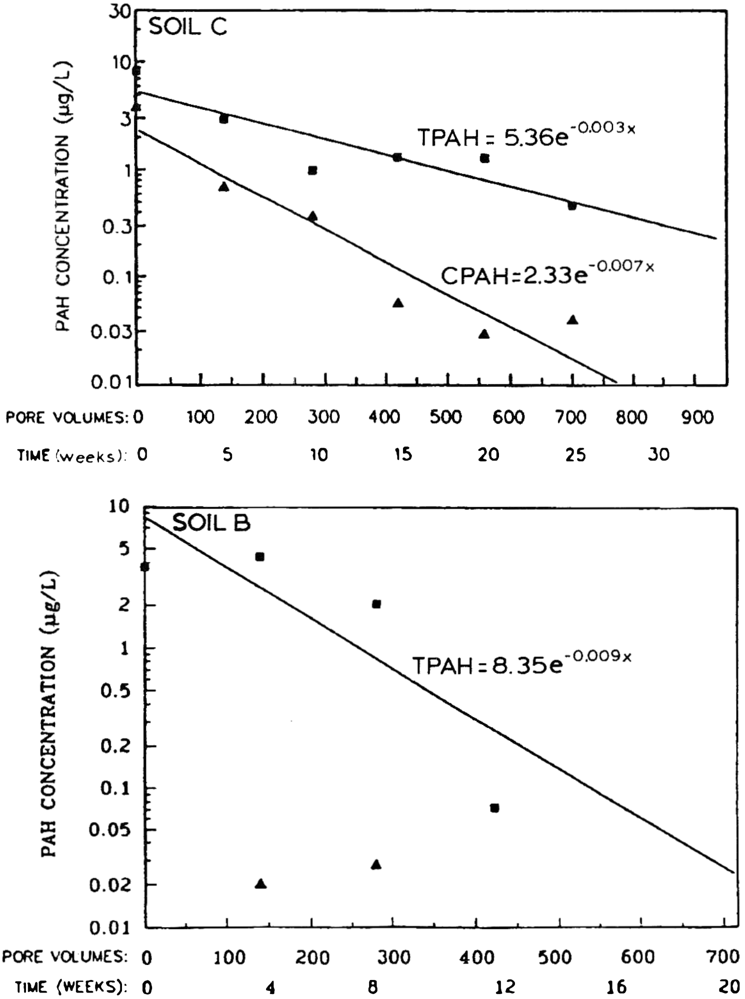


Fig. 3. PAH concentrations in effluents from columns of two creosote-contaminated soils. (■) Total PAH, and (▲) carcinogenic PAH.

concentrations of contaminants in the effluent were analyzed and were found to be insignificant relative to the changes observed. Mass balance calculations for Soil B indicate that less than 0.1% of the PAH removed can be attributed to direct loss in the effluent, suggesting that biodegradation was the primary remediation process. This information, in combination with microbial data, dissolved oxygen profiles and other indirect measurements, support the conclusion that the reductions resulted primarily from biological treatment rather than simple flushing.

Although the results presented represent a limited set of experiments, they provide an indication of both the feasibility and the complexity of *in situ* bioremediation processes for PAH contaminated sites.

Summary and conclusions

Essentially no remediation occurs for three-, four- and five-ringed PAHs in pump-and-treat processes.

The relative performance of pump-and-treat and *in situ* bioremediation can be estimated using simple mathematical models, but the validity of these models requires that partitioning between dissolved and sorbed constituents is fast relative to groundwater movement.

If desorption of PAHs is the rate-limiting step for the *in situ* bioremediation of an aquifer, the most cost-effective process will be that which provides slightly more dissolved oxygen than that required to satisfy the instantaneous oxygen demand of the site.

The rate of desorption and the extent of bioavailability of PAHs is site specific and not readily predictable.

Site specific treatability studies are recommended before predicting the kinetics or extent of biodegradation that can be achieved at PAH-contaminated sites.

Further research is required to understand the factors which control desorption and microbial degradation in soil systems containing low concentrations of PAHs.

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Review

Subsurface microbial ecology and bioremediation*

J.M. Thomas and C.H. Ward

National Center for Ground Water Research, Department of Environmental Science and Engineering, Rice University, P.O. Box 1892, Houston, TX 77251 (USA)

Abstract

A minireview of subsurface microbial ecology as it relates to ground water contamination and remediation is presented. Microorganisms have been detected unequivocally at depths of 500 to 600 m below the surface. Microbial numbers and activity are higher in sandy transmissive sediments than in those with high clay content and low transmissivity. Many of these organisms are active and can metabolize a variety of organic compounds which are of environmental concern. Biodegradation in the subsurface is favored by the presence of acclimated organisms and essential nutrients and the absence of toxicants and inhibitors. Natural bioremediation in the subsurface is enhanced by transporting an electron acceptor and essential nutrients to microorganisms in the zone of contamination. A better understanding of microbial processes in the subsurface may provide better solutions to ground water contamination problems.

Introduction

The biosphere under the root zone is largely uncharacterized in terms of ecological diversity and importance in geochemical processes and more recently, in the fate of environmental pollutants. Lack of interest in subsurface microbial ecology is probably a result of early investigations which indicated that bacterial numbers decreased with depth below the surface [1]. In addition, the expense and logistical difficulties of collecting representative samples have steered research away from subsurface microbiology [2]. As a consequence, it was assumed that the subsurface below the root zone was generally void of life until scientists at the United States Environmental Protection Agency readdressed the question [2,3]. The results of renewed investigations

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Correspondence to: J.M. Thomas, National Center for Ground Water Research, Department of Environmental Science and Engineering, Rice University, P.O. Box 1892, Houston, TX 77251 (USA). Fax: (713) 527-5203.

of the subsurface indicate that subsurface microorganisms exist and can be metabolically active. The heretofore relatively unexplored subsurface may provide a better understanding of biogeochemical processes, harbor organisms with novel metabolic pathways and provide solutions to ground water and subsurface contamination. The following sections will concentrate on subsurface microbial ecology as it relates to subsurface remediation.

Numbers, distribution and activity of microorganisms

Below the rhizosphere where the terrestrial environment is no longer classified as soil, microorganisms have been found unequivocally at depths of 500 to 600 m [4]. Although earlier works suggested that microorganisms could be found at even greater depths, the results of these studies were considered equivocal because methods for sample collection did not exclude the likelihood of contamination from the surface and drilling operations [2,5]. After development of methods that excluded contamination of shallow subsurface samples around 1980 [6,7], credible data on the numbers, diversity and distribution of microorganisms in the shallow subsurface were reported. In addition, analyses of samples of subsurface material instead of ground water was emphasized because water drawn from wells may contain nonindigenous microorganisms [8]. Initial investigations were conducted to determine the microbial ecology of shallow uncontaminated and contaminated subsurface material, the zone from the rhizosphere to about 10 to 20 m from the surface. Later investigations included samples from the uncontaminated deep terrestrial subsurface at depths of 500 to 600 m, which required specialized sampling equipment [9,10].

In general, the numbers, types, and distribution of microorganisms in shallow and deep subsurface sediments are similar, depend on subsurface characteristics, and are microsite specific. Investigations of the microbial ecology of the shallow subsurface have indicated that bacteria are the predominant type of microrganism present [7,11–14], although protozoa, algae and fungi have been detected as well [15,14,16]. Studies conducted using samples from the deep subsurface also have indicated the presence of the same inhabitants, with bacteria predominating [17–19]. In shallow and deep samples of subsurface materials, direct counts of bacteria are fairly uniform with depth and range from about 10^6 to 10^7 cells/g dry weight [7,11,12,17,20]. Direct counts in this range are lower than those of bacteria in samples of surface soil, around 10^8 to 10^{10} cells/g dry soil [21], and may be explained by the oligotrophic nature of most uncontaminated subsurface environments [5]. Viable counts are usually less than direct counts and range from nondetectable to as high as the direct count [7,11,12,15,17,20,22]. However, within the different strata of a subsurface profile, the bacterial populations may vary, with higher numbers and activity detected in sandy aquifer sediments rather than those high in clay [15,17,19,20,23,24].

TABLE 1

Microbial ecology of ucontaminated and contaminated samples from the same sites

Spill	Variable	Uncontaminated	Contaminated	Reference
Creosote[a]	Predominant cell type	Gm$^+$	Gm$^-$	[13]
	Biomass[b] (nmol/GDW[c])	0.6(0.5)	1.0(0.8)-1.9(0.5)[d]	[13]
	Direct Counts (10^6/GDW)	1.2(1.2)-16(8)	8(2)	[25]
		1.4(0.6)-2.3(0.9)	1.3(0.5)-2.4(0.8)	[26]
			0.9(0.4)-2.1(0.8)	
	Viable counts[e] ($\times 10^6$/GDW)	$<10^2$-0.1(0.02)	$<10^2$-2.9(0.2)	[26]
	ATP (ng/GDW)	0.017	0.009	[25]
Coal tar	Direct counts ($\times 10^6$/GDW)	1-100	1-700	[14]
	Viable counts ($\times 10^2$/GDW)	1-100	1-10,000	[14]
	Protozoa (No./GDW)	<50	<50-19,000	[14]
	Fungi (No./GDW)	10	10	[14]
	Actinomycetes (No./GDW)	10-1000	10-10,000	[14]
Unleaded	Viable counts[e] ($\times 10^6$/GDW)	1.6(0.1)-1.8(0.5)	0.3(0.03)-65.5(9.2)	[27]
Gasoline jet fuel	Direct counts ($\times 10^6$/ml)	0.001-0.02(0.008)	0.7(0.1)-13	[28]
	Viable counts[e] ($\times 10^3$/ml)	<1	62-1,400	[28]
Oil products	Glucose uptake V_{max} (μg/L h)	0	0.2	[29]

[a] All measurements of microbial numbers and activity in samples from a creosote spill are from the same site.

[b] Biomass measured as total extractable phopholipid.

[c] Range of measurements can represent different depths in unsaturated and saturated zones and for the contaminated samples, different concentrations of contaminants.

[d] GDW: grams of dry weight of subsurface material.

[e] Range of counts on different types of media.

The microbial ecology of aquifers contaminated with organic pollutants is strikingly different from that found in uncontaminated aquifers. Provided that the nature or concentrations of pollutants are not toxic and there are sufficient nutrients to support growth, the addition of organic contaminants to the uncontaminated subsurface may stimulate microbial growth and activity. A comparison of microbial numbers and potential activity in samples of uncontaminated and contaminated materials from the same site has been conducted by several investigators (Table 1). In general, environmental spills of organic compounds may increase microbial numbers and activity.

Biodegradation in the subsurface

The microflora from uncontaminated and contaminated shallow and deep subsurface materials has been reported to metabolize a variety of naturally-occurring organic compounds including carbohydrates, amino acids, organic acids, methane, cellulose, and lignin-type compounds [30–32]. In addition, compounds from several classes of industrial chemicals that have been shown to biodegrade in shallow subsurface material include petroleum-derived hydrocarbons [17,26,27,30,33–35], chlorinated aliphatic solvents [31,36], phenols [37–39], and polar solvents [39–42]. Studies of the biodegradation of industrial chemicals in the deep subsurface have been limited; however, phenol [43], naphthalene, toluene, the xylene isomers, dibenzothiophene, *p*-cresol [44], nitrogen-containing aromatic compounds [45], and trichloroethylene [19], have been biodegraded by microorganisms from the deep subsurface.

Factors which may affect biodegradation in the subsurface

The same variables which affect biodegradation in terrestrial and aquatic environments also apply to the subsurface. Conditions which favor biodegradation include the presence of acclimated microorganisms, adequate substrate concentration and availablity, the presence of essential nutrients, the absence of toxicants and inhibitors, and appropriate values for pH, temperature, salinity and osmotic pressure [46].

Acclimation is defined as the amount of time between exposure of microorganisms to a substrate and detection of substrate biodegradation. Acclimation may occur as a result of an increase in the number of contaminant-degrading organisms, genetic changes which confer degradation capabilties, enzyme induction, and depletion of a substrate which is preferentially metabolized [47]. Detection of pollutant biodegradation within a relatively short incubation period (days to weeks) also has been reported for samples of uncontaminated subsurface material [7,38,48], suggesting that a lengthy prior exposure to the contaminants before biodegradation can ensue is not required. However, microorganisms in uncontaminated environments may incorporate more of a contaminant into biomass rather than mineralize it [30]. As a result of lengthy exposure to contamination, it has been reported that subsurface microorganisms may shift their metabolism from less cellular incorporation to more mineralization of the contaminants [48]. Investigations which compare contaminant biodegradation in samples of uncontaminated and contaminated material from the same site can be used to indicate the presence of acclimated microorganisms and the potential for biodegradation of subsurface pollutants (Table 2).

The absence of biodegradation in the subsurface may be a result of the presence of toxins or inhibitors. The lack of biological activity in samples collected from deep subsurface material contaminated with trichloroethylene was thought to result from the high concentrations of contamination (>200 mg/kg sediment and >300 mg/L pore water) present [19]. In another study, mi-

TABLE 2

Biodegradation of organic compounds in samples of uncontaminated and contaminated subsurface material from the same site

Compound	Biodegradation[a]		Reference
	Uncontaminated	Contaminated	
Naphthalene	no	yes	[33]
	no	yes, no[b]	[26]
	no	yes, no	[14]
2-Methylnaphthalene	no	yes	[33]
Dibenzofuran	no	yes	[33]
Fluorene	no	yes	[33]
Acenaphthene	no	yes	[33]
1-Methylnaphthalene	no	yes	[33]
Phenanthrene	no	yes, no	[26]
	no	yes, no	[14]
Benzene	no	yes	[49]
	no	yes	[27]
Toluene	no	yes	[49]
	yes	yes	[27]
	yes	yes[c]	[48]
Ethylbenzene	yes	yes	[27]
m-Xylene	no	yes	[49]
	yes	yes	[27]
o-Xylene	no	yes	[49]
	no	no	[27]

[a] Disappearance of parent compound or mineralization.

[b] Samples from several zones and locations in the subsurface were analyzed.

[c] More was biodegraded in the contaminated than uncontaminated samples.

neralization of naphthalene, phenanthrene, and glucose was detected in samples from the saturated but not the unsaturated zone of subsurface material heavily contaminated with creosote; the lack of activity was thought to result from toxic concentrations of creosote present in the unsaturated zone [26].

Nutrient availabilty also may limit biodegradation in the subsurface. Unlike surface environments, the subsurface microflora rely on the transport of nutrients and electron acceptors from ground water recharge from rivers and streams or percolation from the surface, which are most often slow processes. As a result, biodegradation in the subsurface may be limited by the transport of essential nutrients and electron acceptors to the microorganisms [33], which is ultimately dependant on the permeability of the formation. Several investigators have reported that the addition of inorganic nutrients to samples of subsurface material enhanced or had no effect on contaminant biodegradation [26,27,38]. Most likely, the effect of nutrient amendments depends on the native fertility of the subsurface material.

Biodegradation potential in saturated sediments appears to be related to subsurface characteristics rather than to depth or dissolved organic carbon content [43]. As with numbers, types, and distribution of microorganisms, microbial activity and biodegradation potential are higher in sandy transmissive sediments than in those with high clay content [19,43]. Investigations of microbial activity in the subsurface have indicated that biodegradation potential of acetate and phenol is positively correlated to viable cell counts and pH and negatively related to clay content [43]. However, these correlations were not observed for more recalcitrant compounds such as aniline, quinoline, and pyridine, for which other factors may be involved in their biodegradation [45]. Similarly, biodegradation potential of methanol and phenol in samples of surface soil and subsurface material was positively correlated with viable cell counts, whereas a negative correlation was observed for the more recalcitrant compound, *t*-butyl alcohol [39].

Although many organic pollutants have been shown to biodegrade under aerobic as well as anaerobic environments, biodegradation, when it occurs, is usually faster when oxygen (O_2) is used as the terminal electron acceptor. In addition, initiation of the major biodegradative pathways for many organic pollutants, especially aromatic hydrocarbons, requires O_2. Even readily metabolizable compounds such as carbohydrates have resisted biodegradation in environments devoid of O_2 [50]. The results of several laboratory and field experiments have shown that the presence or addition of O_2 enhances biodegradation of many of the pollutants found in the subsurface. Biodegradation of several polycyclic aromatic hydrocarbons was enhanced by the addition of O_2 to the subsurface and samples of ground water collected from a site contaminated with creosote [51,52]. At this same site, transport of O_2 to contaminant-degrading microroganisms in aquifer material contaminated with creosote was thought to control the size and shape of the resulting plume [33,53]. In a field experiment conducted in a shallow, unconfined sand aquifer, biodegradation of benzene, toluene, and the xylene isomers was controlled by the availabilty of dissolved oxygen, and the compounds persisted in layers which were oxygen-poor [54].

Contrary to past research that indicated that O_2 is required in the biodegradation of aromatic hydrocarbons [55], more recent studies have shown that these compounds can be metabolized under anaerobic conditions. Several monoaromatic compounds have been reported to biodegrade under methanogenic [56,57], denitrifying [58,59], sulfate-reducing [60], and ferric iron-reducing conditions [61]. A better understanding of the fate of these compounds under anaerobic conditions is warranted because unsaturated and saturated subsurface materials frequently are driven anaerobic as a result of a contamination event. In addition, use of electron acceptors other than O_2 may be advantageous because of the limited solubility of O_2 in water.

Application of microbial ecology to subsurface bioremediation

Many contamination events may go unnoticed because of natural bioremediation [62]. When the rate of natural bioremediation is not fast enough to prevent the spread of contamination, resulting in health and environmental risks, intervention by one of many remedial techniques will be required. Bioremediation is one of those techniques and usually is used in conjunction with several other remedial options. Subsurface microorganisms were stimulated to bioremediate ground water contaminated with hydrocarbons by R.L. Raymond and coworkers as early as 1974 [63]; however, it was not until the early 1980s that the U.S. Environmental Proctection Agency launched a major program to investigate the potential role of microorganisms in the fate of subsurface contaminants [64]. Until then, the potential of subsurface bioremediation as a remedial option was not considered by federal agencies or industry. Most of the bioremediation technologies that since have been developed are variations of those used by Raymond and his coworkers. In addition, most of these refined processes have been used mainly to bioremediate hydrocarbons.

Application of bioremediation to the subsurface involves designing a system that will provide limiting nutrients and an electron acceptor to the microorganisms in the zone of contamination [65]. The system can be designed to treat the unsaturated or saturated zones or both zones simultaneously. Treatment of the unsaturated zone may be accomplished using several methods: by 1) percolating a nutrient solution from the surface down into the unsaturated zone using an infiltration gallery, 2) raising the water table so that a nutrient solution can be perfused through the affected area, and 3) bioventing, a process which combines soil venting with biodegradation and is used for compounds which can be volatilized relatively easily [66]. Figure 1 was designed as a composite to illustrate the three methods that can be used for remediating the

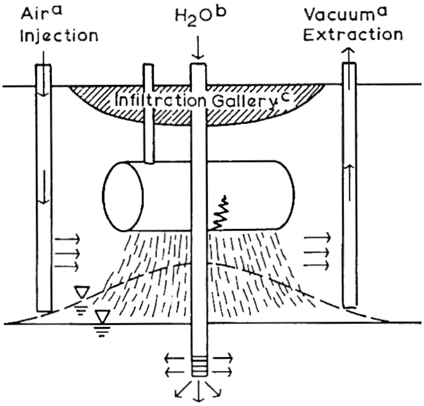

Fig. 1. Composite diagram of different treatment schemes for contamination of the unsaturated zone: (a) vacuum extraction for bioventing, (b) water injection to raise water table, and (c) infiltration gallery to supply nutrients and electron acceptor.

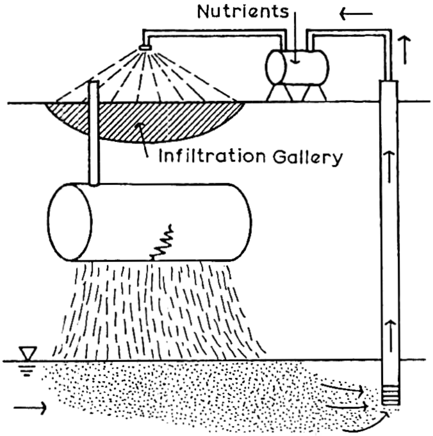

Fig. 2. Schematic diagram of unsaturated and saturated zone treatment in a closed-loop system.

unsaturated zone; this figure should not be used as a basis for process design. The saturated zone may be treated by perfusing the contaminated area with a nutrient solution using injection wells or injection and recovery wells in a closed loop system. Treatment of both the unsaturated and saturated zones simultaneously (Fig. 2) can involve the use of infiltration galleries and recovery wells [65].

All of the above methods, except for bioventing, involve dissolving the electron acceptor, usually oxygen, in water before addition to the subsurface. Using the treatment of monoaromatic hydrocarbons in the bioremediation scenario, large amounts of water will be required to degrade the contaminants because of: (1) the low solubilty of oxygen in water, about 8 mg/L when air is used and about 40 mg/L when pure oxygen is used (depending on temperature), and (2) the 2:1 ratio of oxygen to hydrocarbon that will be required [62]. As a result, hydrogen peroxide, which is infinitely soluble in water, has been used as a source of oxygen in subsurface bioremediation [67]. Hydrogen peroxide decomposes to yield $\frac{1}{2}O_2$ and H_2O so that concentrations as low as 100 mg/L can provide more O_2 per unit volume than using either air or pure O_2. However, peroxide concentrations as low as 100 mg/L can be toxic to microorganisms [68]. To avoid toxicity, peroxide is added in a step-wise manner from about 50 to as high as 1000 mg/L, to allow the subsurface microflora to adapt to the oxidant. Other problems associated with the use of peroxide include rapid decomposition and off gassing of O_2 to the surface and/or plugging of the region undergoing treatment [69]. Bioventing is another approach to increasing the supply of O_2 to the subsurface because more O_2 can be transported in air than water [66].

Also promising is the use of nitrate as an electron acceptor during bioremediation of the subsurface. The use of nitrate alone or in combination with oxygen is attractive because nitrate is more soluble than O_2 in water. Although denitrification was once thought to occur under strict anaerobic conditions, combinations of O_2 and nitrate to enhance biodegradation may be possible [59,70,71]. In the presence of both, O_2 could be used to initiate biodegradation while nitrate could serve as the terminal electron acceptor. Subsurface bioremediation using nitrate as a terminal electron acceptor in the field has been attempted [72–74].

Innovative approaches to subsurface bioremediation

By studying the niche of microorganisms, several innovative approaches to subsurface bioremediation have been developed or proposed. These include the cometabolism of chlorinated aliphatic solvents, transport of microorganisms through the subsurface to aid in contaminant removal, and the production of bioemulsifiers and biosurfactants by subsurface microorganisms.

The process of cometabolism, during which microbial growth results from metabolism of a primary substrate and a secondary substrate is fortuitously metabolized, has been exploited in attempts to remediate materials contaminated with the chlorinated aliphatic solvents. Cometabolism of the chlorinated compounds is effected by broad-specificity mono- and dioxygenases in bacteria which grow on certain hydrocarbons [75–79]. The ammonia monooxygenase of the autotroph *Nitrosomonas europea* is thought to oxidize many chlorinated compounds as well [80]. Trichloroethylene (TCE) also is cometabolized aerobically by heterotrophic enrichment cultures from subsurface material contaminated with the solvent; TCE biodegradation occurs after growth has ceased in cultures amended with methanol, methane, propane, and tryptone-yeast extract as energy sources [81]. Cometabolism of the chlorinated aliphatic solvents in the field has been attempted by stimulating the growth of indigenous methanotrophs with methane and oxygen [31]. The methanotrophs contain a broad-specificity enzyme, methane monooxygenase, which oxidizes the chlorinated compounds [75,76].

The addition of microorganisms to the subsurface during bioremedial processes would be advantageous in situations where contaminant-degrading organisms are absent. Although microorganisms have been added during subsurface bioremediation operations, their contribution to contaminant removal has not been differentiated from that of the indigenous microflora [82]. For added microorganisms to be effective in degradation, they must be transported through the subsurface to the zone of contamination, colonize and grow in the subsurface matrix, compete with the indigenous microflora for nutrients, and maintain their ability to degrade the contaminants. Properties of the subsurface matrix and the organism will affect its transport. Matrix properties which favor transport include large grain size and related high values of hydraulic conductivity and the presence of cracks or fissures which allow channeling [83–87]. Organismal properties which may affect transport include the size, shape, motility, condition, and stickiness of the cells [84,87–89]. In addition, microbial transport may be enhanced when the cells are injected in a low ionic strength solution to reduce adsorption [87,90]. It has been demonstrated in the field that microorganisms can be transported through aquifers [91,92], however, not for the purpose of contaminant degradation.

Another innovative approach to subsurface bioremediation is the exploitation of bioemulsifier and biosurfactant production to enhance removal of contaminants sorbed and/or entrained in the subsurface matrix. Although the dissolved phase of the contaminants is the most easily treated, the sorbed and entrained phases often represent the majority of the contamination and are extremely difficult to remediate. Biosurfactants and emulsifiers could be exogenously supplied or produced in situ or organisms producing these compounds could be transported to the zone of contamination to enhance contaminant extractability and bioavailablity. The presence of these types of organisms in the subsurface has been reported. A survey of samples of biostimulated (nutrient and oxygen addition), contaminated and uncontaminated subsurface material from a site contaminated with aviation fuel indicated that bioemulsifiers were present in all samples; however, the biostimulated zone contained the best emulsifiers, the contaminated zone contained the greatest diversity of emulsifiers, while the uncontaminated zone contained the poorest emulsifiers [93].

Summary

Research investigating the microbial ecology of the subsurface has indicated that microorganisms exist unequivocally at depths of 500 to 600 m below the surface. Although bacteria are the predominant forms of microorganisms present, protozoa, algae, and fungi also have been detected. The subsurface microflora is able to metabolize a variety of naturally-occurring and industrial chemicals; however, biodegradation of many organic compounds may be site and even microsite specific. The availability of dissolved oxygen has been found to be the major factor limiting biodegradation in the subsurface. Subsurface bioremediation usually involves transporting oxygen and nutrients to the indigenous microflora in the zone of contamination. Most subsurface bioremediation operations have involved the treatment of hydrocarbons. Innovative approaches to subsurface bioremediation include the use of alternate electron acceptors, cometabolism to aerobically degrade the chlorinated aliphatic solvents, transport of contaminant-degrading organisms in the subsurface and stimulation of biosurfactant production by the subsurface microflora. A better understanding of the microbial ecology of the subsurface may provide better answers and solutions to ground water contamination problems.

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Column studies on BTEX biodegradation under microaerophilic and denitrifying conditions*

S.R. Hutchins[a], S.W. Moolenaar[b] and D.E. Rhodes[b]

[a]*United States Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, OK 74820 (USA)*
[b]*Rice University, Department of Environmental Science and Engineering, P.O. Box 1892, Houston, TX 77251 (USA)*

Abstract

Two column tests were conducted using aquifer material to simulate the nitrate field demonstration project carried out earlier at Traverse City, Michigan. The objectives were to better define the effect nitrate addition had on biodegradation of benzene, toluene, ethylbenzene, xylenes, and trimethylbenzenes (BTEX) in the field study, and to determine whether BTEX removal can be enhanced by supplying a limited amount of oxygen as a supplemental electron acceptor. Columns were operated using limited oxygen, limited oxygen plus nitrate, and nitrate alone. In the first column study, benzene was generally recalcitrant compared to the alkylbenzenes (TEX), although some removal did occur. The average benzene breakthroughs were 74.3 ± 5.8%, 75.9 ± 12.1%, and 63.1 ± 9.6% in the columns with limited oxygen, limited oxygen plus nitrate, and nitrate alone, respectively, whereas the corresponding average effluent TEX breakthroughs were 22.9 ± 2.3%, 2.9 ± 1.1%, and 4.3 ± 3.3%. In the second column study, nitrate was deleted from the feed to the column originally receiving nitrate alone and added to the feed of the column originally receiving limited oxygen alone. Benzene breakthrough was similar for each column. Breakthrough of TEX decreased by an order of magnitude once nitrate was added to the microaerophilic column, whereas TEX breakthrough increased by 50-fold once nitrate was removed from the denitrifying column. Although the requirement for nitrate for optimum TEX removal was clearly demonstrated in these columns, there were significant contributions by biotic and abiotic processes other than denitrification which could not be quantified.

Introduction

Leaking underground storage tanks are a major source of ground water contamination by petroleum hydrocarbons. There are approximately two million

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Correspondence to: S.R. Hutchins, United States Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, OK 74820 (USA). Fax: (405) 332-8256.

underground tanks storing gasoline in the U.S., and there have been 90,000 confirmed releases reported in the last two years [1]. Gasoline and other fuels contain benzene, toluene, ethylbenzene, and xylenes (collectively known as BTEX) which are hazardous compounds regulated by the U.S. Environmental Protection Agency [2]. Aerobic biorestoration, in conjunction with free product recovery, has been shown to be effective for many fuel spills [3,4]. However, success is often limited by the inabilityto provide sufficient oxygen to the contaminated zones due to the low water solubility of oxygen [5,6].

Nitrate can also serve as an electron acceptor and results in anaerobic biodegradation of organic compounds via the processes of nitrate reduction and denitrification [7]. Because nitrate is less expensive and more soluble than oxygen, it may be more economical to restore fuel-contaminated aquifers using nitrate rather than oxygen. Several investigators have observed biodegradation of aromatic fuel hydrocarbons under denitrifying conditions [8–11]. However, these processes are not well understood at field scale where several other processes, including aerobic biodegradation, can proceed concomitantly. Although several field studies have demonstrated partial success in BTEX removal under denitrifying conditions [12–14], the complexity of the field sites and the limited monitoring data have precluded a thorough evaluation of the process.

Background

The use of nitrate to promote biological removal of fuel aromatic hydrocarbons was investigated for a JP-4 jet fuel spill at Traverse City, Michigan, through a field demonstration project in cooperation with the U.S. Coast Guard. Laboratory tests had indicated that denitrification would be a suitable alternative for biorestoration of the aquifer, although benzene was not degraded [11]. The field work showed that BTEX was degraded under denitrifying conditions in conjunction with low oxygen (microaerophilic) levels [14]. However, a suitable control site was not available to test the effects of treatment without nitrate addition. Therefore, the relative contribution of nitrate to BTEX biodegradation in the field study required further clarification. In addition, although benzene was recalcitrant under strictly denitrifying conditions in the laboratory study, degradation occurred at the field site prior to nitrate addition.

The purpose of this research was to compare BTEX biodegradation by aquifer microorganisms using different electron acceptors and to investigate whether any advantages can be expected under a mixed oxygen/nitrate system. This might prove advantageous in that the demand for oxygen can be supplemented rather than replaced by alternate electron acceptors. This concept, first advanced by Britton [15], was found to hold true for phenol biodegradation by a mixed culture obtained from activated sludge, a contaminated landfill, and ground water. Theoretically, enough oxygen could be provided to allow the initial oxidation of compounds such as benzene by mono- or dioxygenases, which could then yield oxidized intermediates more susceptible to anaerobic biodegradation using nitrate.

Materials and methods

Five columns, 1.5 m × 10 cm I.D., were constructed of beaded process Pyrex glass with Teflon-lined seals and packed under aerobic conditions at room temperature. Columns were packed with fresh aquifer material representing both the contaminated and the uncontaminated zones from the JP-4 site at Traverse City, outside of the zone of influence from the pilot demonstration project on nitrate bioremediation. Both the site and field project have been described elsewhere [14]. Uncontaminated material was obtained from depths of 4.9 to 9.1 m below land surface in an area not impacted by the fuel spill. The water table was at 4.6 m below land surface. The contaminated material was obtained at several locations outside of the demonstration project area at depths from 4.0 to 4.6 m below land surface. The average JP-4 content of the contaminated aquifer material was 3750 ± 1600 mg/kg (mean ± standard error), based on the analytical technique of Vandegrift and Kampbell [16].

The columns were designed to be operated in an up-flow condition. Packing material consisted of glass wool followed by 2.5 cm of porcelain berl saddles at the bottom of the columns. A series of three screens (#40 mesh, #80 mesh, #40 mesh) were placed on top of the column packing followed by 2.5 cm of clean aquifer material. This was followed by 7.6 cm of contaminated aquifer material to simulate the contaminated region in the field demonstration project (Fig. 1). The aquifer material was wet-packed by systematically distributing and mixing 2.5-cm depth aliquots (approximately 200 g) with the lower layers using a 5-cm steel blade attached to a rod. The remainder of each column

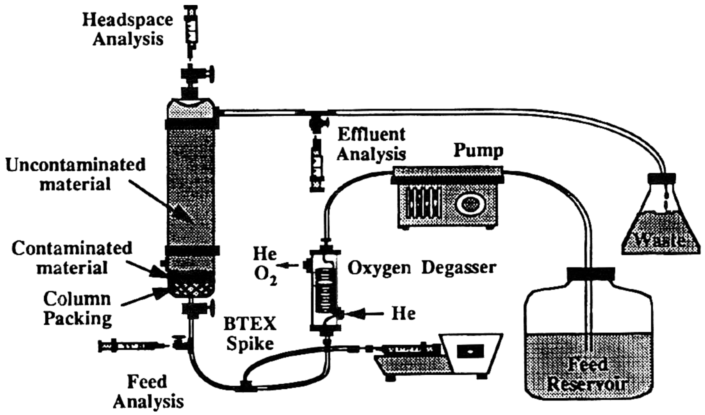

Fig. 1. Column design schematic.

received 1.4 m uncontaminated aquifer material. The column packing, in combination with a flow rate of 0.5 mL/min, was designed to represent the entire treatment zone of the field site on a residence-time basis. That is, the contaminated interval should have had a residence time of 8 h and the entire column should have had a residence time of approximately one week.

The basic feed solution for the columns consisted of a mixture of groundwater obtained from a local artesian well (Byrd's Mill Spring) mixed 1:1 with deionized water to yield a groundwater whose chemistry approximated that found in Traverse City. The feed solution was delivered to each column using a peristaltic pump with Tygon tubing. Because this could allow gas transfer and sorb organics, degassing and BTEX addition was conducted down-gradient. Degassing was accomplished by passing a gas stream into a chamber containing a gas-permeable feed solution flow line (Fig. 1). The chamber was constructed of a plexiglass column (30 cm×5 cm I.D.) with rubber stoppers and contained either 1 or 2 solution lines, each 7.6 m in length, of 2.4 mm O.D.×0.8 mm ID silicone tubing. All tubing was stainless steel beyond this point to prevent gas transfer and sorption of organics. Sample tees containing stainless steel Luer-Lok valves were placed in-line at several points for BTEX addition and sample collection. The solution BTEX spike was continuously added using a syringe pump to deliver a controlled rate of flow. The column effluent end-piece was also modified to allow removal of accumulated gases during operation (Fig. 1).

Columns were operated as illustrated in Fig. 2. Each column was designed to represent a unique treatment scheme, or appropriate control, without rep-

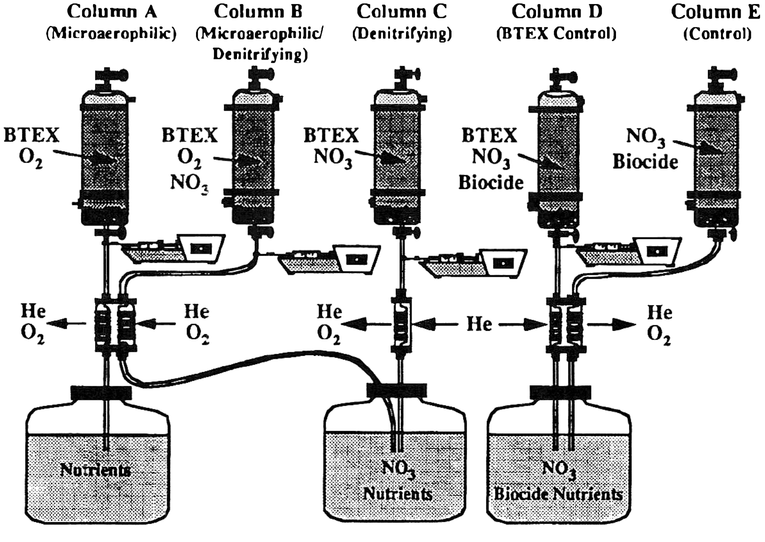

Fig. 2. Column designation and system operation.

licates. The column designations and initial operating parameters were as follows: (a) Column A (microaerophilic), receiving BTEX and low oxygen levels without nitrate addition; (b) Column B (microaerophilic/denitrifying), receiving BTEX and low oxygen levels with nitrate addition; (c) Column C (denitrifying), receiving BTEX and nitrate alone, with the solution flow diverted through a separate degasser to eliminate oxygen; (d) Column D (control), receiving BTEX and nitrate in an analogous manner as the previous column, but with biocide added to the feed reservoir to inhibit microbial activity; and (e) Column E (BTEX control), similar to the previous control column except that no BTEX was added. This last columnwas designed to assess the degree of BTEX removal which occurred through leaching only.

Operation of the columns began initially without nutrient, nitrate, or biocide addition. Feed solution of 50% Byrd's Mill Spring water (50% BMW) was prepared without filtering or autoclaving, and amended with sodium bromide to provide a tracer concentration of 50 mg/L bromide. The feed solution flow rate was 0.50 mL/min. For Columns A and B, the degassers were purged with a mixed gas stream containing 21 mL/min helium and 3.4 mL/min air. The remaining column degassers were purged with helium only at 43 mL/min. Solution BTEX spikes were prepared aseptically in an anaerobic glovebox by injecting the compounds directly through Teflon Mininert valves into 160-ml serum bottles containing sterile distilled water, without headspace, and stir bars. The spikes were mixed overnight, combined, and dispensed into each of four 100-mL glass syringes. The syringes were then removed from the glovebox and loaded onto the syringe pumps, and the flowrate was set at 0.005 mL/min. Following breakthrough of the bromide tracer, bromide addition to the feed reservoirs ceased and nutrients, nitrate, and biocides were added to the appropriate feed reservoirs as shown in Fig. 2. Stock solutions were prepared and autoclaved prior to use, and the final feed concentrations were 5 mg/L ammonia-nitrogen as NH_4Cl and 2 mg/L phosphate-phosphorus as KH_2PO_4 for the nutrients, 10 mg/L nitrate-nitrogen as KNO_3 for the nitrate, and 100 mg/L $HgCl_2$ for the biocide. Feed solutions were replaced once weekly and flow rates and effluent volumes were recorded each week.

The column influents and effluents were sampled 1 to 2 times per week, except during the tracer study when sampling was more frequent. For the tracer study, 2-mL samples were obtained and analyzed for bromide using ion chromatography with a 590 pump (Waters Associates) and conductivity detector (Dionex). The mobile phase consisted of 0.75 m*M* $NaHCO_3$ and 2.2 m*M* Na_2CO_3 at a flow rate of 1.6 mL/min through an HPIC AS4A column (Dionex). The quantitation limit was 0.1 mg/L Br. Samples for BTEX, nitrate, nitrite, ammonia, phosphate, sulfate, pH, and alkalinity were obtained without headspace using glass 50-ml syringes. The volatile aromatic hydrocarbons were analyzed by purge-and-trap gas chromatography using a Tekmar LSC-2000 liquid sample concentrator and an HP5890 GC with a flame ionization detector. Hydrocarbons were purged onto a Tenax trap for 6 min at 34°C followed by a 2 min dry purge and desorbed for 4 min at 180°C. For the first column test, samples were chromatographed using a 30 m×0.32 mm megabore DB-5 capillary column with a 1.0 μm film thickness. The injector temperature was 120°C, and the oven temperature was programmed from 32°C (4-min hold) to 110°C (1-min hold) at 8°C/min with a flow rate of 5 ml/min. This method did not result in separation of all three xylene isomers, and the column was replaced with a 30 m×0.53 mm ID megabore DB-wax capillary column with a 1.0 μm film thickness for the second column test. The new temperature program was from 50°C (4-min hold) to 120°C at 8°C/min, and then to 180°C (4-min hold) at 30°C/min. The quantitation limit for these compounds was 0.2 μg/L. The remaining sample was analyzed for the other parameters using standard EPA methods [17].

Samples for dissolved gases were obtained using plastic 10-mL or 60-mL syringes which had been stored for one week in the anaerobic glovebox. For the dissolved gases, including oxygen initially, 9 mL were injected under water into evacuated 12-mL headspace vials which had been sealed with butyl rubber stoppers and pressurized and evacuated three times with helium. The vials were then shaken at room temperature for 20 min to equilibrate, and headspace samples were analyzed on an HP 5890 GC with a thermal conductivity detector. The injector and detector temperatures were both set at 120°C, and the samples were chromatographed on a CTR I 2-m concentric column set with 3.2-mm O.D. inner column packed with a Poropak mix and a 6.4-mm O.D. outer column packed with activated Molecular Sieve (Alltech Associates) with helium carrier gas at 29 mL/min. The quantitation limits were 0.005% (v/v), 0.02%, 0.02%, 0.07%, and 0.5% for carbon dioxide, nitrous oxide, methane, oxygen, and nitrogen, respectively. In addition, headspace samples were analyzed for trace nitrous oxide using a Varian 6000 GC with electron capture detector. The injector and detector temperatures were 120°C and 300°C, respectively. Samples were chromatographed at 35°C on a 2 m×3.2 mm O.D. stainless steel column containing 100/120 mesh Poropak Q using a mixed carrier gas stream of 95% argon/5% methane at 30 mL/min. The quantitation limit for nitrous oxide was 0.23 ppm (vol/vol) using this method. Aqueous dissolved gas concentrations were calculated for the original solutions using Henry's constants and correcting for total mass in the gas and liquid phases. For the second column test, the analytical procedure for dissolved oxygen was changed to a modified Winkler titration due to problems of inconsistent air contamination of the syringe needle prior to injection of the headspace gas sample into the GC. The standard Winkler titration method [17] was modified for 55-mL volumes and the reagents were prepared in the anaerobic glovebox. Samples were obtained using 60-mL plastic syringes and reagents were withdrawn directly into the samples and mixed in the glovebox. The fixed samples were then titrated outside the glovebox using 0.0075 *N* $Na_2S_2O_3$ with starch indicator.

Results and discussion

Because of the large number of parameters which were continually monitored, a complete evaluation of all of the column data is beyond the scope of this discussion. Rather, this report focuses on (1) the controlling parameters (electron acceptors), (2) benzene, and 3) the alkylbenzenes, considered as a single group. Data on individual compounds, nutrients, pH and dissolved gases are published elsewhere [18].

Column Test I

The first column test was run for 100 days. Initial operation of the five columns commenced using no nutrients or biocides to simulate the initial flooding period required to establish the water table mound in the Traverse City field project. The columns were operated in this manner for approximately 40 days to deplete internal oxygen reserves. Figure 3 shows the bromide tracer data for the first 30 days of operation, and indicates that the average column residence time is six days, with some variability among the columns. On Day 38, nutrient and biocide addition were initiated for the appropriate columns. During the following weeks it became evident that the mercuric chloride biocide was not being properly distributed throughout the control Columns D and E, thereby allowing microbial growth and subsequent BTEX biodegradation. Attempts to mobilize the biocide were not successful, and hence these columns cannot be considered as appropriate controls. The following discussion therefore focuses on Columns A, B, and C.

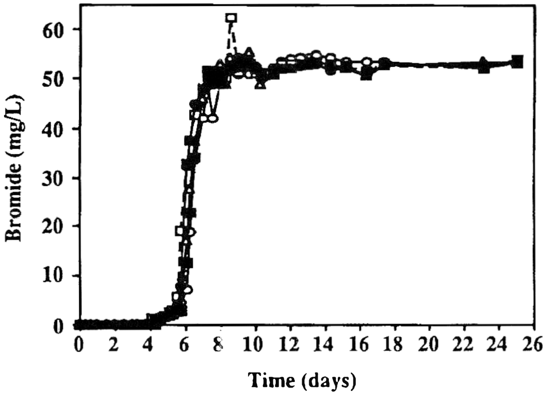

Fig. 3. Breakthrough of bromide tracer in column effluents A (○), B (□), C (△), D (●), and E (■).

To avoid a layering effect, the columns had been packed in an unsaturated mode and then flooded, leading to the formation of numerous gas pockets. It was thought that, because of these pockets, it would be difficult to induce anaerobic conditions in the columns. However, as shown in Fig. 4, effluent dissolved oxygen profiles dropped to 1 mg/L oxygen in about 20 days. This is identical to what was observed in the field study [14]. However, unlike the field study, dissolved oxygen continued to drop to 0.2 to 0.4 mg/L in the column effluents, even though influent oxygen concentrations were maintained at 0.8 to 1.0 mg/L in Columns A and B (Fig. 4). Hence, there was a significant oxygen demand (approximately 0.5 mg/L) in Columns A and B during the study. After Day 63, influent oxygen levels in these two columns appeared to drop, but this was found to be an artifact caused by the column design. The proper levels of oxygen were being supplied by the degassers, but growth of microorganisms in the inlet lines subsequent to BTEX addition resulted in oxygen consumption prior to samples being obtained through the influent monitoring ports. This problem was corrected for Column Test II.

Nitrate and nutrient addition began on Day 38. Nitrate removal was observed in Columns B and C, with losses ranging from 2 to 7 mg/L nitrate-nitrogen once nitrate began to break through in the column effluents (Fig. 5). Effluent nitrate concentrations began to stabilize at Day 60 and were not significantly different, despite the fact that Column B was also receiving approximately 1.0 mg/L dissolved oxygen as an additional electron acceptor. From Day 45 to Day 98, the average nitrate-nitrogen loss was 4.1 ± 0.4 mg/L and 3.6 ± 0.3 mg/L in Columns B and C, respectively. As was also observed in the field study, there was a transient production of nitrite in Columns B and C effluents, with concentrations dropping and stabilizing at 0.6 to 0.8 mg/L nitrite-nitrogen by the end of the test (Fig. 6). Only very low concentrations of

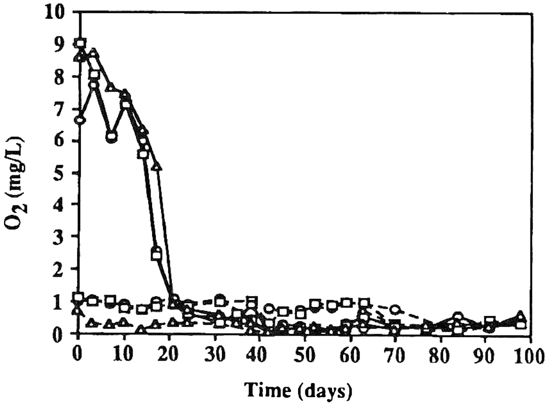

Fig. 4. Dissolved oxygen profiles in Columns A (○, microaerophilic), B (□, microaerophilic/denitrifying), and C (△, denitrifying) during Column Test I. The effluent values are fairly constant in time. (---) Influent, and (—) effluent values.

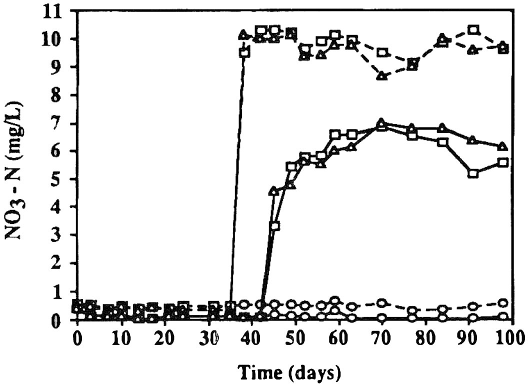

Fig. 5. Nitrate-nitrogen profiles in Columns A (○, microaerophilic), B (□, microaerophilic/denitrifying), and C (△, denitrifying) during Column Test I. (- - -) Influent, and (—) effluent values.

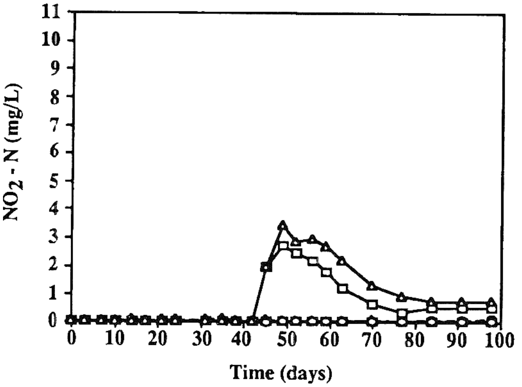

Fig. 6. Nitrite-nitrogen profiles in Columns A (○, microaerophilic), B (□, microaerophilic/denitrifying), and C (△, denitrifying) during Column Test I. (---) Influent, and (—) effluent values.

nitrous oxide were produced, and appearance of this intermediate was transient as well (data not shown). The columns did not appear to be nutrient-limited. Complete breakthrough of ammonia-nitrogen occurred on Day 56 for Columns B and C and on Day 63 for Column A, although some phosphate limitation may have occurred since phosphate did not begin to break through in the column effluents until Day 91 of the test (data not shown).

For several reasons, it was difficult to maintain consistent influent BTEX concentrations during the column tests. These problems were never fully corrected, but the effects were mitigated to the point that conclusions could be made regarding BTEX removal in the separate columns. The majority of this discussion focuses on benzene, the compound of primary interest. The other alkylbenzenes, generally labile under denitrifying conditions, are discussed as a single group consisting of the summation of toluene, ethylbenzene, *m*-, *p*-, and *o*-xylene, and 1,2,4-trimethylbenzene concentrations (TEX). Compared to the alkylbenzenes, benzene was generally recalcitrant during treatment in the separate columns, although some removal did occur (Fig. 7). Lacking a proper control column, it was not possible to determine whether this removal was biological in nature. Despite the variability in influent benzene concentrations, however, it was possible to compare the extent of benzene breakthrough among the three columns by considering the average percent breakthroughs from Day 45 to Day 98; this represents the time period that nitrate and nutrients were available to the columns. In addition, data from Column E, the control column which did not receive BTEX spike, showed that the total leached BTEX concentration from the contaminated zone of this column was generally less than 10 μg/L after Day 42 (data not shown). Hence, BTEX breakthrough from Day 45 to Day 98 would not represent contributions from leach-

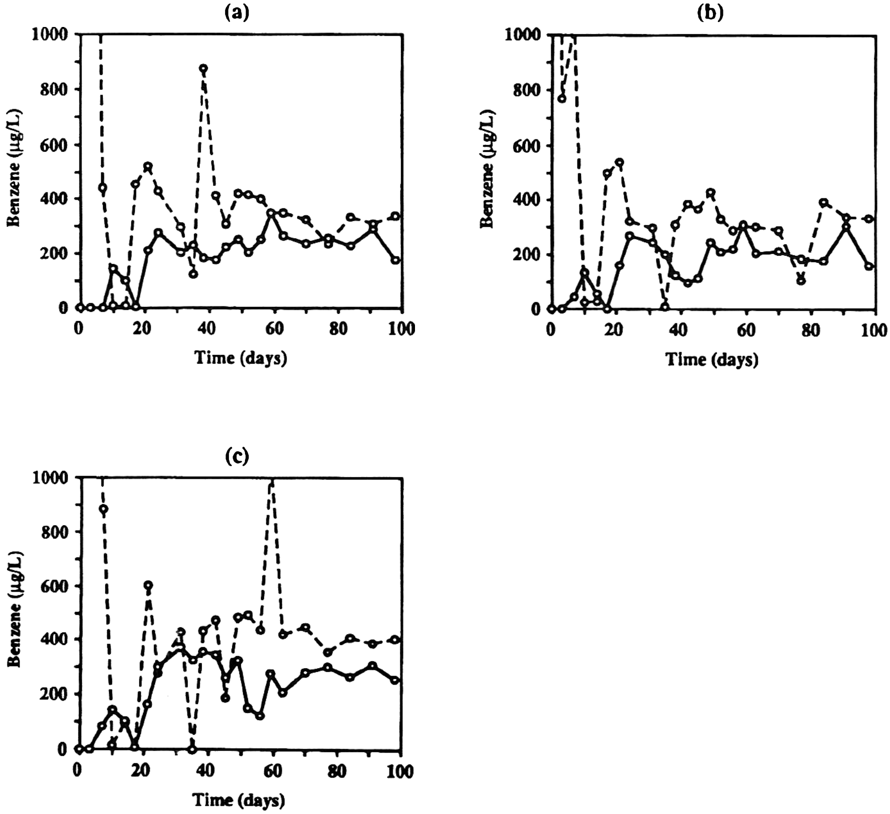

Fig. 7. Influent and effluent benzene concentrations in (a) Columns A (microaerophilic), (b) B (microaerophilic/denitrifying), and (c) C (denitrifying) during Column Test I. (- - -) Influent, and (—) effluent values.

ing of background BTEX from the previously contaminated interval. Based upon this analysis, the average benzene breakthroughs (effluent concentration/influent concentration, expressed as percent) were 74.3±5.8%, 75.9±12.1%, and 63.1±9.6% in Columns A, B, and C, respectively. This indicates that there was little benefit in using nitrate with limited oxygen on benzene removal, compared to either limited oxygen or nitrate alone. Although this does not agree with results from a previous batch microcosm test [19], it may more realistically approximate field conditions.

In contrast to benzene, the alkylbenzenes (TEX) were removed more extensively in each column (Fig. 8). Again, without an appropriate control, it was not possible to determine to what extent this removal was due to biodegradation. This did, however, correlate well with batch microcosm data [11]. After nutrient addition on Day 38, effluent TEX concentrations in each column declined, although the rate of decline was more significant in Columns B and C,

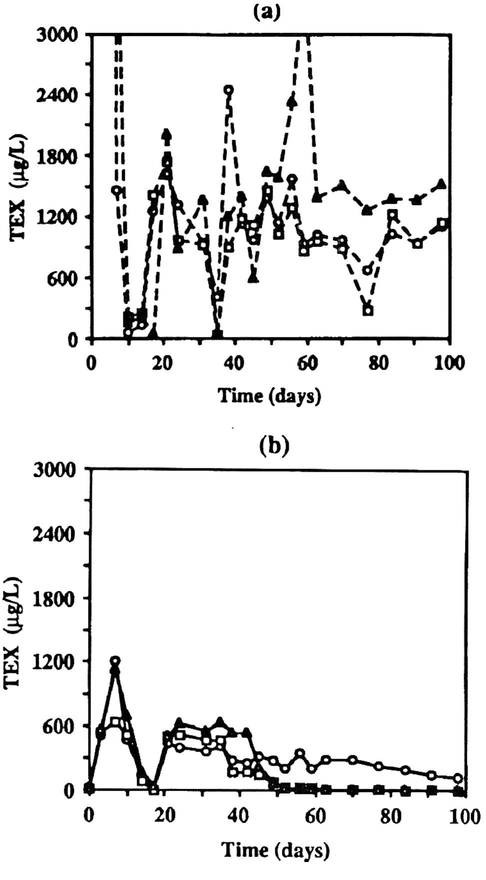

Fig. 8. (a) Influent and (b) effluent TEX concentrations in Columns A (□, microaerophilic), B (○, microaerophilic/denitrifying), and C (△, denitrifying) during Column Test I.

which received nitrate as well as nutrients (Fig. 8). It is of interest to note that effluent dissolved carbon dioxide concentrations, which generally exceeded influent concentrations, exhibited a transient sharp increase in Columns B and C subsequent to the observed rapid decline in effluent TEX concentrations in the respective columns (Fig. 9). This may be due to an increase in mineralization of the utilized labile compounds, but it is not clear why the levels continued to drop to below those of the Column A effluent after the initial peak. The cause of the continued decline in effluent TEX concentrations in the microaerophilic Column A is also unclear. No other exogenous electron acceptors were added, and methane was not detected in the column effluent at any time. In addition, there was little sulfate removal from the influent (data not shown). The aquifer solids could conceivably contain exchangeable iron, manganese, and other potential electron acceptors which might augment the role of nitrate and oxygen, but this possibility could not be assessed with the current test design. From Day 45 to Day 98, the average effluent TEX breakthroughs were 22.9±2.3%, 2.9±1.1%, and 4.3±3.3% in Columns A, B, and C, respectively. As observed in a previous batch microcosm study [19], these alkylbenzenes were degraded equally well with or without limited oxygen under denitrifying conditions, and final effluent concentrations were generally less than 10 μg/L for total TEX.

An approximation of total mass of hydrocarbon removed and electron acceptor consumed can be made by calculating the average difference between influent and effluent concentrations for any given column, and then multiplying by the total effluent volume collected during that period. This was done for the time during which nitrate was available to the columns. From Day 45 to Day 98, the total effluent volume was 38.8±0.1 L for Columns A, B, and C.

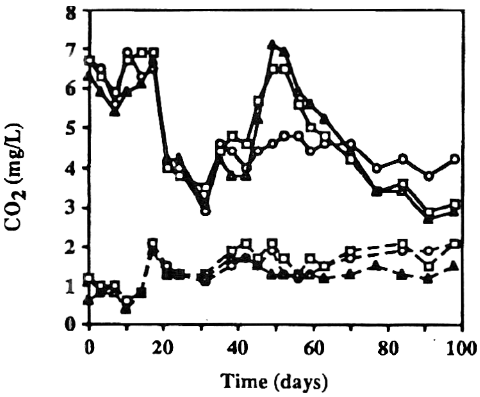

Fig. 9. Influent (---) and effluent (—) dissolved carbon dioxide concentrations in Columns A (O, microaerophilic), B (□, microaerophilic/denitrifying), and C (△, denitrifying) during Column Test I.

The following theoretical stoichiometric relationships were then used to calculate how much of the observed hydrocarbon removal could be attributed to mineralization under either aerobic or denitrifying conditions:

$$C_{61}H_{67}+62.2H^{+}+62.2NO_3^{-}\rightarrow 61CO_2+31.1N_2+64.6H_20$$

$$C_{61}H_{67}+155.5NO_3^{-}\rightarrow 61CO_2+155.5NO_2^{-}+33.5H_20$$

$$C_{61}H_{67}+75.75O_2\rightarrow 61CO_2+33.5H_20$$

This assumed that the nitrate which did not account for nitrite production was completely denitrified. In the column study, no significant nitrous oxide accumulation was observed (data not shown). It was also assumed that the nitrogen requirement for cell biomass was satisfied by the ammonium supplement, and that the hydrocarbons were completely mineralized to carbon dioxide and water. These data are summarized in Table 1, and indicate that the actual BTEX removal was approximately twice that of the theoretical removal for Column A, whereas it was only 35% and 80% of the total theoretical removal in Columns B and C, respectively. For the latter two columns, it is quite possible that additional hydrocarbons present in the contaminated interval exerted a significant electron acceptor demand for nitrate; this was also observed in the field study, but to a much greater extent [14]. Although the higher nitrate consumption observed in Column B is consistent with the hypothesis that preliminary oxidation of the hydrocarbons under microaerophilic conditions could lead to increased utilization of nitrate, the data are not sufficient to formulate definitive conclusions. In addition, the loss of BTEX in Column A, in excess of the electron acceptor supplied, indicates that other electron acceptors may have been present and/or other removal processes were operative. Without an appropriate control column, it was not possible to determine the extent to which abiotic processes contributed to BTEX removal.

TABLE 1

Mass balance for BTEX removal and electron acceptor consumption from Day 45 to Day 98 of Column Test I

Parameter	Units	Column A (Microaerophilic)	Column B (Microaerophilic/ Denitrifying)	Column C (Denitrifying)
Oxygen removed	mg	15.5 ± 3.9	15.5 ± 3.9	0.0 ± 3.9
Nitrate-Nitrogen removed	mg	15.5 ± 0.0	155 ± 16	140 ± 12
Nitrite-Nitrogen added	mg	0.0 ± 0.0	50.4 ± 11.6	69.8 ± 11.6
Theoretical BTEX demand	mg	19.4	120	89.6
BTEX removed	mg	36.0 ± 3.3	42.3 ± 4.4	70.8 ± 11.7

Column Test II

The second column test ran from Day 170 to Day 270. Initially, the only test parameters that were changed from Column Test I were that the column operating temperature was raised from 12°C to 20°C, influent oxygen levels to Columns A and B were increased to 1.5 mg/L, and the mercuric chloride biocide was replaced with 0.01 N NaOH for the control columns. However, the 50% BMW used for the stock feed to Columns A, B, and C was replaced with deionized water during the test to eliminate microbial growth in feed lines and reservoirs. On Day 216, nitrate was deleted from the feed for Column C so that this column now had no added electron acceptor. In addition, nitrate was added to the feed for Column A so that the operating parameters were now identical for Columns A and B.

Oxygen removals were similar throughout Column Test II for Columns A and B with an average loss of 1.0±0.1 mg/L dissolved oxygen. There was no net consumption of oxygen in either of the other columns. Removal of nitrate was more complex. Initially, effluent nitrate values were much higher for Column B than the other columns; once the 50% BMW feed was replaced with deionized water on Day 184, nitrate levels began to rise in the effluents of both Columns B and C (Fig. 10). The reason for this is not clear, since the decrease in background total organic carbon available for denitrification (about 0.3 mg/L) would be insufficient to account for this on a mass basis. Nitrate was removed from the Column C feed solution on Day 216, and its effluent nitrate levels dropped to below detection soon thereafter (Fig. 10). Similarly, nitrate was added to the Column A feed solution at the same time, and its effluent nitrate levels increased to those observed for Column B. From Days 231 to 268,

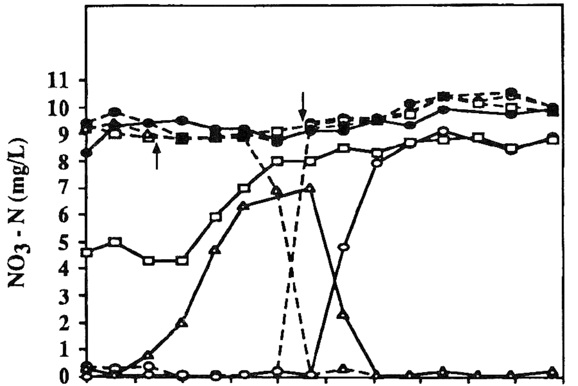

Fig. 10. Influent (---) and effluent (—) nitrate-nitrogen profiles in Columns A (○, microaerophilic), B (□, microaerophilic/denitrifying), C (△, denitrifying), and D (●, control) during Column Test II. The arrows indicate, respectively, the switch to distilled water in the feed and the simultaneous removal of nitrate from feed C and nitrate addition to feed A.

the average nitrate-nitrogen removal was 1.6 ± 0.4 mg/L and 1.3 ± 0.2 mg/L for Columns A and B, respectively. In terms of nitrate removal, therefore, these columns were operating similarly with little or no acclimation period observed for Column A. Unlike the first test, Column D appeared to be an adequate control with respect to denitrification in the second column test (Fig. 10). The average loss of nitrate was only 0.2 ± 0.1 mg/L nitrate-nitrogen in this column. Nitrite levels continued to remain below 0.5 mg/L nitrite-nitrogen in the column effluents, except for a transient production of nitrite in Column C following the switch to deionized water in the feed (Fig. 11). This was accompanied by a transient production in nitrous oxide which peaked at 0.8 mg/L. There was no production of nitrite or nitrous oxide observed in Column D.

Even with the changes incorporated into the operating procedure, there continued to be problems in maintaining consistent BTEX inputs to the columns (Fig. 12). Column E received no BTEX input, and benzene concentrations were typically below 1 μg/L in its effluent; similarly, the total concentrations of the other alkylbenzenes (TEX) were consistently less than 5 μg/L (data not shown). Hence, operation of Column E will not be considered in this discussion. Addition of nitrate to the feed for Column A on Day 216 appeared to have little effect on benzene removal (Fig. 12a), as was expected from the Column B results during Column Test I. Surprisingly, benzene concentrations in the effluent of Column C appeared to decrease once nitrate was removed from the column feed (Fig. 12c), but this decline did not continue. A similar decline was observed for Column D (Fig. 12d), indicating that the drop may have been an artifact, since nitrate was still available in the control column influent. In addition, both of these columns were serviced by the same syringe pump used to deliver BTEX to the column influents and thus failure of the pump may have been responsible. However, a corresponding drop was not ob-

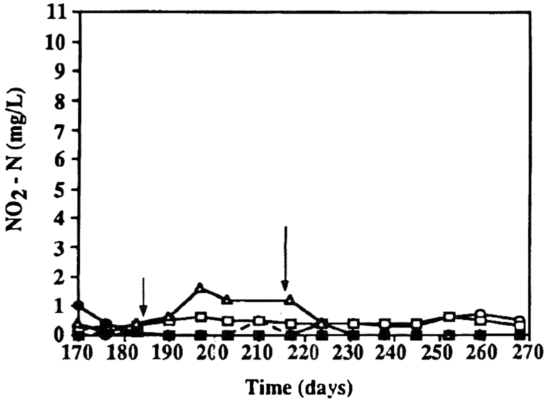

Fig. 11. Nitrite-nitrogen profiles in Columns A (○, microaerophilic), B (□, microaerophilic/denitrifying), C (△, denitrifying), and D (●, control) effluents during Column Test II. Arrows as in Fig. 10.

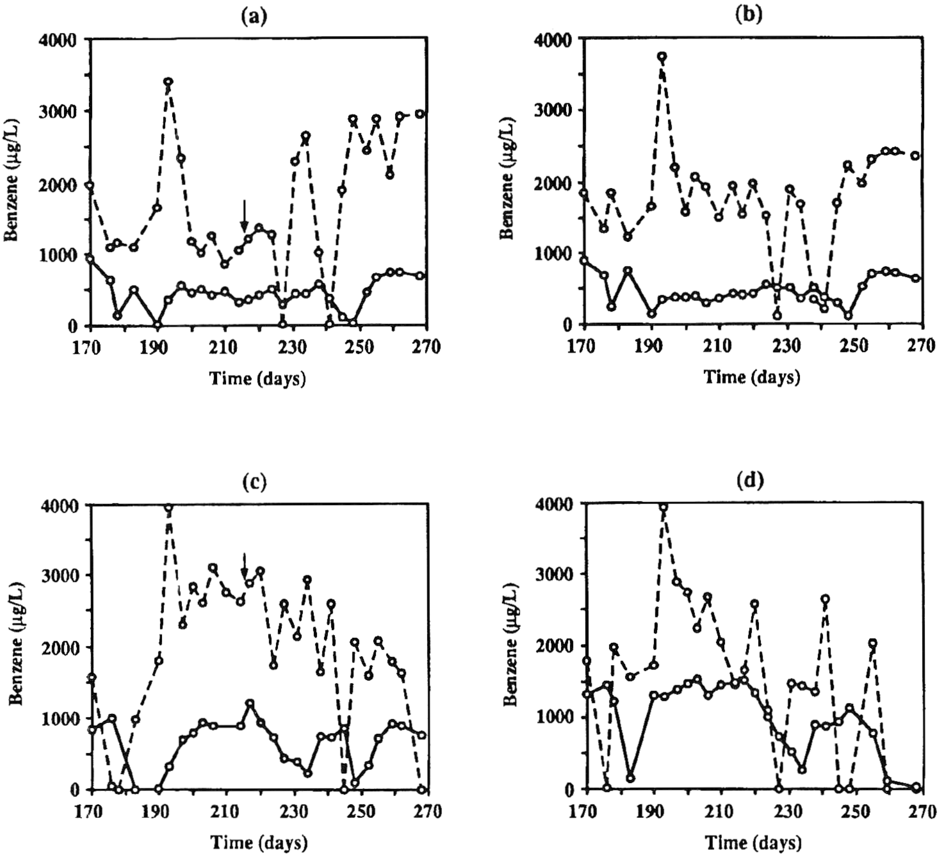

Fig. 12. Influent (- - -) and effluent (—) benzene concentrations in (a) Column A (microaerophilic), (b) B (microaerophilic/denitrifying), (c) C (denitrifying), and (d) D (control) during Column Test II. The arrows in (a) and (c) denote, respectively, the addition and removal of nitrate in the feed.

served in effluent TEX concentrations for Column C (Fig. 13), as would be expected based on syringe pump failure. The reason for this decline is therefore not clear. As shown in Fig. 13, TEX concentrations gradually increased in Column C following nitrate removal from the feed, and decreased in Column A following addition of nitrate to the feed.

Despite the fluctuating BTEX levels in the column influents, an analysis of the effects of the operating parameters on BTEX removal was possible by calculating average percent breakthroughs of the various components during selected time intervals (Table 2). Average percent breakthroughs were considered during the entire test period for Columns B and D, since electron acceptor levels were not changed in the feed solutions. For columns A and C, two time periods were considered, corresponding to the initial part of the test prior to

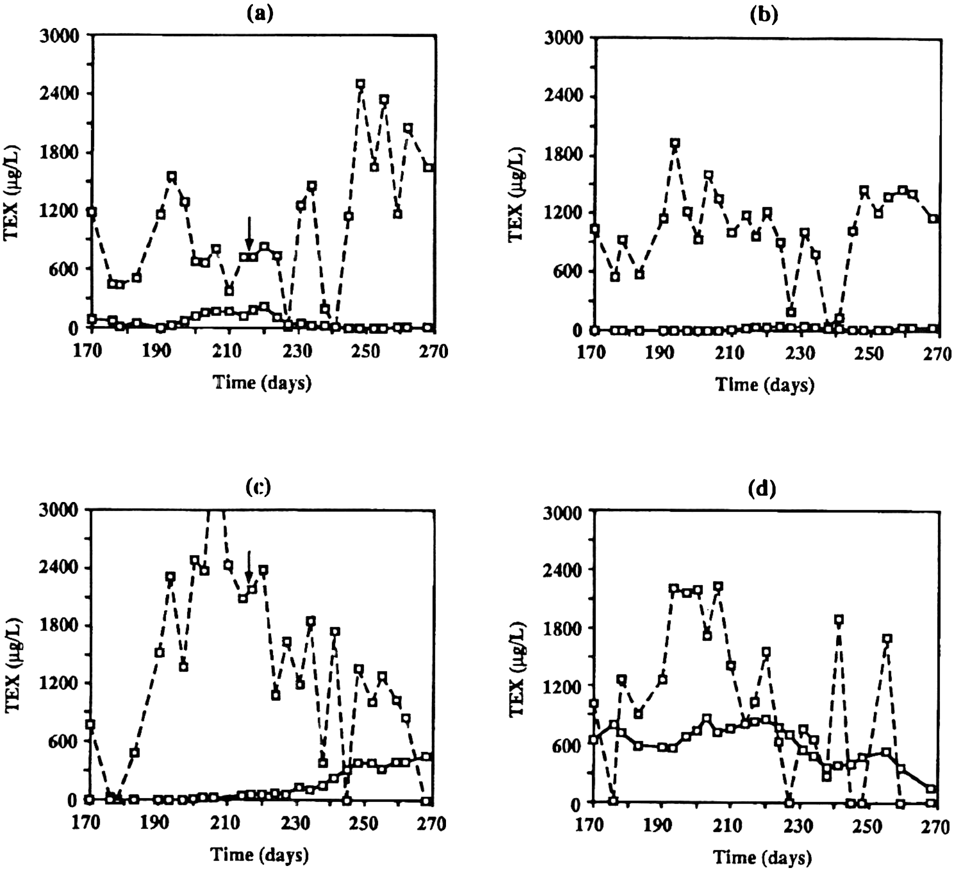

Fig. 13. Influent (- - -) and effluent (—) TEX concentrations in (a) Column A (microaerophilic), (b) B (microaerophilic/denitrifying), (c) D (denitrifying), and (d) D (control) during Column Test II. Arrows as in Fig. 12.

switching the feed solutions (Days 169 to 210), and to the time of nitrate breakthrough in the Column A effluent after switching the feed solutions (Days 231 to 262). Table 2 shows that benzene breakthrough was similar for Columns A, B, and C during each time period, with the exception of a slight decrease in Column A following nitrate addition. While this decrease is in agreement with the results of the previous batch microcosm data using limited oxygen plus nitrate [19], it is not statistically significant given the variability in influent benzene concentrations during the test. At least part of the removal of benzene in the first three columns may have been due to biological processes, since breakthrough in the control column was approximately twice that of the others (Table 2). The requirement for nitrate as an electron acceptor became more apparent with the labile alkylbenzenes (TEX). Breakthrough of TEX decreased by an order of magnitude once nitrate was added to the microaerophilic

TABLE 2

Breakthrough of benzene and TEX during selected time intervals of Column Test II

Compound breakthrough	Time period (days)	Column A (Microaerophilic)[a]	Column B (Microaerophilic/ Denitrifying)	Column C (Denitrifying)[a]	Column D (Control)
Benzene	169-210	29 ± 5%	-	31 ± 7%	-
Benzene	231-262	21 ± 4%	-	32 ± 5%	-
Benzene	169-262	-	26 ± 2%	-	65 ± 6%
TEX	169-210	11 ± 2%	-	0.5 ± 0.2%	-
TEX	231-262	1.1 ± 0.3%	-	26 ± 3%	-
TEX	169-262	-	1.7 ± 0.3%	-	59 ± 3%

[a] Initial conditions. Nitrate added to Column A feed and removed from Column C feed on day 216.

column A, whereas TEX breakthrough increased by 50-fold once nitrate was removed from the denitrifying Column C (Table 2). Even so, TEX breakthrough was still twice that in the control column, indicating that other biotic processes may have been operative. Although nitrate and nitrite concentrations dropped rapidly in the Column C effluent once the feed amendment was stopped, TEX concentrations rose much more gradually (Fig. 13c). Therefore, although the requirement for nitrate for optimum TEX removal was clearly demonstrated in these columns, there were significant contributions by biotic and abiotic processes other than denitrification which could not be quantified using the given experimental design.

Conclusions

These studies have shown that alkylbenzenes can be degraded under denitrifying conditions, even when a limited amount of oxygen is present. There is some evidence that the addition of a limited amount of oxygen can facilitate benzene removal under denitrifying conditions, but the controlling parameters have not been defined. However, there were no adverse effects observed with the use of oxygen in addition to nitrate in the column studies, indicating that a mixed oxygen/nitrate system could be used for biorestoration of fuel-contaminated aquifers. The column data show that nitrate is required for optimal BTEX removal, although some removal does occur without nitrate addition. The nature of these processes could not be determined with the given column design, but appeared to be biotic for at least a portion of the removal. If these results are extrapolated to the field, they show that nitrate addition had a significant effect on BTEX removal in the field demonstration project at Traverse City.

Acknowledgements

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Limiting factors in ground water remediation*

Clinton W. Hall[a] and Jeffrey A. Johnson[b]

[a]*Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA)*
[b]*Dynamark Corporation, Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA)*

Abstract

If one is charged with restoring a contaminated aquifer today, the procedure of pumping contaminated water to the surface for treatment and discharge is most often the state-of-practice technology. The perceived success of pump-and-treat technology can be misleading if the hydrology and contaminant characteristics at the site are not adequately understood. A failure to understand the processes controlling contaminant transport can result in extremely long pumping periods and, consequently, costly and inefficient remediation. Effects of tailing, sorption, and residual immiscible fluids on time required for pump-and-treat remediation of ground water are discussed.

Introduction

The remediation of ground water contamination is one of the most challenging problems that faces the environmental field today. In the past ground water contamination was resolved by simply leaving the problem in place and moving water supply wells to a new location. Today, the use of ground water resources as well as the number of potential contaminant sources coupled with the contemporary environmental ethic has made this approach unacceptable.

Ground water is one of our most important resources. Everyday in the United States the ground water resource is utilized by over 50% of the population and approximately 220 million gallons (0.84 km^3) of ground water are extracted for use. Furthermore, ground water development is increasing; on the average over 40 new wells are drilled every hour to produce additional supplies. Clearly, ground water is a resource that should be properly managed and understood.

Although the supply of clean water is abundant, it is under constant assault by both past and present land use and waste disposal practices. The Congressional Office of Technology Assessment (OTA) has identified over three dozen categories of ground water contamination. Of these industrial landfills, surface

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Correspondence to: C.W. Hall, Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA). Fax: (405) 332-8800.

impoundments, septic tanks and cesspools, disposal wells, fertilizers, oil and gas wells and underground storage tanks pose the greatest threats. More specifically, there are over 1,400 hazardous waste disposal sites covered under the Resource Conservation and Recovery Act (RCRA), and according to the General Accounting Office over 70% may be leaking [1]. In addition, the U.S. Environmental Protection Agency (EPA) has documented over 180,000 surface impoundments – pits, ponds, and lagoons – for waste disposal. More than 98% of these are located within one mile of a drinking water well or potential drinking water source [2]. One of the most prevalent threats to clean ground water is leaking underground storage tanks. The EPA estimates that over 75,000 tanks are annually releasing 11 million gallons of gasoline to the subsurface. Furthermore, over 1,000 locations have been placed on the National Priorities List of hazardous waste sites by the EPA, and it is estimated that this number could potentially rise to 30,000 [3].

The most widely used approach for remediation of ground water contamination is the extraction of the contaminated water followed by treatment at the surface. This method is commonly referred to as pump-and-treat remediation. An ideal pump-and-treat remediation project would involve the installation of extraction wells at defined locations, the pumping of these wells to contain and remove the contaminant plume, treating the extracted water at the surface via carbon adsorption or other means, and then discharging the clean water at the surface or recharging it back to the subsurface. Although successful pump-and-treat projects have occurred, for the most part, pump-and-treat is not the simple solution once envisioned. Specifically, the complexities of the subsurface environment coupled with the diverse nature of the contaminants make the extraction of the contaminants difficult and costly.

Transport effects

The interaction of the processes affecting the transport of contaminants significantly influences the effectiveness and efficiency of pump-and-treat technology. In particular, these processes hinder the removal of contaminants from the subsurface. The resultant effect is the slow, gradual decrease in contaminant levels as water is pumped from an aquifer. This effect is termed tailing. Tailing acts to prolong the expected time of extraction, increase the volume of water necessary for treatment, and, thus, increase the cost of remediation [4].

Numerous mechanisms control the movement of contaminants through porous media. The transport processes associated with even the simplest forms of contamination, conservative, non-reactive dissolved constituents, involve advection, dispersion, and molecular diffusion. Advection is the primary process of contaminant transport and is the movement of the contaminant in the ground water flow system. Dispersion involves the movement of contaminants via fluid mixing that results from heterogeneities within the pore spaces of the aquifer. In general, dispersion acts to attenuate the contaminant concentration while increasing the size and rate of transport of the contaminant plume (Fig. 1). Diffusion is the slow movement of ions or molecules in response to concentration gradients. Because molecular diffusion is time dependent, its effect on the overall transport is more significant at low velocities. As a result, diffusion is an important process in finer grained aquifer materials and can significantly affect pump-and-treat remediation.

Thus, the migration of dissolved contaminants through aquifers is controlled to a great degree by the permeability of aquifer material. In homogeneous strata of high to moderate hydraulic conductivity, such as in sand and gravel aquifers, advection is the predominant process of transport while in

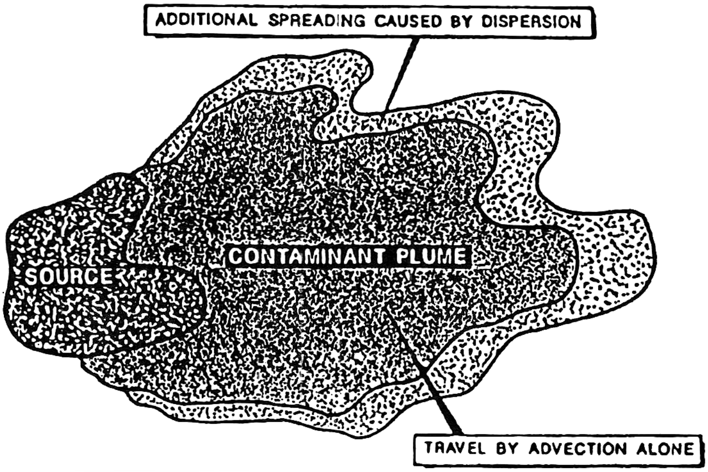

Fig. 1. Plan view of contaminant migration by advection and dispersion.

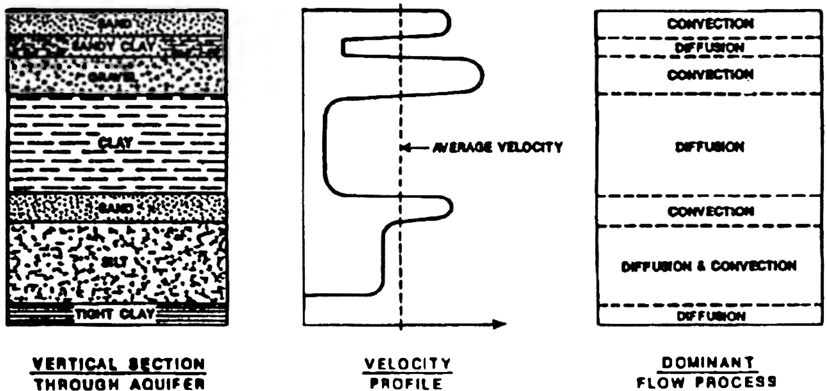

Fig. 2. Effects of geologic heterogeneity on contaminant transport.

heterogeneous strata of low hydraulic conductivity contaminants migrate slowly, primarily by diffusion (Fig. 2). Over time, greater volumes of the contaminants migrate into areas of low permeability — those zones containing the smallest pores. As a result, when pumping is initiated to extract the contaminants, the fluids in the aquifer are not uniformly mobilized. Fluids in the larger, open pores move more readily while the fluids in the smaller, closed pores are retained. In short, pumping creates preferential movement of the contaminants in the larger pores. Given time, the contaminants present in the finer pores eventually migrate by diffusion to the larger open pores. However, this preferential migration resulting from heterogeneities in hydraulic conductivity increases the time required to extract all the contaminants, and thus, creates a tailing effect.

Chemical effects

Additional complexities develop when the contaminants react with the aquifer materials via sorption and/or chemical and biochemical reactions. Sorption is the transfer of contaminants between ground water and mineral and organic surfaces. Several processes act to remove contaminants from the ground water to the solid phase: adsorption, the attraction of a contaminant to the solid surface; absorption, the incorporation of the contaminant into the interior of the solid; and ion exchange, adsorption with a charge-for-charge replacement of the ionic species in solution with ionic species in the solid. The overall effect of sorption is to retard the migration of the contaminant plume. Although this behavior reduces the size of the plume, it increases the difficulty in extracting the contaminant from the aquifer. Most of the sorption reactions processes are completely or partially reversible; as a result, contaminants are not permanently removed from the aquifer by sorption, rather these constituents are simply stored in the solid phase. Desorption adds contaminants to the fluid phase from the solid phase by reversing the reactions.

As water is pumped from the aquifer during pump-and-treat remediation, the dissolved portion is removed and replaced by clean water drawn in from outside the contaminate plume. This situation alters the previously existing equilibrium, and the contaminant continues to partition from the solid phase to the aqueous phase to establish an equilibrium. As a result, the contaminant levels will initially decrease upon migration of the clean water into the aquifer but will eventually increase as a new equilibrium condition develops. Hence, an aquifer may have to be flushed several times to successfully redissolve all the contaminant from the solid surfaces. Furthermore, if the velocities developed by the pumping are too rapid to allow contaminant levels to establish equilibrium conditions, the affected water may be removed before allowing maximum contaminant dissolution. This results in a low contaminant removal efficiency, increased pumping time, and larger volumes of water requiring treatment.

Sorption and desorption are complex processes and are a function of the type of contaminant, the composition of the solid, the chemistry of the aqueous phase and the distribution of contaminant between the solid and fluid phases. Petroleum hydrocarbons, chlorinated solvents, and PCBs are examples of common contaminants that have a high affinity to sorb. Likewise, clay minerals, because of their large surface areas that carry an overall negative charge, are aquifer materials that have a strong tendency to sorb chemicals from the fluid phase. The pH of the ground water can also influence sorption reactions. Since sorption reactions are reversible, the distribution of the contaminant between the fluid phase and solid is important; this distribution is described by the linear partition coefficient, K_d. The parameter K_d is the ratio of the mass concentration in the aqueous phase to the mass concentration sorbed on the solid phase.

$$K_d = C_s/C_a \tag{1}$$

where C_a denotes the mass concentration in the aqueous phase, and C_s is the mass concentration sorbed in the solid phase. A large K_d value indicates strong sorption while a small K_d value indicates the constituent is retained with the aqueous phase.

By determining the linear partition coefficient, it is possible to define the retardation, R, of the contaminant resulting from sorption.

$$R = 1 + (K_d P_s / (P_a \times \epsilon) \tag{2}$$

where P_s is the soil bulk density, P_a the density of water, and ϵ the porosity.

More importantly in the design of pump-and-treat systems is the velocity of the contaminant (V_c), which can be described as the ratio of the water velocity to the retardation factor.

$$V_c = V_w/R \tag{3}$$

Hence, an estimate of the time required to extract a contaminant can be determined. The following example is a simple scenario illustrating the time required to extract a contaminant from an aquifer [5]. Given a relatively homogeneous, uniform sand aquifer with a thickness of 55 feet (17.5 m) and having a porosity of 30%, assume approximately 10 acres (4 ha) of the aquifer are contaminated by chloride from a salt storage area. The volume of contaminated ground water is approximately 55 million gallons or 210 000 m^3 (10 acres × 43560 ft^2/acre × 55 feet × 0.3 void space per acre × 7.5 gal/ft^3 = 53,905,500 gal). Under these ideal conditions, it would be possible to exchange the water in the ten-acre plume in about a year by pumping at a rate of 100 gallons per minute (365 days/y × 24 h/day × 60 min/h × 103 gal/min = 54,136,800 gallons). Assuming that the extraction well is at the center of a radial plume, the velocity of the ground water from the periphery of the plume to the well is about 370 feet per year or approximately 1 foot per day.

However, assuming that sorption is an active process, a more realistic condition, the time required to extract the contaminant increases. For example, given the conditions previously described with a linear partition coefficient of 0.5, a soil bulk density of 100 lb/ft^3, and a ground water density of 62.4 lb/ft^3, then the contaminant velocity would be approximately 75 percent slower than the water velocity ($V_c = 372$ ft/y/1+0.5(100 lb/ft^3/(62.4 lb/ft$^3\times$0.3)) $V_c =$ 101 ft/y).

This slower velocity could prolong the pumping time to over three years. It is evident from this illustration that sorption and heterogeneities in the aquifer material can pose significant difficulties in pump-and-treat technology.

NAPL Effects

The existence of non-aqueous phase liquid (NAPL) contaminants present additional difficulties in pump-and-treat remediation. These water-immiscible phases are of two general forms: lighter-than-water non-aqueous phase liquids, termed L-NAPLs, such as gasoline and oil; and denser-than-water non-aqueous phase liquids, termed D-NAPLs, such as halogenated solvents and creosote/coal tars. L-NAPLs float on the ground-water table and are generally contained within the capillary fringe. In contrast, D-NAPLs sink downward through the aquifer and can migrate independently of the ground water direction. Pump-and-treat remediation is relatively successful in extracting floating product. Current methods can remove over 90% of the floating L-NAPL source [6]. The extraction of D-NAPLs has not been effective simply because these contaminants are rarely located within the aquifer. As a result, the D-NAPL contaminant source remains slowly dissolving in the aquifer for time periods ranging from decades to hundreds of years.

When dealing with NAPLs, remediation is further complicated by their affinity for sorption to aquifer materials. This creates a major problem as even after the product is removed surface tension forces retain this fluid phase. As a result, after the removal of the free product by pumping an L-NAPL can occupy up to 50% of the soil pore space — primarily in the finer pores [7] (Fig. 3). This trapped immiscible fluid is termed the residual saturation or residual phase and cannot be removed in any substantial quantity by pumping.

When the residual phase is a contaminant such as gasoline, its benzene, toluene, and xylene components can partition into the passing ground water. The rate of transfer and the concentration within the aqueous phase depends on the contaminant characteristics and the location of the residual phase with respect to the flowing water. In the case of gasoline and other complex fluids, the rate of contaminant transfer into water will change as the gasoline ages, or

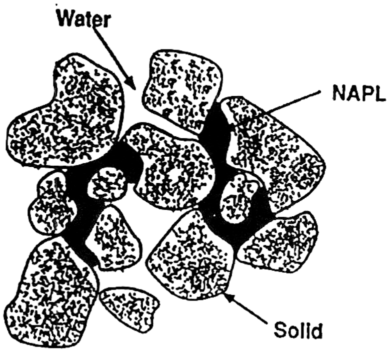

Fig. 3. Residual saturation within aquifer voids.

as its composition changes. Thus, the residual phase may act as a source for future contamination.

It is this relatively slow rate of contaminant transfer which is deceiving when attempting to remove contaminants using increasingly higher pumping rates. The concentration may initially appear to be reduced or even eliminated due to dilution as large amounts of uncontaminated water enter this area of the aquifer, or by lowering the water table below the source of contamination, or both. In any event, when pumping ceases, the residual phase water soluble components will again dissolve into the ground water, and the contaminant concentration will return to the previous level. To place this in perspective, assuming similar contaminant conditions as the previous scenario and only a 10% residual saturation of toluene, it would take about 1,500 years' pumping at 100 gallons per minute to reduce the initial amount of toluene by 80% if no other processes of transformation were active.

Summary

Although pump-and-treat is not the quick fix once envisioned, it is still a viable remediation method. In particular, it is useful when the contaminants are mobile, and the aquifer is homogeneous and has a high hydraulic conductivity. Conversely, pump-and-treat is not extremely useful under the opposite conditions — when the contaminants are NAPLs, have a high sorption affinity, and when the aquifer is heterogeneous and has a low hydraulic conductivity (Fig. 4).

The design of pump-and-treat remediation systems is improving to increase the effectiveness of the technology. For example, pulsed pumping may improve the efficiency of this technology by allowing contaminants located in low permeability zones to diffuse outward into areas of higher hydraulic conductivity during nonpumping times. Likewise, this non-pumping time allows sorbed contaminants and residual NAPLs to reequilibrate with the ground water.

Favorable Conditions	**Unfavorable Conditions**
SOURCE TERM	
Source Removed	NAPLs at Residual Saturation
CHEMICAL PROPERTIES	
Mobile chemicals	Chemicals sorbed or precipitated
HYDROGEOLOGY	
High hydraulic conductivity (e.g., $K > 10^{-6}$cm/s)	Very low hydraulic conductivity (e.g., $K < 10^{-7}$cm/s
Homogeneous	Highly heterogeneous

Fig. 4. Conditions favorable and unfavorable to pump-and-treat remediation.

Hence, during the subsequent pumping cycle the minimum volume of contaminated ground water is removed at a maximum contaminant concentration. In addition, low permeable barriers can be constructed along the periphery of the plume to minimize the movement of the contaminants, to reduce the volume of fresh water being contaminated by remediation, and to ultimately lower the volume of water requiring treatment.

Continuing research in the complexities of subsurface transport and transformation of contaminants will further increase the effectiveness and efficiency of pump-and-treat remediation. However, since the understanding of subsurface processes is currently fragmented and not complete, it is important to appreciate the conditions in which a remediation method, such as pump-and-treat, is effective so that successful remediation can be achieved at minimal cost.

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Ground water contaminant modeling for bioremediation: A review*

P.B. Bedient and H.S. Rifai

Department of Environmental Science and Engineering, Rice University, P.O. Box 1892, Houston, TX 77251 (USA)

Abstract

This paper presents an overview of biodegradation as a remediation technology for contaminated ground water. A discussion of design issues for the remediation process and a review of models applied to biodegradation in groundwater are included. Following a description of BIOPLUME II numerical degradation model, the authors discuss its application to field studies of an aviation fuel spill in Traverse City, Michigan.

Introduction

One of the remediation methods that has been gaining more widespread attention recently is bioremediation, the treatment of subsurface pollutants by stimulating the native microbial population. The technology is not novel, the biodegradation potential of organic contaminants has been recognized and utilized in the wastewater treatment process for years. The biodegradation process is simply a biochemical reaction which is mediated by microorganisms where an organic compound is oxidized (loses hydrogen electrons) by an electron acceptor which itself is reduced (gains hydrogen electrons). Several electron acceptors have been identified to date: oxygen, nitrate, sulfate, or carbon dioxide. The utilization of oxygen as an electron acceptor is termed aerobic biodegradation and that of nitrate is called anaerobic biodegradation. An example of the simple aerobic biodegradation reaction for benzene is given by:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \qquad (1)$$

The ultimate goal of the biodegradation process is to convert organic wastes into biomass and CO_2, CH_4, and inorganic salts. Two essential criteria must

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Correspondence to: Dr. P.B. Bedient, Department of Environmental Science and Engineering, Rice University, P.O. Box 1892, Houston, TX 77251 (USA).

be in place before biodegradation or biorestoration can occur. First, the subsurface geology must have a relatively large hydraulic conductivity to allow the transport of oxygen and nutrients through the aquifer. Secondly, microorganisms must be present in sufficient numbers and types to degrade the contaminants of interest. Because of the heterogeneous nature of the subsurface, hydraulic conductivity should be evaluated at multiple locations on a site. Formations with K-values greater than 10^{-4} cm/s or greater are most amenable to *in situ* biorestoration.

Laboratory and field pilot studies of biodegradation are needed to ensure the successful implementation of the bioremediation technology at the field scale. There are several questions that need to be answered in these experiments: is a given organic compound biodegradable and under what conditions? What numbers and types of microorganisms are required for degradation? Would the microorganisms respond to stimulation if growth-limiting nutrients are added? and at what rates would a given organic chemical degrade under natural or enhanced conditions?

In ground water, the problem of determining whether a compound is degradable or not and under what conditions is complicated by several factors. The combination of soil and water imposes a mixed-media analysis approach and the complexity of the physical and chemical processes which control the transport and fate of the organic contaminants provide a challenge for designing indicator parameters for biodegradation in the subsurface. The current state-of-the-art does not offer a concise and uniform methodology for laboratory and field quantitative estimation of biodegradation.

To date, the most aerobically biodegradable compounds in the subsurface have been light petroleum hydrocarbons such as gasoline, crude oil, heating oil, fuel oil, lube oil waste, and mineral oil [1]. Other compounds such as alcohols (isopropanol, methanol, ethanol), ketones (acetone, methyl ethyl ketone) and glycols (ethylene glycol) are also aerobically biodegradable.

Design issues for the bioremediation process

The basic steps involved in an *in situ* biorestoration program [1] are: (1) site investigation, (2) free product recovery, (3) microbial degradation enhancement study, (4) system design, (5) injection and pumping operation, and (6) system maintenance. It is important to define the hydrogeology and the extent of contamination at the site prior to the initiation of any *in situ* effort. The parameters of interest at a field site include the direction and rate of ground water flow, the depths to the water table and to the contaminated zone, the specific yield of the aquifer, and the heterogeneity of the soil. In addition, other parameters such as hydraulic connections between aquifers, potential recharge and discharge zones, and seasonal fluctuations of the water table should be considered. A number of monitoring wells should be installed and slug tests and pump tests should be performed for determining the hydraulic conductivity. Water levels should be measured in the wells to determine a potentiometric map of the site. Secondly monitoring wells should be sampled for presence of hydrocarbon contamination and a plume should be mapped for the site. The pumping rate that can be sustained in the aquifer is an important consideration because it limits the amount of water that can be circulated in the system during the bioremediation process.

After defining the hydrogeology, recovery of free product, if any, at the site should be completed. The pure product can be removed using physical recovery techniques such as a single pump system that produces water and hydrocarbon or a two-pump, two-well system that steepens the hydraulic gradient and recovers the accumulating hydrocarbon. Physical recovery often accounts for 30 to 60% of the hydrocarbon before yields decline [2].

Prior to the initiation of a bioremediation activity, it is important to conduct a feasibility study for the biodegradation of the contaminants present at the site. First, contaminant-degrading microorganisms must be present, and second the response of these native microorganisms to the proposed treatment method must be evaluated. In addition, the feasibility study is conducted to determine the nutrient requirements of the microorganisms. These laboratory studies provide a reliable basis for performance at the field level only if they are performed under conditions that simulate the field.

The chemistry of a field site will affect the types and amounts of nutrients that are required. Limestone and high mineral content soils, for example, will affect nutrient availability by reacting with phosphorous. Silts and clays at sites may induce nutrient sorption on the soil matrix, and hence decrease the amount of nutrients available for growth. In general, a chemical analysis of the ground water provides little information about the nutrient requirements at a field site, it is mostly the soil composition that is of significance.

In situ biorestoration usually requires the addition of an electron receptor such as oxygen. The rate of aerobic biodegradation is usually limited by the amount of oxygen that can be transported to the organisms in the zone of contamination. A number of methods are available to supply oxygen to ground water including the addition of air, pure oxygen, or hydrogen peroxide, with increasing concentrations, respectively. Addition of hydrogen peroxide must be carefully monitored to avoid being toxic to microorganisms at elevated concentrations [3]. Aquifer plugging due to precipitation of inorganic nutrients is a possible side effect.

A system for injection of nutrients into the formation and circulation through the contaminated portion of the aquifer must be designed and constructed [4]. The system usually includes injection and production wells and equipment for the addition and mixing of the nutrient solution [5]. A typical system is shown in Fig. 1. Placement of injection and production wells may be restricted by the presence of physical structures. Wells should be screened to accommodate sea-

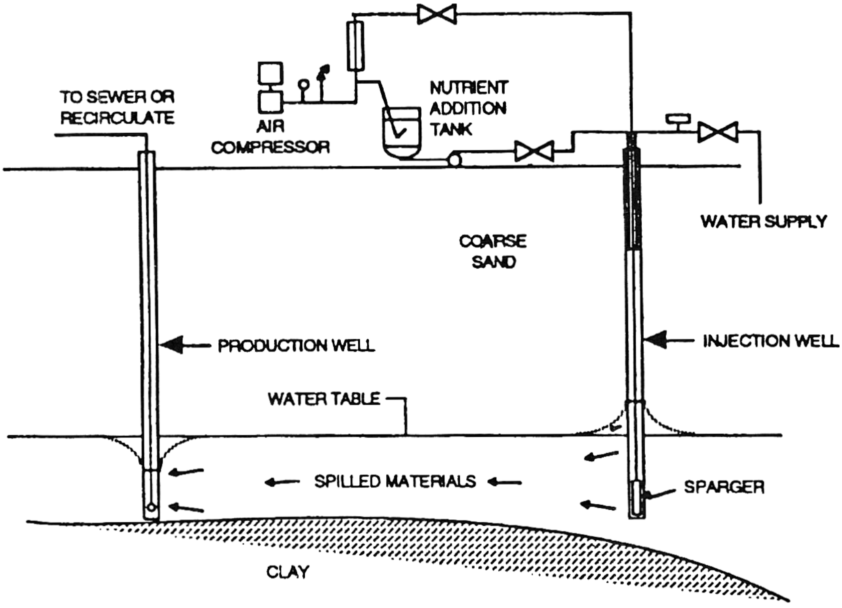


Fig. 1. Typical system.

sonal fluctuations in the level of the water table. Wells are often installed within the contaminant plume to monitor concentrations of hydrocarbon, nutrients, microbes, and other parameters. Monitoring of the process is critical for evaluating its success or failure. Microbial cell counts and contaminant breakthrough curves are indicators of how well the process is performing.

Well installation should be performed under the direction of a hydrogeologist to ensure adequate circulation of the ground water. Produced water can be recycled to recirculate unused nutrients, avoid disposal of potentially contaminated ground water, and avoid the need for make-up water. Inorganic nutrients can be added to the subsurface once the system is constructed. Continuous injection of the nutrient solution is labor intensive but provides a more constant nutrient supply than a discontinuous process. Continuous addition of oxygen is recommended because the oxygen is likely to be a limiting factor in hydrocarbon degradation.

Bioremediation is not without its problems, however. The most important being the lack of well documented field demonstrations that show the effectiveness of the technology and what if any are the long term effects of this treatment on ground water systems. The lack of documented field studies may be attributed in part to the significant commercial potential of the technology which basically means that the information is proprietary. Other problems include the possibility for generating undesirable intermediate compounds during the biodegradation process which are more persistent in the environment than the parent compound.

Enhanced aerobic bioremediation for a petroleum spill is essentially an engineered delivery of nutrients and oxygen to the contaminated zone in an aquifer. Oxygen sources include air, pure oxygen (gaseous and liquid forms), and hydrogen peroxide. Sparging the ground water with air and pure oxygen can supply only 8 to 40 mg/L of oxygen depending on the temperature of the injection fluid [2].

Hydrogen peroxide, which dissociates to form water and half a molecule of oxygen, is infinitely soluble in water [6]; however, hydrogen peroxide can be toxic to microorganisms at concentrations as low as 100 ppm [3]. A stepping-up procedure is usually utilized to allow the microorganisms to adapt to the higher concentrations of the oxidant. Other problems have to do with the stability of hydrogen peroxide. The key to success in using hydrogen peroxide as an oxygen source is to add a relatively large quantity to water and have oxygen released in a controlled manner as it advances through the aquifer. If hydrogen peroxide is destabilized, oxygen will come out of solution as a gas, and the process becomes less efficient [7]. Proprietary techniques have been developed to stabilize hydrogen peroxide.

Review of models applied to biodegradation in ground water

The problem of quantifying biodegradation in the subsurface can be addressed by using models which combine physical, chemical and biological processes. Developing such models is not simple, however, due to the complex nature of microbial kinetics and degradation pathways, the limitations of well monitored sites, the general lack of field data on biodegradation, and the lack of robust numerical schemes that can simulate the physical, chemical, and biological processes simultaneously. Several researchers have developed ground water biodegradation models. The main approaches utilized for modeling biodegradation kinetics have included:

(1) First-Order Decay
(2) Biofilm Models (including kinetic expressions)
(3) Instantaneous Reaction Model
(4) Dual-Substrate Monod Model

McCarty et al. [8] modeled the biodegradation process using biofilm kinetics. They assumed that substrate concentration within the biofilm changes only in the direction which is normal to the surface of the biofilm and that all the required nutrients are in excess except the rate-limiting substrate. The model employs three basic processes: mass transport from the bulk liquid, biodecomposition within the biofilm, and biofilm growth and decay. The authors evaluated the applicability of the biofilm model to aerobic subsurface biodegradation using a laboratory column filled with glass beads. The experimental data and the model predictions were relatively consistent.

Kissel et al. [9] developed differential equations describing mass balances on solutes and mass fractions in a mixed-culture biological film within a completely mixed reactor. The model incorporates external mass transport effects, Monod kinetics with internal determination of limiting electron donor or acceptor, competitive and sequential reactions, and multiple active and inert biological fractions which vary spatially. Results of hypothetical simulations involving competition between heterotrophs deriving energy from an organic solute and autotrophs deriving energy from ammonia and nitrite were presented.

Molz et al. [10] and Widdowson et al. [11] presented one-dimensional and two-dimensional models for aerobic biodegradation of organic contaminants in ground water coupled with advective and dispersive transport. A microcolony approach was utilized in the modeling effort, microcolonies of bacteria are represented as disks of uniform radius and thickness attached to aquifer sediments. A boundary layer of a given thickness was associated with each colony across which substrate and oxygen are transported by diffusion to the colonies.Their results indicated that biodegradation would be expected to have a major effect on contaminant transport when proper conditions for growth exist. Simulations of two-dimensional transport suggested that under aerobic conditions microbial degradation reduces the substrate concentration profile along longitudinal sections of the plume and retards the lateral spread of the plume. Anaerobic conditions developed in the plume center due to microbial consumption and limited oxygen diffusion into the plume interior.

Widdowson et al. [12] also extended their previous work to simulate oxygen and/or nitrate based respiration. Basic assumptions incorporated into the model include a simulated particle-bound microbial population comprised of heterotrophic, facultative bacteria in which metabolism is controlled by lack of either an organic carbon-electron donor source (substrate), electron acceptor (oxygen and or nitrate), or mineral nutrient, or all three simultaneously.

Borden and Bedient [13] developed the first version of the BIOPLUME model. They developed a system of equations to simulate the simultaneous growth, decay, and transport of micro-organisms combined with the transport and removal of hydrocarbons and oxygen. Simulation results indicated that any available oxygen in the region near the hydrocarbon source will be rapidly consumed. In the body of the hydrocarbon plume, oxygen transport will be rate limiting and the consumption of oxygen and hydrocarbon can be approximated as an instantaneous reaction. The major sources of oxygen, the researchers concluded, are transverse mixing, advective fluxes and vertical exchange with the unsaturated zone.

Borden et al. [14] applied the first version of the BIOPLUME model to simulate biodegradation at the Conroe Superfund site in Texas. Oxygen exchange with the unsaturated zone was simulated as a first-order decay in hydrocarbon concentration. The loss of hydrocarbon due to horizontal mixing with oxygenated ground water and resulting biodegradation was simulated by generating oxygen and hydrocarbon distributions independently and then combining by superposition. Simulated oxygen and hydrocarbon concentrations closely matched the observed values.

Srinivasan and Mercer [15] presented a one-dimensional, finite difference model for simulating biodegradation and sorption processes in saturated porous media. The model formulation allows for accommodating a variety of boundary conditions and process theories. Aerobic biodegradation was modeled using a modified Monod function; anaerobic biodegradation is modeled using Michaelis-Menten kinetics. In addition, first-order degradation was allowed for both substances. Sorption was incorporated using linear, Freundlich, or Langmuir equilibrium isotherms for either substance.

MacQuarrie et al. [16] utilized a similar approach to Borden et al. [14] and Rifai et al. [17,18] to develop a biodegradation model. The advection-dispersion equation was coupled with a dual-Monod relationship. The system of equations was solved using an iterative principal direction finite element technique. Comparisons of numerical results with the results of a laboratory column experiment showed that the model equations adequately describe the behavior of toluene, dissolved oxygen, and the microbial population, without considering solute diffusion through stagnant fluid layers or biofilms. The authors conclude that in a two-dimensional shallow aquifer setting, an organic plume experiences mass loss, spreading controlled by the availability of dissolved oxygen, and skewing in the direction of ground water flow.

MacQuarrie and Sudicky [19] utilized the model developed by MacQuarrie et al. [16] to examine plume behavior in uniform and random flow fields. In uniform ground water flow, a plume originating from a high-concentration source will experience more spreading and slower normalized mass loss than a plume from a lower initial concentration source because dissolved oxygen is more quickly depleted. Large ground water velocities produced increases in the rate of organic solute mass loss because of increased mechanical mixing of the organic plume with oxygenated ground water.

Recently, Odencrantz et al. [20] presented a contaminant transport model which allows for different biodegradation kinetics. Monod kinetics and biofilm kinetics are compared in a two-dimensional transport model, where the differential equations are solved using a nonlinear operator splitting. Results indicated that the two models could differ for a large enough biofilm thickness.

Celia et al. [21] presented two papers on developing a numerical biodegradation model designed to handle co-metabolism, multiple substrates, and aerobic and anaerobic metabolism. The model is currently one-dimensional and therefore has limited applications to field sites.

Description of the BIOPLUME II model

Rifai et al. [17,18,22] developed one of the first numerical biodegradation models (BIOPLUME II) by modifying the USGS two-dimensional solute transport model [23]. The basic concept applied in developing BIOPLUME II includes the use of a dual-particle mover procedure to simulate the transport of oxygen and contaminants in the subsurface.

Biodegradation of the contaminants is approximated by the instantaneous reaction model proposed by Borden and Bedient [13]. The ratio of oxygen to contaminants consumed by the reaction is determined from an appropriate stoichiometric model (assuming complete mineralization). In general, the transport equation is solved twice at every time step to calculate the oxygen and contaminant distributions:

$$\frac{\partial(Cb)}{\partial t}=\frac{1}{R_c}\left[\frac{\partial}{\partial x_i}\left(bD_{ij}\frac{\partial C}{\partial x_j}\right)-\frac{\partial}{\partial x_i}(bCV_i)\right]-\frac{C'W}{n} \tag{2}$$

$$\frac{\partial(Ob)}{\partial t}=\left[\frac{\partial}{\partial x_i}\left(bD_{ij}\frac{\partial O}{\partial x_j}\right)-\frac{\partial}{\partial x_i}(bOV_i)\right]-\frac{O'W}{n} \tag{3}$$

where C and O are the concentration of contaminant and oxygen respectively, C' and O' the concentration of contaminant and oxygen in a source or sink fluid, n is the effective porosity, b the saturated thickness, t the time, x_i and x_j the cartesian coordinates, W the volume flux per unit area, V_i the seepage

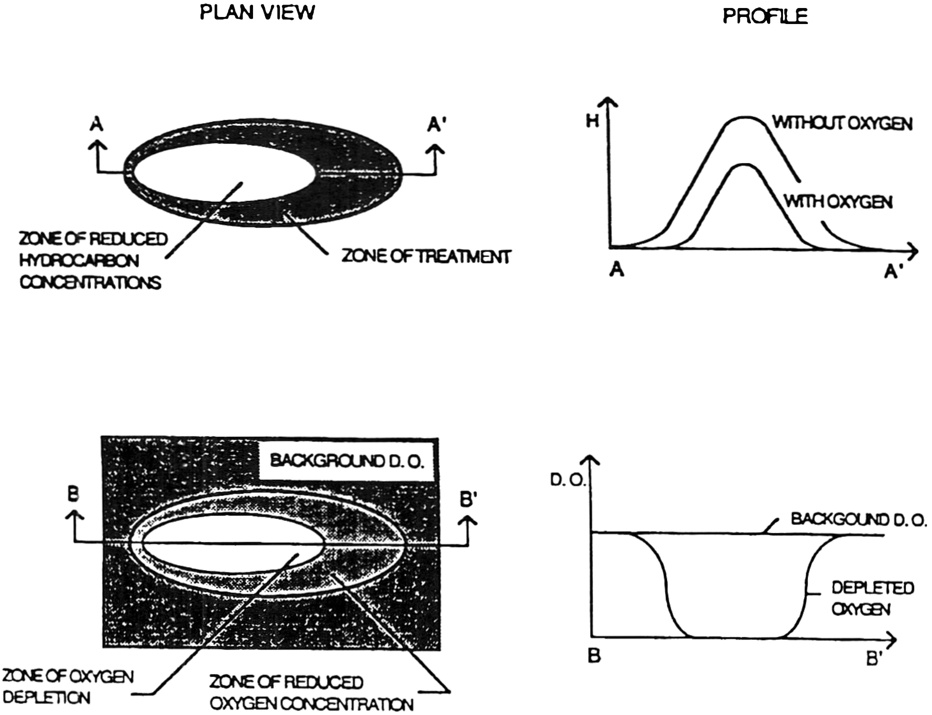


Fig. 2. Principle of superposition for organics and oxygen in BIOPLUME II model.

velocity in the direction of x_i, R_c = retardation factor for contaminant, and D_{ij} the coefficient of hydrodynamic dispersion. It is emphasized that the BIOPLUME II model simulates dissolved contaminant concentrations which are vertically averaged over the thickness of the aquifer.

The two plumes are combined using the principle of superposition (Fig. 2) to simulate the instantaneous reaction between oxygen and the contaminants, and the decrease in contaminant and oxygen concentrations is calculated from:

$$DC_{RC} = O/F; \quad O = 0 \quad \text{where} \quad C > O/F \tag{4}$$

$$DC_{RO} = C \times F; \quad C = 0 \quad \text{where} \quad O > C \times F$$

where DC_{RC}, DC_{RO} are the calculated changes in concentrations of contaminant and oxygen, respectively, due to biodegradation.

The only model input parameters to BIOPLUME II which are required to simulate biodegradation include the amount of dissolved oxygen in the aquifer prior to contamination, and the oxygen demand of the contaminant determined from a stoichiometric relationship.

Examples of recent field studies

In a controlled field experiment at the Canada Forces Base Borden site, two plumes of gasoline contaminated ground water were introduced into the aquifer. Immediately upgradient of one plume, ground water spiked with nitrate was added so that a nitrate plume would overtake the organic plume [24]. The success of the field experiment was limited [25]. The dissolved organic contaminant mass (BTEX) decreased rapidly due to residual oxygen concentrations in the aquifer prior to the nitrate overlap. Organic mass left in the aquifer was not adequate to evaluate anaerobic biotransformation.

Semprini et al. [26] presented the results from a field evaluation of *in situ* biodegradation of trichloroethylene (TCE) and related compounds. The method that was used in the field demonstration relied on the ability of methane-oxidizing bacteria to degrade these contaminants to stable, non-toxic, end products. The field site is located at the Moffett Naval Air Station in Mountain View, California and the test zone is a shallow confined aquifer composed of coarse grained alluvial sediments. Results from the biotransformation experiments at the site indicates that biodegradation of TCE was on the order of 30% of the mass injected.

Semprini and McCarty [27] presented two papers on modeling the in-situ biodegradation of chlorinated aliphatics. Their model solves ordinary differential equations by standard numerical integration, and the model was applied to two sets of field data at the above site.

Major et al. [28] investigated the biodegradation of benzene, toluene and the isomers of xylene (BTX) in anaerobic batch microcosms containing shallow aquifer material. BTX loss occurred with the addition of either nitrate or oxygen. Denitrification was confirmed by nitrous oxide accumulation. When a limiting amount of nitrate was added, there was a corresponding limit to the loss of BTX and a limited amount of nitrous oxide production.

Borden and Bedient [29] conducted a three-well injection-production test at the United Creosoting Company (UCC) site in Conroe, Texas, to evaluate the significance of biotransformation in limiting the transport of polycyclic aromatics present in the shallow aquifer. During the test, chloride, a non-reactive tracer and two organic compounds, naphthalene and paradichlorobenzene (*p*DCB), were injected into a center well for 24 hours followed by clean ground water for six days. Ground water was continuously produced from two adjoining wells and monitored to observe the breakthrough of these compounds. A significant loss of naphthalene and *p*DCB attributed to biotransformation processes was observed during the test.

Rifai et al. [22] studied the naturally occurring biodegradation at an aviation fuel spill in Traverse City, Michigan. Contamination data from approximately 25 wells at the site were utilized to define the dissolved benzene, toluene and xylene plume over a two year period. Rifai et al. [22] calculated a biodegradation rate of 1.0% a day at the Traverse City site (Fig. 3) and indicated that the pump and treat system at the site was removing a very small percentage of the total dissolved mass present at the site. A modeling effort was completed using the BIOPLUME II model. The modeling results along the centerline of the contaminant plume are shown in Fig. 4. In general, the BIOPLUME II model results match the field results except in the area between monitoring

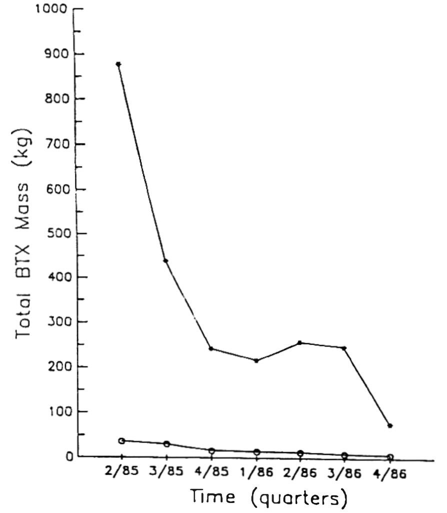


Fig. 3. Variation in total BTX with time at Traverse City.

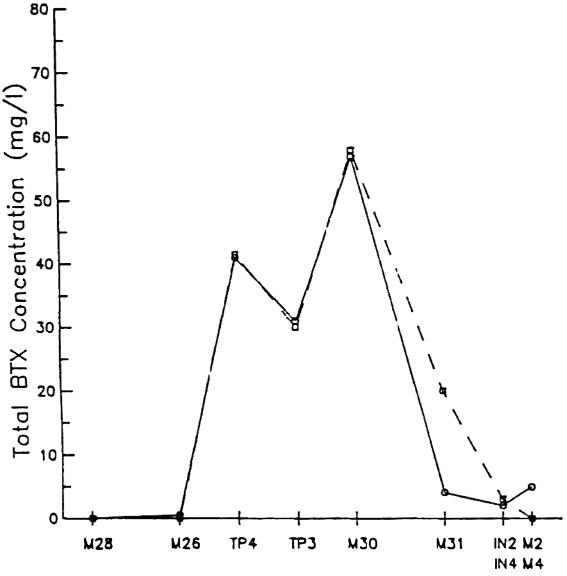


Fig. 4. Calibrated (—) versus observed (-) BTX concentrations at Traverse City.

wells M30 and the pumping wells. The researchers discuss the possibility of anaerobic biodegradation taking place in that zone.

Chiang et al. [30] characterized soluble hydrocarbon and dissolved oxygen in a shallow aquifer beneath a field site by sampling ground water at 42 monitoring wells. Results from 10 sampling periods over three years showed a significant reduction in total benzene mass with time in ground water. The natural attenuation rate was calculated to be 0.95% per day. Spatial relationships between DO and total benzene, toluene, and xylene (BTX) were shown to be strongly correlated by statistical analyses and solute transport modeling.

Modeling natural biodegradation with BIOPLUME II

Modeling studies using the extensive data from field programs at Traverse City, Michigan (TCM) were run to understand and aid in the evaluation of natural biodegradation at the site. Modeling studies at the TCM site were performed to: (1) help understand rates of natural biodegradation, (2) model sensitivity of certain key parameters, (3) determine conditions favorable to use of natural biodegradation as a remedial scheme, and (4) aid in the calibration, formulation and understanding of modeling overall bioremediation at the site.

The Coast Guard Air Station is the site of an aviation fuel spill which occurred somewhere near the Hangar Administration Building in 1969, pictured in Fig. 5. A plume of contamination migrated in the shallow drinking water

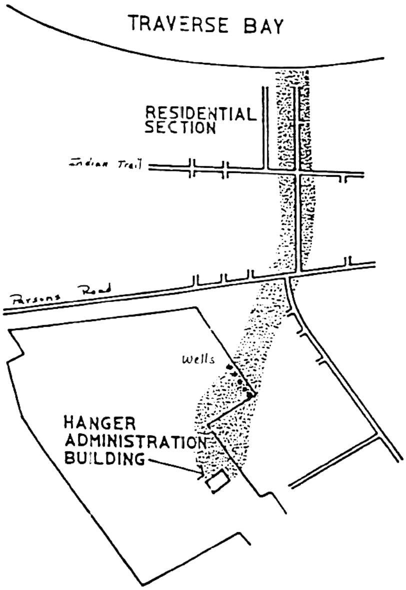


Fig. 5. Traverse City site map.

aquifer from the spill toward the bay and underneath a residential area. Investigation into the spill revealed that 10,000 to 20,000 gallons of aviation fuel had been released into the ground when a flange failed on one of the tanks. Alkylbenzenes (BTEX) from the fuel were found in the ground water in concentrations ranging from 30 μg/L to 30,000 μg/L near the source area [31].

Extensive studies have been carried out at the site since the mid 1980's by the U.S. Coast Guard Station, U.S. Environmental Protection Agency Robert S. Kerr Environmental Research Laboratory, the Traverse Group, Inc., and Rice University. Clean-up of the Air Station is underway using purge wells (pump and treat). An interdiction well field (Fig. 5) was installed in April of 1985 to limit the contamination to the site and to pump and treat contaminants intersected by the wells. These wells have been very effective in stopping contaminant migration downgradient of the interdiction field (Fig. 6). Within about 24 months of the pumping system installation, the rapid dissipation of the downgradient BTEX plume underlying the residential area was observed at a number of wells located north of the site and is the subject of this modeling study. *In situ* bioremediation and soil venting pilot studies have been underway at the base since 1988 [22,31]. Preliminary results of the current effort were presented at a meeting in San Diego in 1990 [32].

Site characterization at TCM

The study area is underlain by lacustrine glacial deposits consisting of an upper sand and gravel layer and underlying clay layer. The upper 15 to 20 feet

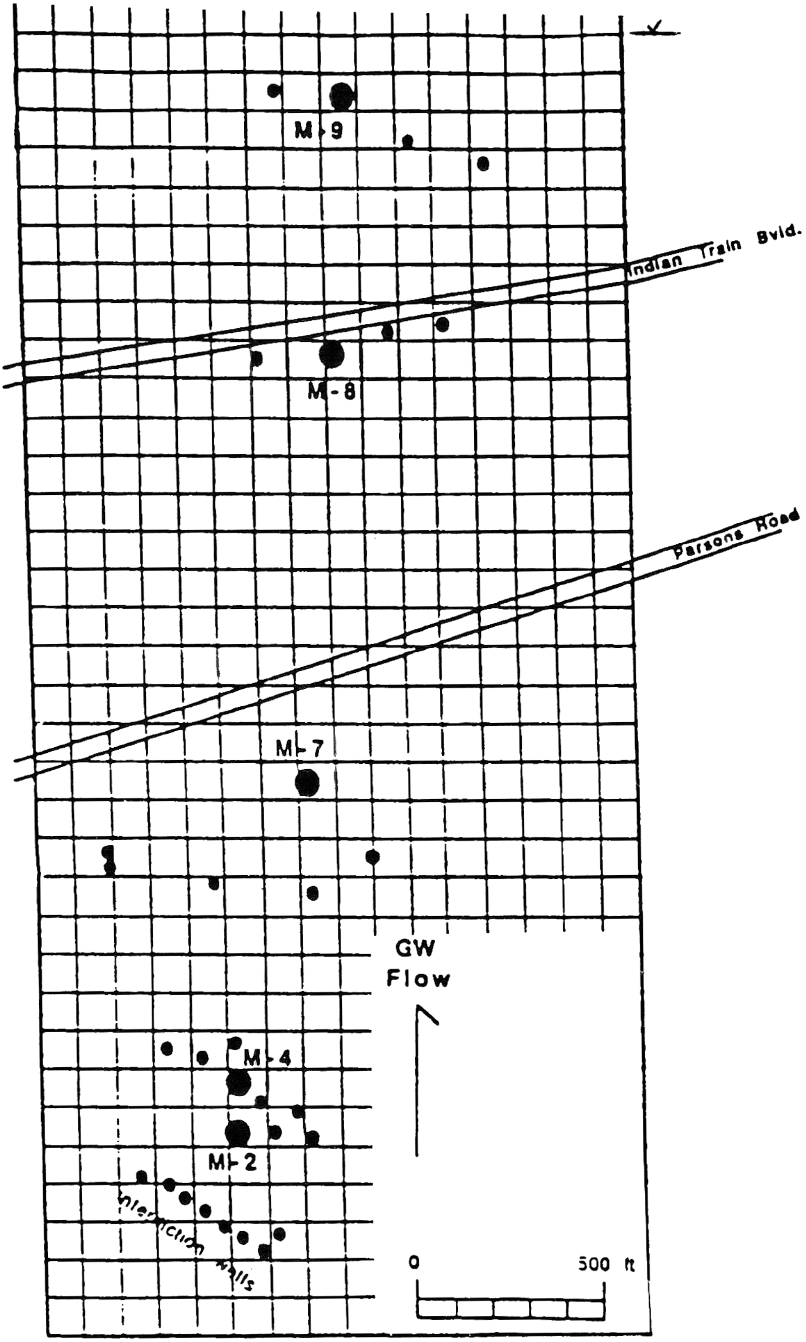


Fig. 6. Model and grid wells.

of this unit, the zone in which the water table occurs, is generally fine to medium grained sand. Below this, gravel and coarse to very coarse sand are more abundant. Based on wells in the area the thickness of the upper sand and gravel unit ranges from 29 to 118 feet. The underlying clay unit is relatively impermeable and its thickness in the study area is not known as no wells have pene-

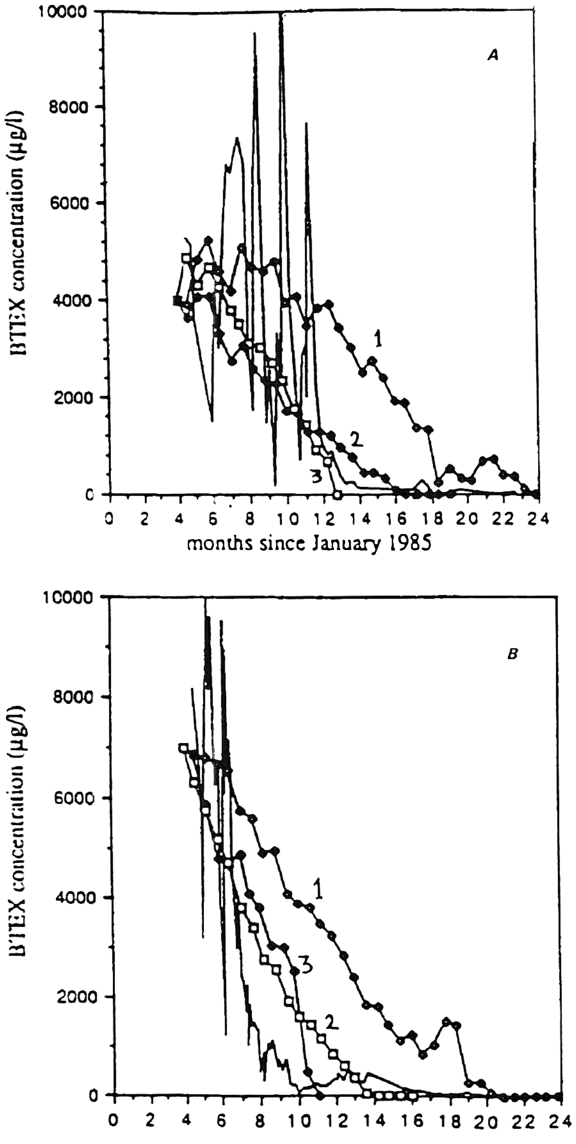
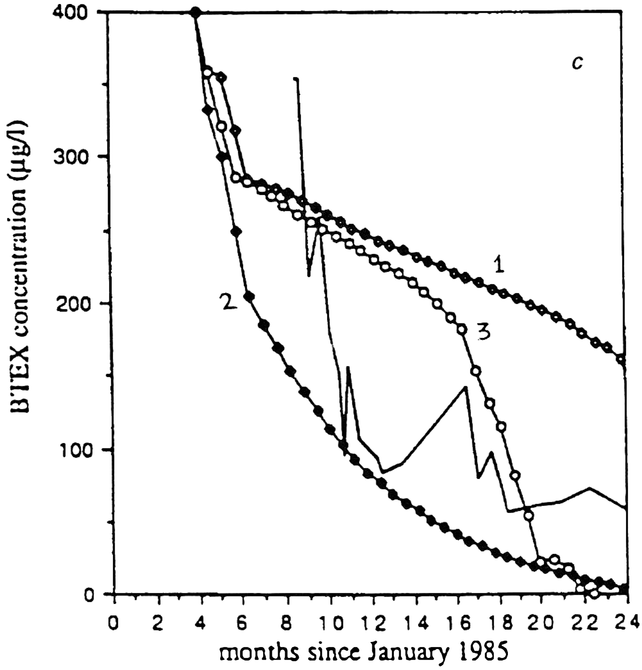


Fig. 7. Results for (a) M-4, (b) M-2, and (c) M-9. (—) Observed, (1) 95 ft/day, (2) 95 ft/day at $r=0.01\ d^{-1}$ and (3) 150 ft/day.



trated it fully [33]. Cone penetrometer data [34] show a distinct change in the density of the sand unit at approximately 20–25 feet, which corresponds to the change in sediment type reported by Twenter at 15–20 feet.

Hydraulic conductivity ranges from 100 ft/day to 150 ft/day based on pump test data acquired several years ago in the initial site investigation [33]. Slug tests performed in 1988 by Smythe confirm these results for the upper sands. However, the lower dense sands have a hydraulic conductivity of about 20 ft/day according to permeameter tests performed under *in situ* conditions [34]. The hydraulic gradient averages 0.005 and effective porosity is in the range of 0.30.

Model application and parameter selection

The model study represents a unique application of the BIOPLUME II model to contaminant migration and biodegradation. Previous uses of the model have dealt mostly with modeling plumes with a variable source component. The lack of definition of source terms has always presented a serious problem in predicting the fate and transport of plumes, since it creates poorly defined mass rates of contaminant feeding a plume and therefore does not allow for biodegradation to be evaluated accurately. This application, given that the interdiction field has effectively cut off the source and created a well-defined flush out of the aquifer, offers a real advantage in modeling the biodegradation process at a real field site.

The modeling approach taken here starts with a well-defined initial source concentration in the aquifer below the pump and treat wells and attempts to match observed dissipation results from a number of well-monitored points downstream. Both hydraulic conductivity and degree of biodegradation, using both an instantaneous reaction method and a reaeration coefficient, were used to fit to the observed dissipation in the aquifer over a two year period.

Modeling of the plume downgradient of the interdiction field (Fig. 5) was performed using BIOPLUME II [17,18]. This study was performed under steady state conditions using an effective porosity of 30%, a longitudinal dispersivity of 5 feet, a ratio of transverse to longitudinal dispersivity of 0.3, and a 16 by 58 grid (Fig. 6). Saturated thickness ranges from 30 to 100 feet and the hydraulic gradient averages 0.005. These parameters are in line with previous geologic and model studies of the site (Smythe et al., 1989).

Initial model runs were made without biodegradation to evaluate the sensitivity of the model to observed total BTEX concentrations, based solely on the hydraulic flushout of the system over about a 24 month period. An initial contaminant plume configuration at the time of the interdiction field start-up of April of 1985 was used for input. This plume was defined based on measurements made by the Traverse City Group Inc. (TGI) and EPA RSKERL in 1985. Three monitoring wells were selected to allow for the comparison of calculated to observed total BTEX concentrations. These wells are M-2, M-4, and M-9 (Fig. 6). Also the seven interdiction wells that were pumping as of April of 1985 are included in the model and are modeled with an average pumping rate of 20 gpm per well as reported for the period of the simulations.

A large number of model runs were made to evaluate the effect of biodegradation as simulated using an instantaneous reaction assumption and a reaeration coefficient. Initial background dissolved oxygen values were input as a grid over the site. A number of results have been reported elsewhere (Bedient et al., 1992) and only are summarized here.

Results of natural biodegradation modeling

Model results for wells M-2, M-4, and M-9 are shown in Figure 7a, 7b, and 7c. These plots indicate that the most reasonable match is found using a hydraulic conductivity of 150 ft/day (with biodegradation) or by using a hydraulic conductivity of 95 ft/day coupled with a reaeration coefficient of 0.01 day^{-1}. Comparisons with lower hydraulic conductivities (48 or 72 ft/day) produced much poorer results since the rate of flushout was reduced. With these higher hydraulic conductivities values, the observed increases attributed to reaeration were expected due to the results seen in the sensitivity analysis study. However in well M-9, Figure 7c, the match was more difficult due to the fact that the well M-9 is not on the centerline of the plume and is in a zone where the plume has narrowed. It would have been useful to have another well between M-2 and M-9, but no other data was available.

Biodegradation modeling at the Traverse City aviation spill site for the portion of the plume downgradient of the interdiction well system indicated some interesting results. The modeling of the dissipation of BTEX concentrations was greatly simplified by the cutoff of the variable source 1500 ft upgradient. This allowed the remaining plume to flush out naturally and biodegrade according to natural kinetic rates for the site. The success of the modeling effort was largely a function of the accuracy of the initial downgradient plume and the hydraulics of the system. The modeling results show a distinct and reasonable comparison to observed dissipation in 3 wells downgradient of the interdiction well field. Measured hydraulic conductivities (K) ranged from 48 to 150 ft/day, and a range of values were used to help fit the observed declines at the wells. The higher the K value used, the faster the flush out and decline, and the lower the K value used, the more biodegradation was required to match the decline. It was found that using a hydraulic conductivity of 150 ft/day coupled with biodegradation simulated with both an instantaneous reaction and a reaeration coefficient gave a good match to observed contaminant declines. A similar match to observed contaminant declines was obtained by using a hydraulic conductivity of 95 ft/day coupled with both an instantaneous reaction and a reaeration coefficient of 0.01 day^{-1}.

Conclusions

Biodegradation modeling has progressed significantly since the mid 1980s with more than a dozen papers and modeling studies reported in the general literature since 1985. However, the need still exists for well-documented field sites where biodegradation is being measured as part of a cleanup operation. There has always been a real problem in extrapolating from degradation rates measured in the laboratory to the field for certain classes of compounds. Only through more detailed monitoring and modeling efforts at real field sites can we ever hope to gain a better understanding of natural or enhanced biodegradation processes.

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Organic substances in the subsurface: Delineation, migration, and remediation*

Ishwar Murarka[a], Edward Neuhauser[b], Michael Sherman[b], Barbara B. Taylor[c] and David M. Mauro[c], John Ripp[d] and Terry Taylor[d]

[a] *Land and Water Quality Studies, Electric Power Research Institute, 3412 Hillview Ave., Palo Alto, CA 94303, (USA)*
[b] *Niagara Mohawk Power Company, Syracuse, NY (USA)*
[c] *META Environmental, Inc., 49 Clarendon St., Watertown, MA 02172 (USA)*
[d] *Atlantic Environmental Services, Inc., Colchester, CT (USA)*

Abstract

The Electric Power Research Institute (EPRI) and Niagara Mohawk Power Corporation are sponsoring a research program concerning the release, transformation, and migration of organic compounds at a site where coal tar from former manufactured gas plant (MGP) operations was disposed nearly thirty years ago. Work at this site, referred to as EBOS Site 24, has included: determination of the location and chemical content of the tarry source material, delineation of the groundwater contaminant plume, evaluation and implementation of innovative methods for sampling and analysis, and the remediation and restoration of the site. The results of the initial phase of research provided several important insights into the mechanisms of contaminant release and migration. For example, the shape of the groundwater contaminant plume at EBOS Site 24 was dominated by longitudinal advection with little contribution from transverse or vertical dispersion. A long-term monitoring program at EBOS Site 24 was initiated prior to the removal of the source material. The results of the baseline groundwater monitoring along the plume centerline were similar to the values predicted using EPRI's MYGRT™ model for migration of contaminants. After the baseline monitoring was completed, all of the tarry source material was removed in 1991 and used in the production of asphalt and portland cement. The groundwater monitoring program will continue for several years and the field results generated during this time will be used to evaluate and/or calibrate the MYGRT™ model.

Introduction

In recent years, increasing concern has been expressed about the potential threats to human health and the environment from organic substances produced as by-products of former manufactured gas plant (MGP) operations,

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Correspondence to: Dr. B. Taylor, META Environmental, Inc., 49 Clarendon St., Watertown, MA 02172, (USA).

such as the mononuclear aromatic hydrocarbons (MAHs) and polynuclear aromatic hydrocarbons (PAHs) in coal tar. Although the presence of coal tar, and other process residues, at sites where former MGP plants were located has been known for some time, few sites have been investigated thoroughly and even fewer have been remediated.

Starting in 1987, the Electric Power Research Institute (EPRI) initiated a major research effort under the Environmental Behavior of Organic Substances (EBOS) program to help understand what happens to the organic wastes at MGP sites over time as some of their constituents are released to the environment, and what happens to the contamination in the downgradient aquifer after the wastes are removed from the site.

The focus of the EPRI-sponsored research began with a series of field efforts directed toward developing insights concerning the natural processes by which organic substances in tarry materials are released to, transformed in, and move through various environmental matrices. The understanding of these processes is fundamental to selecting the appropriate means of remediation and for determining the efficacy of that remediation. As a better understanding of these processes has evolved, part of the more recent research has focussed on predicting how well remediation efforts will work (based on computer-generated migration simulations using EPRI's MYGRT™ software) and determining how good those predictions are.

The EPRI field work started in late 1987 at a site in the Northeast, referred to as EBOS Site 24, with the assistance and cooperation of the owner utility, Niagara Mohawk Power Corporation. First, preliminary field work was carried out to test both conventional and innovative methods for sampling and analysis of soils and groundwaters. When the methods were well-established, a series of field studies were implemented to locate the tarry material and define the groundwater contaminant plume both aerially and vertically. After the location of the source area was defined, Niagara Mohawk contracted to have all of the known tarry material removed from the site. Finally, EPRI, in cooperation with Niagara Mohawk, recently initiated a long-term monitoring program which will examine the groundwater quality, biotransformation, and plume dissipation for the next ten years to assess both the efficacy of the remedial source removal and the ability of MYGRT™ to predict plume dissipation.

This paper provides a summary of a portion of the work carried out by EPRI and utility contractors at EBOS Site 24 and the major findings of that work. It starts with an overview of the MGP problem and why such research efforts are needed.

Background

From the early 1800s through the 1950s, the production of gas using coal, coke, or oil resulted in the generation of large volumes of various process by-products at MGP operations throughout the United States, as shown in Table 1 [1–4]. As seen in this table, tars and tarry materials were a major part of the MGP waste products. Often, the standard practice of the day was to leave these tarry residues in holders, trenches, ponds, or pits on-site or to move them to off-site locations for disposal [5,6].

Gas production at MGP sites was phased out rapidly after World War II with the development of natural gas pipelines. The tarry remnants of MGP operations remained, even as the former MGP sites were converted for various utility purposes, such as utility maintenance areas or substations, demolished, abandoned, or sold to others. In recent years, however, the leftover wastes generated from the old MGP processes have come under increased scrutiny. This is partly a result of increased awareness of potential problems, as well as an increase in the sale or redevelopment of former MGP sites [3].

Since the concern about potential hazards from MGP wastes has surfaced only in the past several years, little has been known about the environmental fate of MGP-derived tarry materials. Attempting to study the fate of these materials is difficult since the coal or oil tar resulting from different processes can be physically or chemically different [6,7]. Furthermore, where and how the tars have been left for decades can impact their current state. For example, tar left in a deep holder that was demolished and covered over with rubble, fill, and asphalt can be significantly different from a similar tar that was placed in a shallow trench and left exposed to the environment. This is because from the moment of disposal, a variety of physical, chemical, and microbial processes affect the way in which the coal tar constituents are released to, transformed in, and transported through the environment. Natural processes such as dissolution, volatilization, adsorption, microbial degradation, dispersion, and advection combine to determine the ultimate environmental fate of tarry material constituents [1,8]. Table 2 illustrates some of the differences among the

TABLE 1

Typical MGP process by-products

By-products	Processes		
	Coal carbonization	Carburetted water gas	Oil gas
Petroleum oils		×	×
Tars	×	×	×
Spent oxides	×	×	×
Ash/clinker	×	×	×
Sludges/emulsions	×	×	×
Ammonia liquor	×		
Lampback			×

TABLE 2

Comparison of MGP organic compound characteristics[a]

Characteristic	Compound groups		
	MAHs	PAHs	Phenols
Volatility	High	Low	Low
Solubility	Medium	Low	High
Biodegradability	Medium	Low	High
Adsorption tendency	Low	High	Low
Mobility	High	Low	High

[a] There is significant variability in characteristics among individual compounds, such as the PAHs

environmental fate characteristics of three major types of MGP-related organic compounds, MAHs, PAHs, and phenolic compounds.

Understanding how natural processes play a part in the ultimate fate of MGP tar is very difficult. It is especially complicated because tars are very complex mixtures of hundreds, if not thousands, of different organic compounds. These compounds each have their own physical, chemical, and biological properties, which often are very different from each other. For example, one of the most common constituents in MGP tars is naphthalene, a two-ring PAH. It has a pure component, aqueous solubility of about 31 mg/L. This is dramatically contrasted with benzo(a)pyrene, a five ring PAH, which has a pure component, aqueous solubility of only about 0.004 mg/L [9].

Although some properties of the individual tar constituents, such as volatilization and dissolution, have been studied in laboratory experiments [9], the estimation of individual constituent parameters does not accurately describe how the tar mixture will act in the environment. Again, using the example of naphthalene, while the pure component solubility is about 31 mg/L, the aqueous solubility of the naphthalene in some MGP tars has been determined to be about 11 mg/L in laboratory experiments and about 13 mg/L based on Raoult's Law predictions [10].

Clearly, although laboratory experiments on single tar compounds or model simulation concerning the rate of environmental processes in nature provide some important information, field-scale research at MGP sites can help fill in the information gap. This is particularly important in determining appropriate remedial alternatives and predicting how well they will work. Thus, EPRI has emphasized field-scale research at MGP sites.

EBOS Site 24

The EPRI research at EBOS Site 24 began in late 1987, about twenty-five to thirty years after coal tar was removed from an MGP holder, trucked to a rural area a short distance away, placed in a large trench at the side of a country road, and covered over with sand. The amount of tar deposited in the trench has been estimated to be anywhere between about 4,000 and 16,000 gallons, although no records of the actual volume disposed were found.

The tar was left forgotten in the covered over trench and indigenous vegetation grew back on top of the sand fill, giving no indication that this location was anything other than a pleasant open area covered with wild strawberry plants, small shrubs, and grasses. It was not until the early 1980s when a utility worker detected coal tar-derived organic compounds several hundred meters downgradient from the tar that an investigation of the site was initiated.

With support from and in cooperation with Niagara Mohawk, EPRI began its MGP site research at EBOS Site 24. The goals of the research effort were to examine and evaluate both conventional and innovative methods for sampling and analysis at former MGP sites, to help develop insights into the ultimate fate of tarry materials in the environment, and to determine the efficacy of remedial actions.

EBOS Site 24 was an ideal site to use for initial research on environmental processes as they control the release and migration of organic compounds from MGP tars. First, the site was located in a rural area and, other than a country road and electrical transmission lines which transverse through one corner of the site, there were no buildings or other structures to modify subsurface characteristics or influence the natural movement of groundwater. Second, the site had only a single tar source, thereby eliminating the problem of multiple sources and multiple plumes. Third, although there were discontinuous clay lenses in the saturated zone, the aquifer was consistently sandy throughout the site and was composed of coarse to fine silty sands, with a confining clay layer located below the silty sands at a shallow depth of about 22 feet (6.6 m). Finally, the sandy soil contained little organic carbon, indicating that adsorption reactions would not be dominant for chemical attenuation at this site.

Location and volume estimation of the source tar

One of the first steps in the site investigation at EBOS Site 24 was to accurately determine where the tarry source was located. To do this, a square site grid was established at the site with grid points at 50 foot intervals in the source area and 100 foot intervals for the rest of the site. This is shown in Fig. 1. The grid was extended over the entire site and was used throughout the research effort to pinpoint sampling, piezometer, multilevel sampler, and monitoring well locations.

Anecdotal information from a former utility employee indicated that the coal tar trench was located north of the road in a clearing to the west of a small stand of trees. Thus, initial efforts to locate the source area focussed on that part of the clearing. It was soon discovered that anecdotal accounts often are

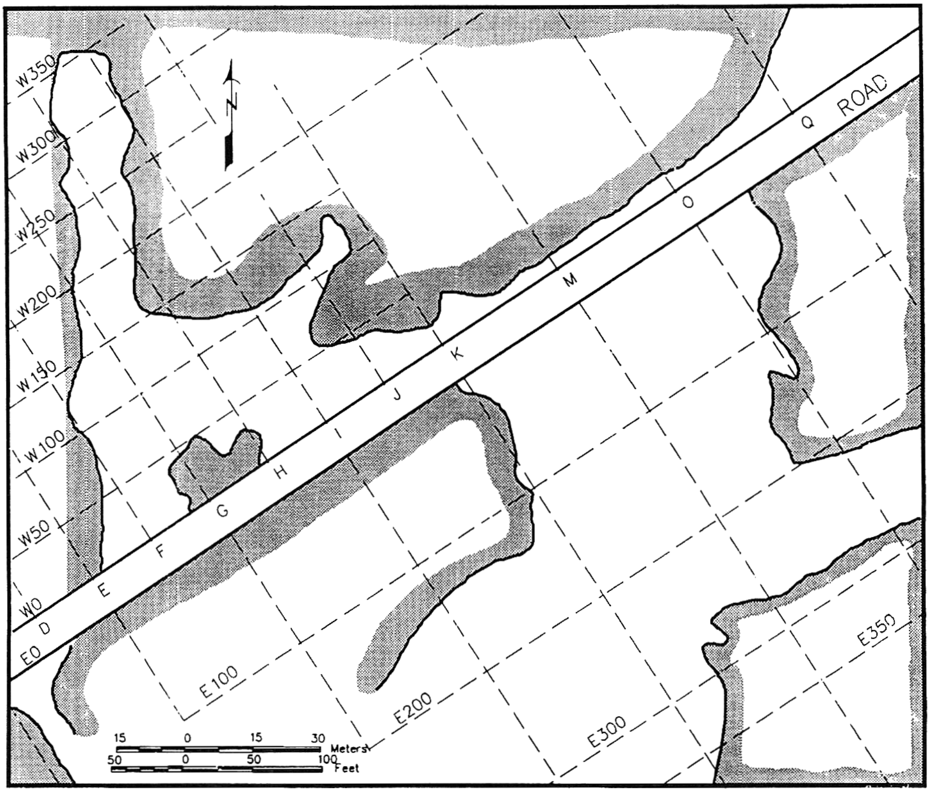

Fig. 1. Site grid for EBOS Site 24.

only partly correct. In this case, the tar indeed was found north of the road, but to the east — rather than the west — of the small stand of trees.

The determination of the areal tar boundaries and the estimation of the tar and tar-contaminated soil volume was made later in the project by a series of rapid borings in the vicinity of the source. The areal extent of the tar and contaminated soils is shown in Fig. 2. Based on the results of the borings, the volume of tar and tar-contaminated soils was estimated to be approximately 8,000 cubic yards (6100 m^3), with most of the tar and highly contaminated material located at or below the water table at depths from about 7 to 22 feet.

Contaminant plume location and definition

The data from piezometers and groundwater wells installed at various locations across the site showed that the groundwater flowed from the source in a southeasterly direction, under the road, and down to a downgradient seep area more than 300 yards away (Fig. 3). This area consisted of numerous small trickling seeps that converged to a small stream that eventually reached a ma-

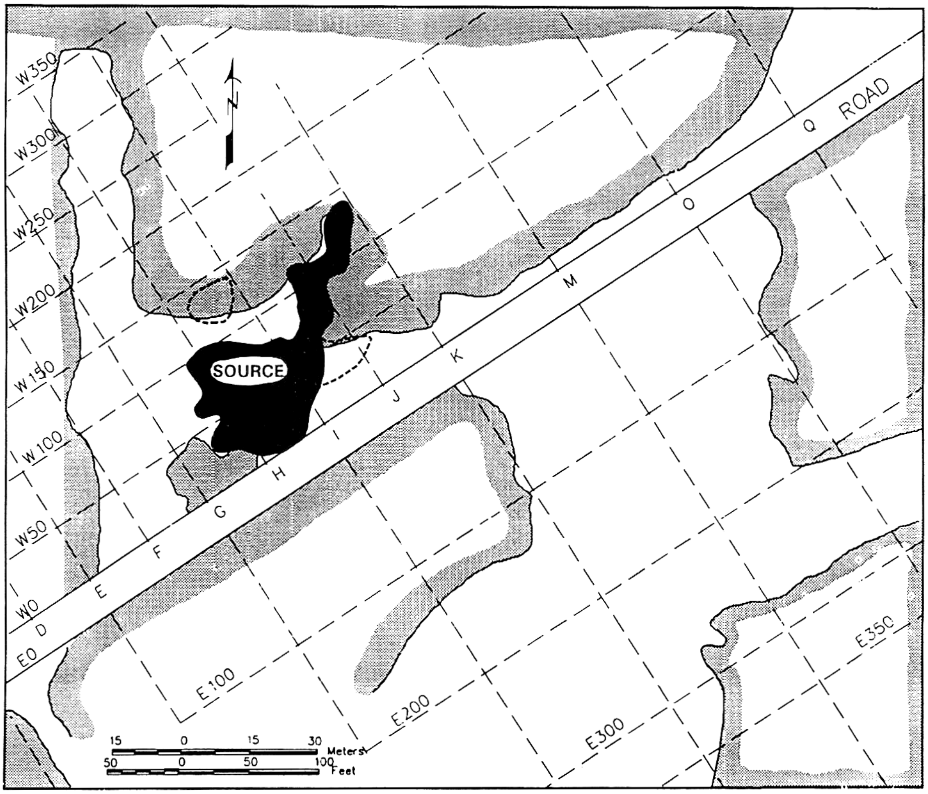

Fig. 2. Location of tarry source material at EBOS Site 24.

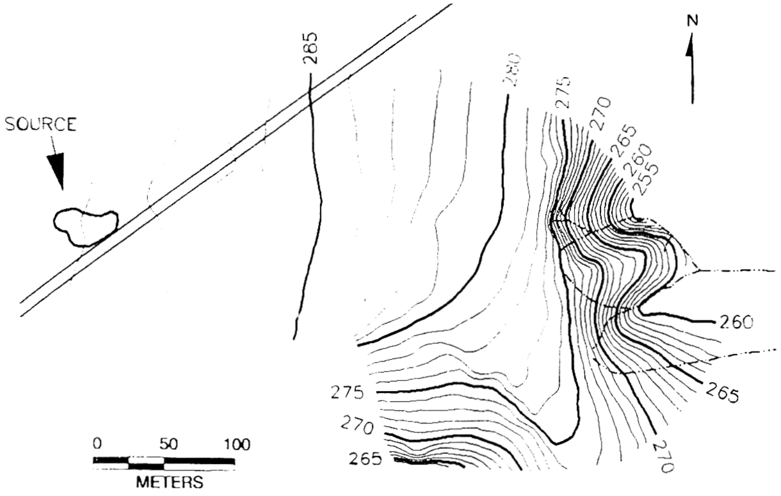

Fig. 3. Groundwater contours.

jor river. Results of a study concerning the seep area showed the presence of naphthalene in the seep sediments, but no PAHs were detected in the stream water entering the river.

One of the major developments for field sampling at MGP sites from this research was the method for determining the lateral and vertical placement of groundwater monitoring wells directly within the plume or at the plume edges. This method used naphthalene as an indicator compound because it was the PAH found in the highest concentration in the source tar and because it is the most soluble and has the least potential for soil adsorption of all of the PAH compounds detected. Thus, it was the most abundant and mobile of the coal tar-derived PAHs for the EBOS Site 24 source tar.

The method for determining where groundwater wells should be placed (both laterally and vertically) and what screen length should be used had several steps. First a series of transects were established to cut across the site in such a way so that they were approximately perpendicular to the expected direction of the groundwater plume (Fig. 4). As a result of the placement of some monitoring wells during the initial reconnaissance phase of the work and the impediment of heavily wooded areas, not all of the transects were parallel.

Second, several borings were made along each transect, starting from the edges and working toward what was thought to be the centerline of the plume. During the boring process, soil samples were collected at appropriate depths and taken to the field laboratory where they were extracted and analyzed. (A

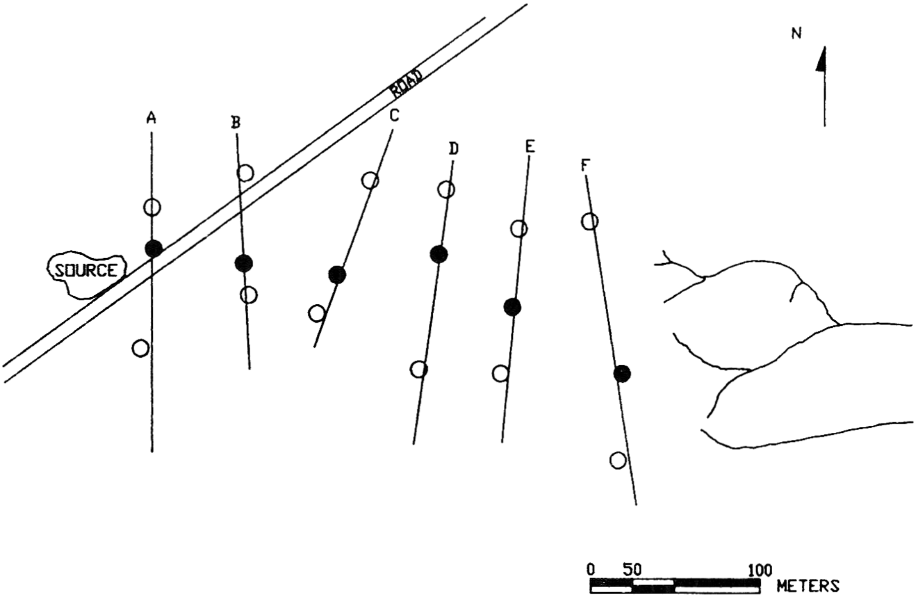

Fig. 4. EBOS Site 24 transects.

field method of soil and groundwater extraction and analysis for PAH compounds was developed during this research effort. It consisted of a micro extraction technique followed by gas chromatography with flame ionization detection (GC/FID). The results of this method compared favorably with conventional Soxhlet extraction followed by gas chromatography with mass spectrometric detection (GC/MS)). Next, the results of the initial borings were used to determine where future borings would be made or from what depth samples should be collected for analysis.

Finally, once all of the data were examined, the areal location of the boring with the highest concentration of naphthalene along each transect was selected for the approximate well location. Then, by studying the vertical distribution of naphthalene concentrations in that boring a determination was made concerning what depth and screen length would place the monitoring well in the zone with the highest naphthalene concentration. Typically, two or three relatively short well screens (usually 2 or 2.5 feet in length) were placed at a single areal location determined to be at or near the plume centerline. Fringe wells were also placed at the edges of the plume in order to clearly delineate the outer boundaries of the plume.

This method of well placement proved to be an excellent technique for placing monitoring wells where the highest concentration of PAHs were found in the plume or at the plume boundaries with a fairly high degree of certainty. However, since soil analysis results were needed within a day or so of collection, it could only be used effectively in conjunction with a rapid turnaround field laboratory.

As an example of how this method worked, Fig. 5 shows the maximum concentration of naphthalene detected in the soils at five locations along Transect C. The place where the highest naphthalene concentration was detected was designated the centerline for Transect C and the soil results from different depths at that location were reviewed to determine the best well depths and screen lengths to use for the monitoring wells. Figure 6 shows how the naph-

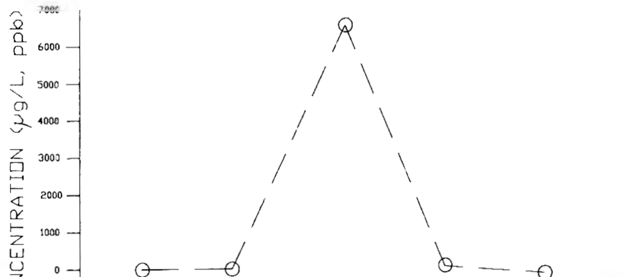

Fig. 5. Maximum naphthalene concentrations in soils across Transect C.

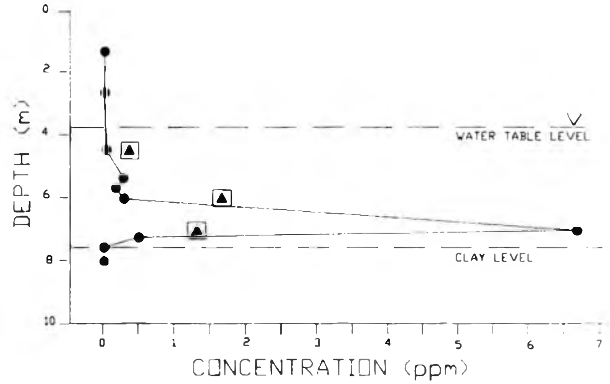

Fig. 6. Soil (●) and groundwater (▲) naphthalene concentrations at the centerpoint of Transect C. (□) Well screen.

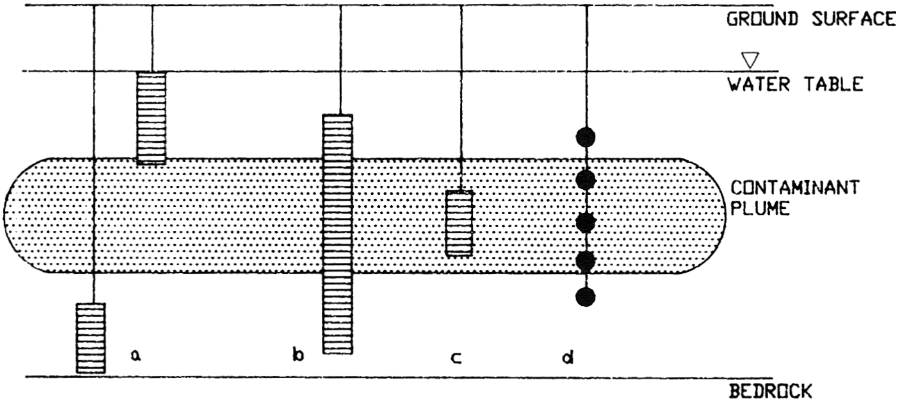

Fig. 7. Different groundwater well configurations. (a) Conventional placement of two wells located at the water table and confining layer to detect the presence of L-NAPL and D-NAPL, (b) a single well with a long well screen, (c) a single well with a short screen placed in the contaminated zone, and (d) a multilevel sampler ports at specific intervals.

thalene concentrations in the soil changed with depth, the placement of the three groundwater wells, and the groundwater naphthalene concentrations found in the three wells. As shown in this figure, the vertical extent of the groundwater plume is very narrow and that the well with the highest naphthalene concentration is the middle well, between the water table and the confining layer.

One of the interesting results from this method was that standard well placement techniques may not always result in proper well placement. For example, often wells are placed so that they are screened at the water table to detect the presence of lighter-than-water non-aqueous phase liquids (L-NAPL) or at the confining layer (or bedrock) to detect the presence of denser-than-water non-aqueous phase liquids (D-NAPL). However, for most locations at EBOS Site 24, such as Transect C illustrated in Fig. 6, the placement of wells at the water table and confining layer would have resulted in groundwater samples with much lower concentrations of naphthalene than in the plume. This is because most of the highest naphthalene concentrations were observed at locations between the water table and the confining layer (except for the near source locations). Wells placed at the two extreme locations or long well screens would have significantly underestimated the contamination present in the plume, this is shown schematically in Fig. 7.

Investigation conclusions

The results of the field investigation at EBOS Site 24 showed that a fairly narrow plume of tar constituents moved away from the source area and that naphthalene moved the furthest distance of any of the PAH compounds studied. Figure 8 depicts the areal extent of the groundwater naphthalene plume across the site. Other PAH compounds did not appear to move through the saturated zone as readily as naphthalene and some did not show any significant movement away from the near source area. This is shown in Fig. 9. In this figure, the concentrations of naphthalene, acenaphthylene, and anthracene in groundwater are shown as a function of distance from the source. It is easily

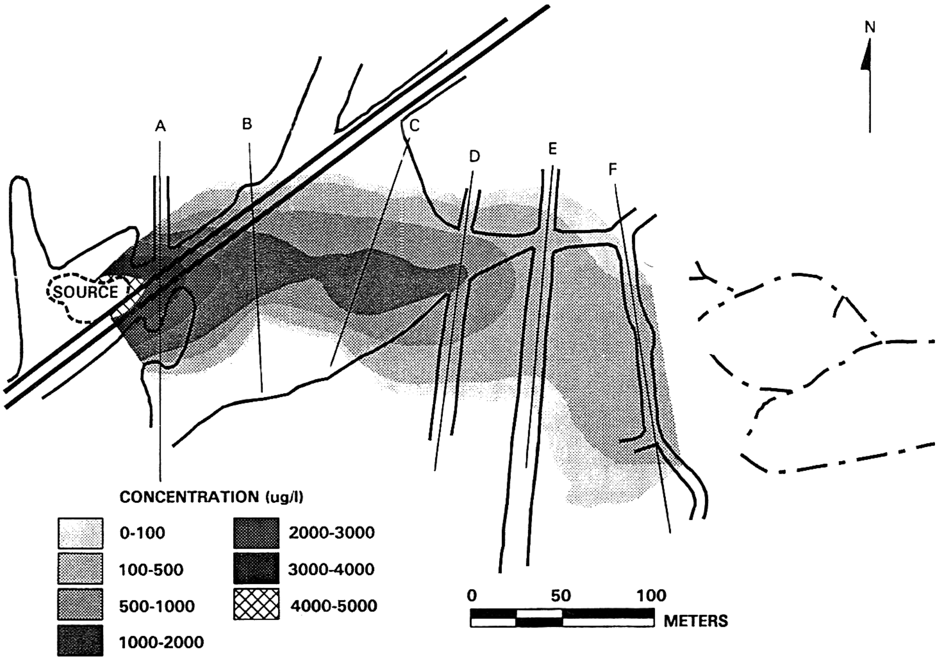

Fig. 8. Aereal extent of the groundwater naphthalene plume.

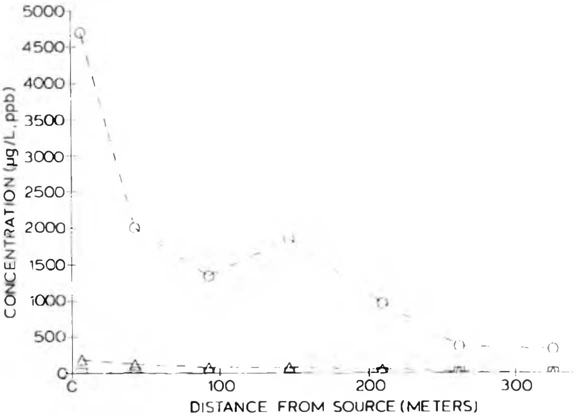

Fig. 9. Groundwater concentrations of naphthalene (○), acenaphthylene (△), and anthracene (□) at wells in the plume.

seen that the high molecular weight PAHs, such as anthracene and benzo[a]pyrene, were not observed at any significant distance away from the source.

At EBOS Site 24, it was apparent that the primary release mode of coal tar constituents to the environment was by dissolution. Thus, the solubility of a particular constituent dictated how much of that compound was allowed to move with the groundwater. Once dissolved, the material moved along with the groundwater flow in an advective manner with very little vertical or transverse dispersion. Although the contaminant plume was near the water table in the near source area, the plume dropped gradually as it moved downgradient and tended to be situated in similar soils located above the clay confining layer, as shown in Fig. 10. And, since this site contained very little organic carbon, adsorption did not appear to play a major role in retarding the movement of the coal tar constituents with the groundwater. Furthermore, there was no evidence of L-NAPL or D-NAPL at any locations away from the immediate source area.

One process which may be important with respect to the fate of some coal tar constituents is subsurface microbial transformation. Research performed at this site by scientists from Cornell University showed that there were indigenous, PAH-degrading, microorganisms in the constituent plume (11). The researchers collected soil samples from locations both in contaminated areas and an uncontaminated background area and from the saturated and unsaturated zones. They then measured the potential of the indigenous organisms to degrade naphthalene and phenanthrene. The results showed that mineralization of naphthalene and phenanthrene occurred only in the samples collected from within the contaminant plume. No such mineralization was observed for the soils from the on-site background location.

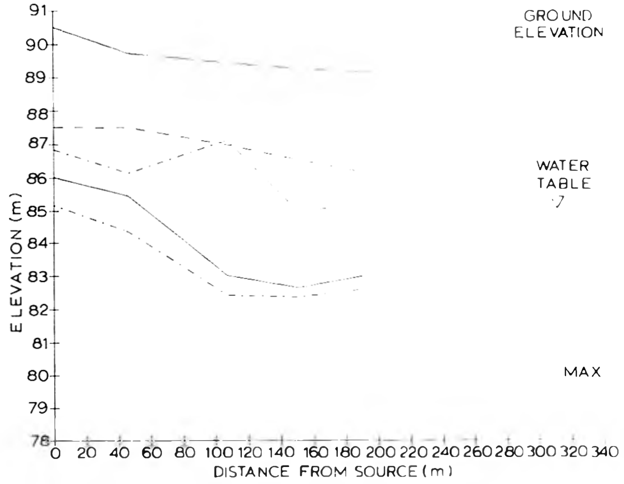

Fig. 10. Location of detectable naphthalene concentrations in soils downgradient from the source.

Source removal

In 1991, Niagara Mohawk contracted with Atlantic Environmental Services, Inc., to oversee the removal of all of the source tars and tarry soils, as well as the restoration of the source area. This work began in May 1991 with the site preparation. First, the entire site was secured using fencing and a locked access gate. To enclose the entire work area, the country road adjacent to the tar trench had to be closed for the duration of the site work and all traffic had to be rerouted from the area.

Next, plastic liners were located near the excavation area so that contaminated soil removed from the source area could be stockpiled until loaded into trucks for transport. In addition, a plastic-lined wastewater pond was constructed to hold all of the water generated during the excavation dewatering. Then, sheetpiles were driven to a depth of about 30 feet, well below the known confining layer, to completely surround the area where tar and tarry soils were located and to form a cofferdam. A schematic drawing of the construction site layout and the location of soil samples is shown in Fig. 11.

Soils were removed from the excavation area using backhoes and were temporarily placed on the stockpile until they were placed in trucks and transported off-site. When the excavation reached the water table, water was pumped from the cofferdam area to the lined wastewater pond.

A total of approximately 9,400 cubic yards (15,000 tons) of tarry soils, tar-contaminated soils, and adjacent clean soils were excavated from the source area. The excavated soils were tested several times and were found not to exhibit any hazard characteristic as defined by the EPA, including: toxicity, ignitability, reactivity, or corrosivity. As a result, the excavated soils could be

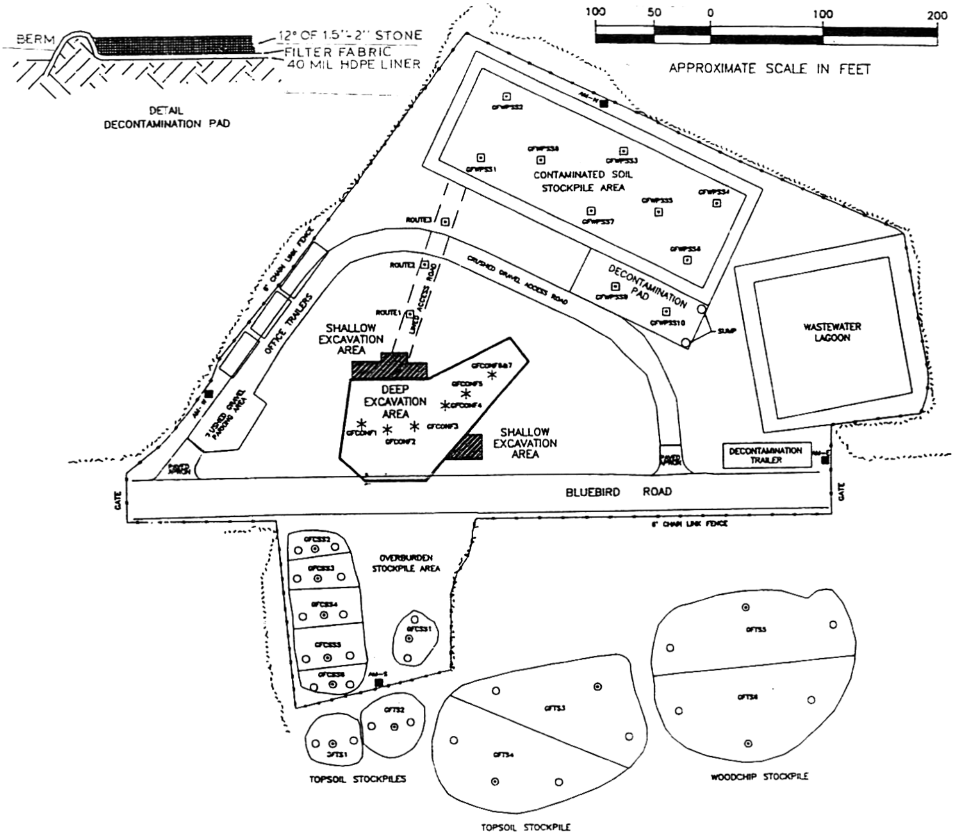

Fig. 11. Remedial construction layout and sample location.

used in processes to form asphalt or portland cement and would not be required to undergo treatment and/or disposal at a hazardous waste facility.

Two facilities did trial studies using the contaminated soils to produce portland cement and one facility did a trial study using the soils to produce hot batch asphalt. All three facilities used thermal desorption techniques with rotary kiln technologies, all three performed the trial burns satisfactorily, all passed audits by the contractor, and all had secure, covered, on-site storage for the contaminated soils. Based on total costs, however, one facility, the asphalt batching plant, was used to treat most of the soils (about 11,500 tons) at a cost of about $106/ton. One of the facilities generating portland cement was used as a secondary and backup treatment plant and processed about 3,600 tons of contaminated soil for about $172/ton. The other facility producing portland cement was used only for the trial burn study and processed about 40 tons at a cost of $210/ton.

The wastewater generated during the excavation dewatering was tested and found acceptable for the local wastewater treatment plant without pre-treatment. Thus, the approximately 737,000 gallons (2800 m^3) of water collected during the remedial work were removed from the site and taken to the wastewater treatment facility for disposal.

By mid-October of 1991, all of the contaminated soils, water, and liners had been removed from the site. After removal of the tar and tar-contaminated soils, the excavated hole was filled with clean native sand and clean soil resulting from excavation activities in areas other than the contaminated location. The sheetpiles were removed, decontaminated, and taken from the site. The EPRI research wells and piezometers which were destroyed during the excavation process were replaced. The disturbed area was leveled, and the ground was fertilized and seeded.

Long-term monitoring

Two rounds of groundwater monitoring were completed in 1989 and 1990 prior to the removal of the source in 1991. The naphthalene results for this baseline monitoring program are shown in Fig. 12. Note how the concentration of naphthalene at Transect A in 1990 is much less than it was during the monitoring from 1989. The reason for this change is that the water table level fell so much between 1989 and 1990 that the well with the highest naphthalene concentration at Transect A could not be sampled in 1990 because it was dry. Thus, data from another well at that location had to be substituted in the 1990 study. The very low water table level also might have impacted the well at Transect B, to a lesser degree.

Figure 13 shows the mean naphthalene concentrations at the plume center-

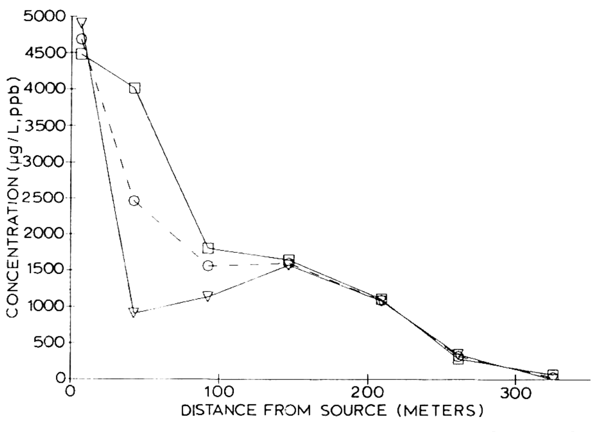

Fig. 12. Naphthalene concentrations at the groundwater plume centerline prior to source removal. (□) September 1989, (▽) June 1990, and (○) mean concentration prior to source removal.

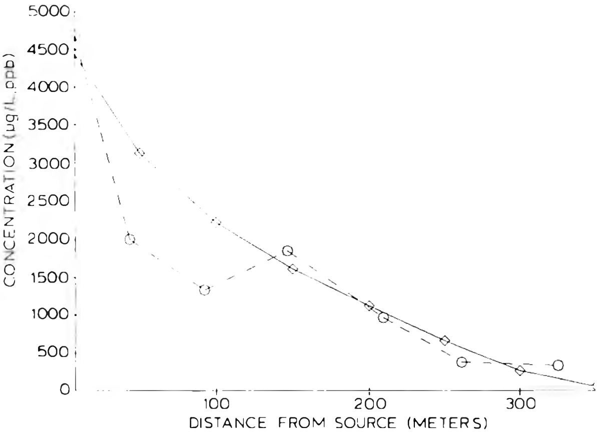

Fig. 13. Measured mean (○) and MYGRT™ predicted (◇) naphthalene concentrations along the plume centerline.

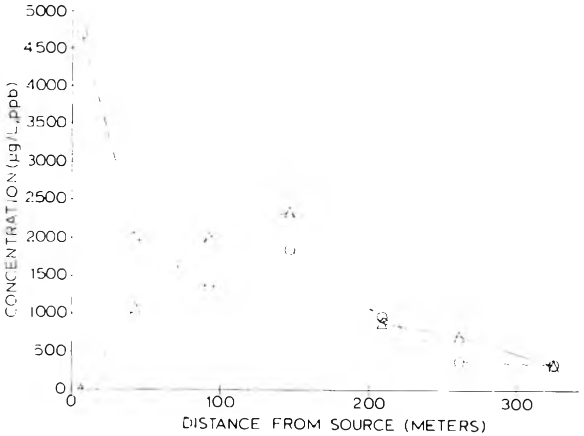

Fig. 14. Naphthalene mean concentrations along the plume centerline prior to (○) and after (△) source removal.

line prior to the source removal along with the predicted naphthalene concentrations from the EPRI MYGRT™ Code 2.0 model. MYGRT™ is a user-friendly IBM PC code designed to evaluate and predict the migration of organic and inorganic chemicals in groundwater [12]. As shown in Fig. 13, the MYGRT™ prediction of naphthalene concentrations at EBOS Site 24 was very close to the measured concentrations prior to source removal. In future studies, MYGRT™ will be used to predict the dissipation of the contaminant plume over the next ten years. During this time, groundwater samples will be collected, analyzed, and the results of these samples will be used to calibrate and/or verify MYGRT™ predictions.

The first round of sampling after removal of the source material was completed in November 1991. The naphthalene results for this sampling event are shown in Fig. 14.

Summary

The results of the EPRI and Niagara Mohawk Power Corporation work at EBOS Site 24 have provided considerable insights into the mechanisms for release, migration, and transformation of MGP tar constituents in the environment. Future work at the site will continue to generate data designated to help understand these mechanisms and to understand the impact of remedial source removal.

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Using an uncertainty analysis of direct and indirect exposure to contaminated groundwater to evaluate EPA's MCLs and health-based cleanup goals*

Brent Finley, Virginia Lau and Dennis Paustenbach

ChemRisk Division, McLaren/Hart Environmental Engineering, 1135 Atlantic Ave., Alameda, CA 94501 (USA)

Abstract

Groundwater which has been contaminated by industrial chemicals has been of significant concern in the U.S. since about 1975. Since then, dozens of regulatory decisions have been made to remediate many of these contaminated aquifers. The selected groundwater clean-up levels will dictate the cost and time frame of the remediation. Most clean-up decisions have been based either on EPA's Maximum Contaminant Levels (MCL) or so-called 'risk-based' levels. For many chemicals, risk-based levels are much lower than the corresponding MCLs. This paper uses an uncertainty analysis of probability density functions (PDF) to assess whether MCLs are sufficient to provide health protection for human populations using remediated groundwater as the sole tap-water source. A case-study involving tetrachloroethylene and chloroform and all the potentially direct and indirect routes of exposure to contaminated water is presented. The results suggest that groundwater need not be cleaned-up to concentrations less than drinking water standards (i.e., MCLs) to achieve health protection.

Introduction

Maximum Contaminant Levels (MCLs) are maximally acceptable concentrations of chemicals in a public water system that are set by U.S. EPA (Environmental Protection Agency) in accordance with the 1972 Safe Drinking Water Act. The MCLs are derived from health-based criteria in conjunction with technologic and economic factors relating to the feasibility of achieving and monitoring for these concentrations in water supply systems. Due to the balancing of health effect considerations with technologic and economic factors, the MCLs for many chemicals are much higher than their respective '*de minimis* risk' concentrations (defined here as the concentration associated with

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Correspondence to: D. Paustenbach, ChemRisk Division, McLaren/Hart Environmental Engineering, 1135 Atlantic Ave., Alameda, CA 94501 (USA). Fax: (510) 521-1547.

one excess cancer case in a million individuals drinking two liters of water per day for 70 years). For example, the primary MCLs for chloroform (100 μg/L), and tetrachloroethylene (5 μg/L) are one to two orders of magnitude higher than their corresponding *de minimis* concentrations (5.7 μg/L and 0.69 μg/L, respectively). This dichotomy is analogous to many of the chemical-specific workplace ambient air standards (Threshold Limit Values, etc.) which are set partially on technical considerations and can be significantly higher than purely 'risk-based' standards [1].

One of the outcomes of such technical and economical concessions is that contaminated groundwater remedial goals, which are often strictly health-based, are sometimes set at concentrations far below drinking water standards. For example, the State of California's 'Recommended Public Health Levels' (RPHLs) for contaminants in drinking water, which are essentially *de minimis* concentrations,have been implemented as cleanup goals at several state and federal Superfund sites in California. The existence of such goals can create technical, financial, and legal dilemmas for the parties faced with cleaning groundwater to concentrations far below the levels that are generally considered safe for daily human consumption. On a more global scale, this issue begs the question as to whether such measures are truly necessary and whether limited resources might be better devoted to other environmental problems.

To date, health-based soil and groundwater remediation goals have largely been driven by the use of fairly conservative point estimates of exposure. For example, current U.S. EPA guidance for risk assessment at Superfund sites [2] suggests using either the maximum or the 95% upper confidence limit of the arithmetic mean of the measured contaminant concentrations and the 90th or 95th percentile of the available estimates of exposure rate and duration (e.g., soil ingestion rates, breathing rates, etc.) to assess contaminant uptake. As has been discussed extensively in the literature, the major shortcoming inherent in this approach is that repeated use of upper-bound values throughout an exposure assessment is likely to result in unrealistic estimates of risk and unreasonable cleanup goals [5,6]. As an alternative, it has been suggested that the exposure assessment process could be refined if probability density functions (PDFs), rather than point exposure estimates, were incorporated into the exposure analysis [3–5]. Specifically, instead of using a single value to represent the exposure parameter, each exposure variable takes on a range of values with a known probability. These PDFs are then analyzed statistically to develop a range of estimated risks and associated probabilities. This 'probabilistic' approach places the point estimate into a full and proper context, and provides more information to the risk managers and the public.

A review of the recent scientific literature indicates that Monte Carlo analysis of exposure parameter PDFs appears to be the current probabilistic approach of choice [4–8]. In the initial step of a Monte Carlo analysis, the available data for each exposure parameter are evaluated with respect to distribution type (e.g., normal, log-normal, etc.) and the mean, maximum, and minimum values are identified. Commercially available software programs (e.g., @RiskTM, Crystal BallTM) then simulate a full distribution frequency for the parameter based on these descriptors. If only the range of values is known, a uniform distribution may be assigned to the exposure parameter. If only the range and mode are known, a triangular distribution may be most appropriate. In addition, if the data set is not accurately described by a standard distribution (normal, lognormal, etc.) it is considered appropriate to use only the empirical data points themselves ('bootstrapping') rather than attempting to simulate a PDF [6]. In the next step, the risk calculation equation is solved several thousand times using a Monte Carlo program which draws values from each exposure PDF. This results in a distribution of risk values and associated probabilities.

In this paper, we examine the health risks associated with daily exposure to MCL concentrations of tetrachloroethylene and chloroform using a Monte Carlo analysis of exposure PDFs. The exposure pathways evaluated are: direct ingestion, dermal contact while showering, indoor inhalation, and garden vegetable ingestion. This scenario comprises all of the likely pathways of exposure to tapwater contaminants in the household. The purpose of this examination is to: (1) assess the degree of conservatism associated with the MCLs, (2) determine whether in fact the MCLs are protective for a vast majority of the population via *all* exposure pathways, and (3) provide a preliminary assessment as to whether groundwater remedial goals should be limited to drinking water standards.

Methods

This section describes the dose equations and data sources for each exposure variable. For the purposes of this evaluation, a single adult age group is considered. Tables 1 through 3 summarize the data distribution characteristics for each exposure variable.

Tapwater ingestion

Contaminant uptake via tapwater ingestion is described by the following equation:

$$Dose=\frac{C\times IR\times EF\times ED}{BW\times AT} \tag{1}$$

where *Dose* is in mg/kg day, *C* denotes the chemical concentration in water (mg/L), *IR* is the ingestion rate (L/day), *EF* the exposure frequency (day/year), *ED* the exposure duration (years), *BW* the body weight (kg), and *AT* the averaging time (days).

For the purposes of this evaluation, the rate of tapwater intake (the sum of water drunk directly as a beverage and water added to foods and beverages

TABLE 1

Probability density functions for exposure duration and frequency, averaging time, and body weight

Parameter	Distribution	Arithmetic mean	Minimum	Maximum	Source
Exposure duration (years)	Empirical	12.9	—	—	Census Bureau [11]
Exposure frequency (days/year)	Constant	350	—	—	USEPA [10]
Averaging time (days)	Constant	25,550	—	—	USEPA [2]
Body weight (kg)	Uniform	—	46.8	101.7	USEPA [12]

during preparation) is taken to be uniformly distributed between 0.4 and 2.2 L/day, as described by data presented by the International Commission on Radiologic Protection in the Report of the Task Group on Reference Man [9]. Exposure frequency is set at a point estimate of 350 days/year, per U.S. EPA guidance [10]. Exposure duration is taken to be an empirical distribution of data collected by the U.S. Census Bureau in 1980 [11]. The arithmetic mean of this distribution, which describes the period of residential tenure of a single household, is 12.9 years. Averaging time is 25,550 days per U.S. EPA guidance [2]. A uniform PDF for body weight is constructed from data collected in the Second National Health and Nutrition Examination Survey (NHANES II), in which adult body weights ranged from 46.8 kg (5th percentile, female) to 101.7 kg (95th percentile, males) [12]. The chemical concentration in water is the chemical-specific MCL.

Dermal contact

Dermal uptake of contaminants in tapwater during showering and bathing is described by the following equation:

$$Dose=\frac{C\times SA\times PC\times F\times CF\times ET\times ED}{BW\times AT} \tag{2}$$

where *Dose* is in mg/kg day, C denotes the chemical concentration in water (mg/L), SA the surface area of exposed skin (cm^2), PC the STCT coefficient (cm/h), F the fraction of skin in contact with water (unitless), CF the conversion factor (10^{-3}L/cm^3), ET the exposure time (h/day), EF the exposure frequency (days/year), ED the exposure duration (year), BW the body weight (kg), and AT the averaging time (days).

TABLE 2

Pathway-specific probability density functions

Pathway	Distribution	Mean	Standard Deviation	Minimum	Maximum	Source
Tapwater ingestion						
Rate (L/day)	Uniform	—	—	0.4	2.2	[9]
Dermal contact						
Skin Surface (cm^2)	Normal	17,000[a]	1,000[a]	—	—	[7]
Shower Exposure Time (h/day)	Log-normal	0.11[b]	1.8[b]	—	—	[14]
Fraction of exposed skin (unitless)	Uniform	—	—	0.4	0.9	[6]
Inhalation						
Water Use Rates (L/h)						
Shower	Log-normal	460[b]	1.4[b]	—	—	[14]
House	Log-normal	37[b]	1.4[b]	—	—	[6]
Air Exchange Rates (m^3/h)						
Shower	Uniform	—	—	4	20	[6]
Bath	Uniform	—	—	10	100	[6]
House	Uniform	—	—	300	1200	[6]
Exposure Time (h/day)						
Shower	Log-normal	0.11[b]	1.8[b]	—	—	[6]
Bath	Log-normal	0.27[b]	1.8[b]	—	—	[6]
House	Uniform	—	—	8	20	[6]
Inhalation rate (m^3/h)	Uniform	—	—	0.21	0.74	[17]
Vegetable ingestion						
Rate (kg/day)	Log-normal	0.062[b]	1.8[b]	—	—	[7]
Fraction homegrown (%)	Empirical	—	—	18%	47%	[17]

[a] Arithmetic mean.
[b] Geometric mean.

The surface area of adult skin is taken to be normally distributed with a mean of 17,000 cm^2 and an arithmetic standard deviation of 1,000 cm^2, as reported in McKone's and Bogen study of household exposure models [7]. The permeability coefficient for each chemical is assigned a uniform distribution between 0.4 and 1.0 cm/h, based on the data reported by Brown et al. [13] for volatile contaminants. Based on data compiled by James and Knuiman [14], the duration of contact during showering is lognormally distributed with a geometric mean of 0.11 hour/day and a generic standard deviation of 1.8 hours/day [6]. The fraction of skin surface area in contact with water is taken to be

TABLE 3

Chemical-specific distributions

Parameter	Distribution	Geometric mean	Mode	Geometric standard deviation	Minimum	Maximum	Source
Dermal permeability coefficient (cm/h)							
PCE[a], Chloroform	Uniform	—	—	—	0.4	1.0	[13]
Transfer efficiency from water to shower air (unitless)							
PCE	Triangular	—	0.6	—	0.1	0.9	[6]
Chloroform	Triangular	—	0.6	—	0.1	0.9	[6]
Transfer efficiency from water to household air (unitless)							
PCE	Triangular	—	0.3	—	0.1	0.9	[6]
Chloroform	Triangular	—	0.3	—	0.1	0.9	[6]
Soil-water partition coefficient (L/kg)							
PCE	Triangular	—	2.4	—	0.0	34	[7]
Chloroform	Triangular	—	0.58	—	0.0	3.0	[7]
Plant-soil partition factor (unitless)							
PCE	Log-normal	0.59	—	4.0	—	—	[7]
Chloroform	Log-normal	2.8	—	4.0	—	—	[7]
Cancer potency factors $(mg/kg\text{-}day)^{-1}$							
PCE							
- oral and dermal	Empirical	5.1×10^{-2}	—	—	—	—	[18]
- inhalation	Empirical	1.8×10^{-3}	—	—	—	—	[18]
Chloroform							
- oral and dermal	Empirical	6.1×10^{-3}	—	—	—	—	[18]
- inhalation	Empirical	8.1×10^{-2}	—	—	—	—	[18]

[a] PCE = Tetrachloroethylene.

uniformly distributed between 0.4 and 0.9 [6]. All other factors are the same as described for tapwater ingestion.

Indoor inhalation from tapwater

Tapwater related sources of indoor air contaminants include baths, showers, toilets, dishwashers, cooking, and washing machines. It has been suggested that contaminant uptake via inhalation of VOCs in tapwater may exceed exposure via direct ingestion [6–15]. In this evaluation, we apply the assumptions of McKone and Bogen [6] and Fisk et al. [16] to estimate indoor air concentrations of tapwater contaminants using the following general equation:

$$C_{\mathrm{air}} = \frac{W_x \times \phi_x \times C_w}{VR_x} \tag{3}$$

where C_{air} is the contaminant concentrations in air (mg/m^3), W_x the water use rate (L/h), ϕ_x the transfer efficiency from water to air (unitless), C_w the contaminant concentration in water (mg/L), and VR_x the air exchange rate (m^3/h).

Following the example of McKone and Bogen [6], the contaminant concentrations in shower air, bathroom air, and household air are estimated using activity-specific estimates of water use rates and air exchange rates and chemical-specific estimates of water to air transfer efficiencies. Based on McKone and Bogen's [6] interpretation of the domestic water use data collected by James and Knuiman [14], the amount of water used during a shower (W_{shower}) is described by a log-normal distribution with a geometric mean of 460 L/h and a geometric standard deviation of 1.4 L/h; total household water use (W_{house}) is represented by a lognormal distribution with a geometric mean of 37 L/h and geometric standard deviation of 1.4 L/h. Air exchange rates in the shower, bathroom, and house (VR_{S}, VR_{B}, and VR_{H}, respectively) are based on the assumption that the volumes of these compartments are 2, 10, and 600 m^3, respectively, and that the number of air changes per hour ranges uniformly from 2–10 in the shower, 1–10 in the bathroom, and 0.5–2 in the house [6].

The dose associated with inhalation of indoor air is then calculated as follows:

$$Dose = \frac{[(C_{\mathrm{S}} \times ET_{\mathrm{S}}) + (C_{\mathrm{B}} \times ET_{\mathrm{B}}) + (C_{\mathrm{H}} \times ET_{\mathrm{H}})] \times IR \times EF \times ED}{BW \times AT} \tag{4}$$

where *Dose* is in mg/kg day, C_{S},C_{B},C_{H} are the contaminant concentrations in shower air, bathroom air, and household air, respectively (mg/m^3), ET_{S},ET_{B},ET_H are the the exposure time in the shower, bathroom, and the house respectively (h/day), *IR* is the inhalation rate (m^3/h), *EF* the exposure frequency (days/year), *ED* the exposure duration (years), *BW* the body weight (kg), and *AT* the averaging time (days).

The amount of time an individual spends in the bathroom (ET_{B}) is represented by a log-normal distribution with a geometric mean of 0.27 h/day and a geometric standard deviation of 1.8 h/day; the amount of time an individual spends in the house (ET_{H}) is taken to be a uniform distribution ranging from 8 to 20 h [6].

The transfer efficiency of tetrachloroethylene from tapwater to shower air has been estimated to be best represented by a triangular distribution with a range of 0.1–0.9 and mode of 0.6; the transfer efficiency for all other tapwater uses has been estimated to be described by a triangular distribution of 0.1–0.9 and a mode of 0.3 [6]. Transfer efficiencies for chloroform have not been similarly examined. However, given the similar physico-chemical characteristics of the VOCs in general, we assign the triangular distributions developed for tetrachloroethylene to chloroform (Table 3).

Inhalation rates during resting and light, moderate, and heavy activities have been measured in adults [17]. For the purposes of this evaluation, inhalation rates are taken to be uniformly distributed from 0.21–0.74 m^3/h. This range is based on the weighted arithmetic means of resting and light activity reported for adult males and females [17], and assumes a 14-h duration (mid-point of ET_H range) during which 8 h are spent sleeping and 6 h are engaged in light activity.

Garden vegetable ingestion

Contaminant uptake via garden vegetable ingestion, which can occur as a result of vegetable irrigation with tapwater, can be described by the following equation:

$$Dose = \frac{C \times SW \times PS \times IR \times FH \times CF \times EF \times ED}{BW \times AT} \qquad (5)$$

where *Dose* is in mg/kg day, *C* the chemical concentration in water (mg/L), *SW* the soil–water partition coefficient (L/kg), *PS* the plant–soil partition factor (unitless), *IR* the vegetable ingestion rate (kg/day), *FH* the fraction of ingested vegetables that are homegrown (unitless), *CF* the conversion factor (10^{-6} kg/mg), *EF* the exposure frequency (days/year), *ED* the exposure duration (years), *BW* the body weight (kg), *AT* the averaging time (days).

The soil–water partition coefficients for tetrachloroethylene and chloroform can be described as triangular distributions, based on the information presented in Salhotra et al. [7]. Table 3 summarizes the mode, minimum, and maximum values for each distribution. The plant–soil partition factors, which are lognormally distributed, are calculated from data presented by Salhotra et al. [7]. Adult vegetable ingestion rates, log-normally distributed with a geometric mean of 0.062 kg/day and a geometric standard deviation of 1.8 kg/day, are also calculated from presented in the 1991 Salhotra et al. report. Data collected by the U.S. EPA have estimated the fraction of consumed vegetables that are from homegrown sources in rural (47%), city (18%), suburban (29%), and all other areas (34%). For the purposes of this evaluation, these data are bootstrapped into the Monte Carlo analysis.

Cancer potency factors

The inhalation and oral cancer potency factors (*CPF*) are constants taken from U.S. EPA's Health Effects Assessment Summary Table [18]. For the purposes of this evaluation, the oral potency factor is used to estimate the cancer risk for the absorbed dermal dose. It is important to note that a great deal of uncertainty and conservatism are present in most potency factors, as they represent the upper 95th percent confidence limit (UCL) of the slope of the dose response curve generated by the cancer bioassay. Indeed, for some chemicals the conservatism in the potency factor may "drown out" or overwhelm the uncertainty and conservatism in the estimates of exposure and uptake. For the purposes of simplification, we use the *CPF*s provided by U.S. EPA.

Results and discussion

Using the @Risk™ computer program, the risk estimate equation ($Dose \times CPF =$ individual increased cancer risk) for each pathway was solved for 5,000 iterations. Figure 1 illustrates the distribution of total risk versus probability for tetrachloroethylene. Table 4 contains the 50th and 95th percentile values of risk for each pathway for each chemical. Total chemical-specific risks (all pathways summed for each chemical) are also presented. Total increased risks at the 50th percentile are 2.6×10^{-6} and 5.9×10^{-6} for tetrachloroethylene and chloroform, respectively; at the 95th percentile, increased cancer risks are 9.3×10^{-6} and 2.0×10^{-5}, respectively. As suggested by McKone and Bogen [6], the inhalation pathway "drives" the risk for both chemicals.

These estimated risks are well within the range of 'acceptable' risks typically established for Superfund sites (10^{-4} to 10^{-7}) [2]. Based on these results, it would seem that MCL concentrations of tetrachloroethylene or chloroform in drinking water are unlikely to pose a significant risk to a resident who uses

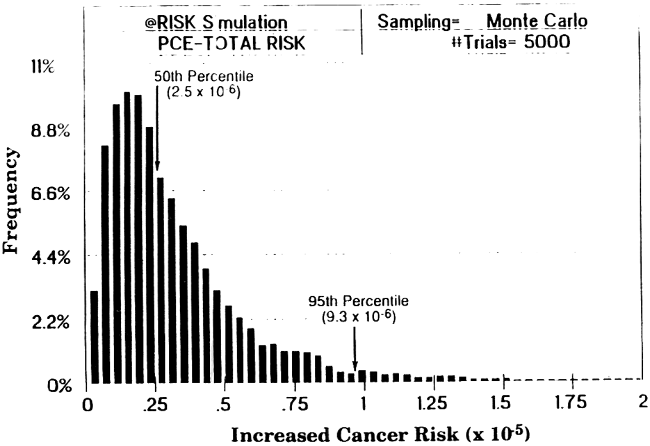

Fig. 1. Distribution of Total PCE risk.

TABLE 4

Estimated individual increased cancer risk

Chemical	Percentile	
	50th	95th
Tetrachloroethylene		
Tapwater ingestion	5.1×10^{-7}	2.8×10^{-6}
Dermal contact	3.4×10^{-7}	2.2×10^{-6}
Inhalation (indoor)	8.5×10^{-7}	6.7×10^{-6}
Vegetable ingestion	4.2×10^{-8}	9.9×10^{-7}
Total risk	2.6×10^{-6}	9.3×10^{-6}
Chloroform		
Tapwater ingestion	1.2×10^{-6}	6.5×10^{-6}
Dermal contact	7.9×10^{-7}	5.7×10^{-6}
Inhalation (indoor)	2.0×10^{-6}	1.6×10^{-5}
Vegetable ingestion	4.5×10^{-8}	1.2×10^{-6}
Total risk	5.9×10^{-6}	2.1×10^{-5}

tapwater as a source of drinking water and for showering, bathing, and garden irrigation. This limited analysis suggests that the "risk-based" remedial goals often implemented at hazardous waste sites might be unnecessarily low and that, at least in the case of tetrachloroethylene and chloroform, MCLs should be considered amply health-protective at most sites. It should be noted that these risk estimates are based on a refinement of exposure assessment *only*; using the probabilistic approach to address pharmacokinetics and cancer potency would likely result in lower estimates of health risk. An important issue in this analysis is how one defines compliance with a clean-up level. For example, is compliance achieved when 95% of the samples are less than the MCL or must each of them be less than that value? Perhaps the best approach to define compliance is to input each sample value into the PDF of water concentrations and routinely check to be sure that the estimated risk remains acceptable.

In this analysis, we specifically address cleanup goals for contaminated groundwater at hazardous waste sites wherein the groundwater may be used as a drinking water source. This implies a finite duration of exposure, as Bureau of the Census studies have shown that most individuals spend far less than a full lifetime in a single residence [11]. For the purposes of evaluating acceptable levels in a public drinking water system, which may be a lifetime drinking water source, it would be inappropriate to assume a less than lifetime exposure.

Case examples such as these are useful for illustrating the conservatism and uncertainty inherent in most risk assessments being performed today. The

Monte Carlo analysis provides the assessor a way to examine the conservatism present in the default point estimate approach and provides a full distribution of risk estimates to risk managers and the public. As stated by Burmaster and Lehr [5]. "We see a way to re-introduce science and fact into risk assessment calculations. The Monte Carlo method gives us a way to distinguish once again risk assessment from risk management." We concur and suggest that the probabilistic approach to exposure and risk assessment be implemented to the fullest extent possible in the coming years. We believe that this refinement will help ensure that our financial resources are properly apportioned to the most pressing environmental and social problems which America faces.

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Chlorinated solvents in groundwater: Field experimental studies of behaviour and remediation*

John A. Cherry

Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, N2L 3G1 (Canada)

Abstract

The chlorinated solvents, such as trichloroethylene, tetrachloroethylene, trichloroethane and methylene chloride have a combination of physical and chemical properties that give them exceptional propensity to cause groundwater contamination. These solvents have been in widespread use in manufacturing and cleaning industries since World War II. Although somewhat diminished in the past decade, industrial use of solvents is still large. Solvents are now one of the most common causes of significant groundwater contamination in industrialized regions of North America and Europe. Because of the importance of chlorinated solvents as an environmental problem and because little was known or understood about the subsurface fate, transport and remediation of these contaminants, the University Consortium Solvents-In-Groundwater Research Program was started in 1988 by a group of universities in Canada and the United States.

Introduction

The University of Waterloo (the lead institution), Colorado State University and the Oregon Graduate Institute are the principal institutions involved in many aspects of the Research Program. The Research Program also has specific collaborative projects with various other institutions including the State University of New York at Buffalo, Queen's University (Ontario), the University of Western Ontario, Stanford University, and the U.S. Geological Survey.

The main thrusts of the current work are the development and assessment of technologies for in situ subsurface remediation of chlorinated solvents above and below the water table; the use of advanced geophysical methods (surface geophysics and borehole geophysics) and mathematical models to assess the spatial distribution of liquid-phase solvents below the water table and progress

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Correspondence to: J.A. Cherry, Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, N26 361 (Canada). Fax: (519) 746-5644.

of *in situ* site remediation methods; and the characterization of D-NAPL (denser-than-water non-aqueous phase liquid) transport, distribution and fate in fractured environments.

Emerging technologies

Emerging technologies are technologies that have been in existence for several years but their performance and limitations warrant assessment. Of the many emerging *in situ* technologies that currently exist, the following are the focus of study:

(i) removal of solvents from the vadose and interface zones by vacuum extraction and soil flushing

(ii) removal of free-phase solvents from the groundwater zone by wells and drains with and without chemically induced interfacial-tension reduction by surfactants

(iii) removal of immiscible phase solvents from the groundwater zone by enhanced solubilization induced by surfactant flushing

New technologies

These remedial technologies have been invented by researchers at universities in the Solvent Research Program and are being assessed in the Solvent Research Program. These technologies are unique to the Research Program:

(iv) passive permeable dehalogenation wall for plume cutoff

(v) void-space air sparge wall for plume cutoff

(vi) permeable bioremediation dispersion wall for nearly passive plume cutoff

(vii) destruction of immiscible-phase solvents by chemical oxidant flushing

(viii) control of solvent contamination areas using sealable-joint steel sheet piling.

The emerging and new technologies are studied through a combination of laboratory experiments, field experimental and mathematical models. Most field experiments are conducted on a relatively large scale in an actual sand aquifer located at Canadian Forces Base Borden in Alliston, Ontario, 75 km northwest of Toronto. In these large field-scale groundwater experiments, many of the difficulties and complications that occur at actual industrial sites are represented. Therefore, the experiments have considerable site realism and yet can be controlled very effectively to allow for quantitative scientific assessment.

At the Borden site, unique field experiments involving controlled release or subsurface emplacement of immiscible-phase chlorinated solvents such as tetrachloroethylene and trichloroethylene into an unconfined sand aquifer are in progress. In the initial stages, these experiments allow the movement of the immiscible-phase solvent liquid and dissolved-phase plumes emanating from the liquid to be studied using various monitoring methods and mathematical models. In later stages, the experiments are used to assess *in situ* technologies for restoration of the contaminated aquifer zones. These experiments are full-cycle experiments in the sense that solvents are introduced to the groundwater zone, their behaviour is studied, and ultimately the solvent mass is removed using *in situ* methods. Of the eight emerging or experimental technologies listed above, six have field trials in progress in addition to associated laboratory studies completed or in progress. The two technologies not yet in field trials are scheduled for trials in 1992.

The Research Program includes fundamental experimental and mathematical modelling pertaining to the behaviour of aqueous-phase and gaseous-phase solvents in the vadose zone and the mechanisms by which solvents in the vadose zone cause contamination of the interface zone at the water table. This research also considers avenues for remediation of the interface zone, which is a particularly difficult remediation task because of the conditions at the capillary fringe.

Experiments at the Borden site involving release of free-phase solvents into the aquifer have been made feasible by creation of impervious cells, which are aquifer segments surrounded by vertical cutoff walls. The walls are constructed of sealable-joint steel sheet pile (referred to as Waterloo sheet piling). The joints on conventional sheet piling have been modified (patent pending) to allow water-tight sealants to be injected into the joints after the walls are driven through the sand aquifer into the underlying clay aquitard. Double-walled cells have been installed for maximum environmental protection. The aquifer segments inside the cells are well suited for performance assessments of new or emerging *in situ* technologies for aquifer restoration. Research is directed at determining what cleanup levels are achievable and developing an understanding of what factors enhance or limit technology performance for various remediation technologies.

Waterloo sheet piling was developed to provide environmentally safe conditions for major experiments involving solvent releases to the Borden aquifer. Through success in this research use, possibilities for scaling-up this technology for application to real industrial or waste disposal sites were recognized. Scaled-up feasibility studies are now underway. The technology has several advantages over conventional cutoff walls. Recently, the barrier has been tested to a depth of 47 feet (14 m) at CFB Borden.

The Waterloo barrier provides a contained subsurface environment for the solvent release experiments, and subsequent aquifer restoration research, and also provides a means for installing *in situ* treatment walls in the Borden aquifer. An *in situ* treatment wall is a vertical wall of permeable material (a narrow trench) placed across a plume. The purpose of the wall is to induce processes, usually chemical or biochemical reactions, that remove contaminants from the plume so that the plume, in effect, is cut off by the wall. To construct a treatment wall the sheet piling cell is driven into the aquifer across or in front of the plume, the cell is dewatered, the aquifer material is removed and replaced with a new reactive material, or with a material or void space of much higher permeability suitable for hydraulic manipulation or air sparging. The sheet piling is then removed from the ground.

The first *in situ* treatment wall to be assessed in the field is a dehalogenation wall. The dehalogenation wall, incorporating catalysed abiotic dehalogenation of chlorinated organics, is currently being evaluated in the remediation and control of a contaminant plume emanating from an emplaced mass of three solvents (TCE, PCE, and TCM) at the Borden site. A biodegradation dispersion wall, which allows for the creation of conditions favourable for the biodegradation of organic contaminants in the subsurface within and downgradient of the wall, is also in place at the Borden site awaiting the start-up of an experiment. An air sparge wall is being designed; the wall will facilitate the introduction of air to a groundwater-zone plume contaminated with volatile organic compounds, with the intent of stripping the VOCs from the plume as it passes through the wall, without disturbance to the plume by pumping. When successful, *in situ* treatment walls offer advantages such as less wastage of clean water and energy and lower long-term cost.

Conclusion

The Borden site is a convenient facility, both with regard to logistics and degree of hydrogeologic complexity, for conducting prototype-scale remediationresearch. If a new or emerging remediation technology cannot be made to function successfully at the Borden site, it can usually be concluded that the technology is not sufficiently advanced for success to be achieved elsewhere.

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Evaluation of soil venting application*

Dominic C. DiGiulio

Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA)

Abstract

This paper discusses performance limitations and containment removal optimization of soil venting technology when remediating a VOC contaminated site. Presented herein is a discussion of influential soil venting performance parameters such as containment volatility, mass transfer, and air permeability. The significance of these and other factors including placement of extraction and observation wells as related to site characterization, field tests and actual remediation projects is considered.

Introduction

The ability of soil venting to inexpensively remove large amounts of volatile organic compounds (VOCs) from contaminated soils is well established. However, the time required using venting to remediate soils to low contaminant levels often required by state and federal regulators has not been adequately investigated. Most field studies verify the ability of a venting system to circulate air in the subsurface and remove, at least initially, a large mass of VOCs. They do not generally provide insight into mass transport limitations which eventually limit performance, nor do field studies generally evaluate methods such as enhanced biodegradation which may optimize overall contaminant removal. Discussion is presented to aid in evaluating the feasibility of venting application. Methods to optimize venting application are also discussed.

Determining contaminant volatility

The first step in evaluating the feasibility of venting application at a hazardous waste site is to assess contaminant volatility. If concentrations of VOCs in soil are relatively low and the magnitude of liquid hydrocarbons present in

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Correspondence to: D.C. DiGiulio, Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA). Fax: (405)332-8800.

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the soil is negligible, VOCs can be assumed to exist in a three-phase system (i.e., air, water, and soil), as illustrated in Fig. 1. The mass ratio of VOCs in the vapor phase to total soil mass can be estimated by:

$$\frac{C_g\phi}{C_t}=\frac{\phi}{(P_g K_{oc} f_{oc}/K_h)+\theta/K_h+\phi} \tag{1}$$

where C_g denotes the vapor concentration of VOCs in gas phase(mg/cm^3 air), C_t the total volatile organic concentration (mg/cm^3 soil), P_g the bulk density (g/cm^3), K_{oc} the organic carbon–water partition coefficient (cm^3/g), f_{oc} the fraction of organic carbon content (g/g), K_h is Henry's constant (mg/cm^3 air/mg/cm^3 water), θ is the volumetric moisture content (cm^3/cm^3), and ϕ the volumetric air content (cm^3/cm^3).

Caution must be exercised when using this approach since this relationship is based on the assumption that solid phase sorption is dominated by natural organic carbon content. This assumption is frequently invalid in soils below the root zone where soil organic carbon is less than 0.1%.

Equation (1) can be used to evaluate individual VOC contaminant reduction trends and attainment of soil-based remediation standards. Vapors should be collected from dedicated vapor probes under static (venting system not operating) conditions. This estimate is valid only for soils in the immediate vicinity of the probe intake. This approach minimizes sample dilution and collection of vapor samples under nonequilibrium conditions. It, however, necessitates periodic cessation of venting. When the vapor concentration for a VOC approaches a corresponding total soil concentration, actual soil samples can be collected to confirm remediation. This approach has several benefits over conventional soil samples collection and analysis. At lower VOC concentration levels, collection of static vapor samples is likely more sensitive than soil collection and analysis due to VOC loss in the latter procedure. Siegrist and Jenssen [1] demonstrated substantial VOC loss during normal soil sample collection, storage, and analysis. Also, comparing contaminant reduction trends strictly with soil samples is difficult due to spatial variability in soils. No two soil samples can be collected at the exact same location. In addition, soil gas analyses can be accomplished more quickly and inexpensively than soil sample collection, thus enabling more frequent evaluation of trends. A potential disadvantage of using this approach is inability to distinguish VOC vapors emanating from soils as opposed to ground water. Hypothetically, soils could be remediated to desired levels with probes still indicating contamination above remediation standards. This concern could be alleviated to some degree by

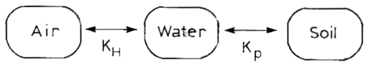

Fig.1. Three-phase system. K_p is the soil-water partition coefficient, and K_H Henry's constant.

determining the presence of a diffusion vapor gradient from the water table using vertically placed vapor probes.

If soils are visibly contaminated or the presence of non-aqueous phase liquids (NAPLs) is suspected in soils based on high contaminant, total organic carbon, or total petroleum hydrocarbon analysis, contaminants are likely present in a four phase system as illustrated in Fig. 2. Under these circumstances, most of the VOC mass will be associated with the immiscible fluid and assuming that the fluid acts as an ideal solution, volatilization will be governed by Raoult's Law.

$$P_a = X_a P_a^o \qquad (2)$$

where P_a is the vapor pressure of component over solution (mmHg), X_a the mole fraction of component in solution, and P_a^o the saturated vapor pressure of pure component (mmHg).

In a four-phase system, contaminant volatility will be governed by the VOC's vapor pressure and mole fraction within the immiscible fluid. The vapor pressure of all compounds increases substantially with an increase in temperature while solubility in a solvent phase is much less affected by temperature. This suggests that soil temperature should be taken into account when evaluating VOC recovery for contaminants located near the soil surface (seasonal variations in soil temperature quickly dampen with depth). For instance, if conducting a field test to evaluate potential remediation of shallow soil contamination in the winter, one should realize that VOC recovery could be substantially higher during summer months, and low recovery should not necessarily be viewed as venting system failure.

As venting proceeds, lower molecular weight organic compounds will preferentially volatilize and degrade. This process is commonly described as weathering and has been examined by Johnson [2] in laboratory experiments. Samples of gasoline were sparged with air and the concentration and composition of vapors were monitored. The efficiency of vapor extraction decreased to less than 1%of its initial value even though approximately 40% of the gasoline remained. Theoretical and experimental work on product weathering indicate

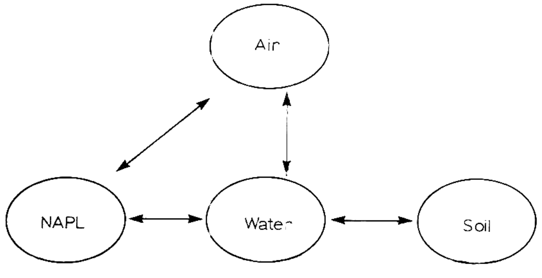

Fig.2. Four-phase system.

the need to monitor temporal variation in specific VOCs of concern in extraction and observation wells.

Evaluating air flow

Air permeability (k_a) in soil is a function of a soil's intrinsic permeability (k_i) and liquid content. At hazardous waste sites, liquid present in soil pores is often a combination of soil water and immiscible fluids. Air permeability (k_a) can be estimated by multiplying a soil's intrinsic permeability (k_i) by the relative permeability (k_r).

$$k_a = k_i k_r \tag{3}$$

The dimensionless ratio k_r varies from one to zero and describes the variation in air permeability as a function of air saturation. Equations developed by Brooks and Corey [3] and Van Genuchten [4] are useful in estimating air permeability as a function of air saturation or liquid content. The Brooks–Corey equation to estimate relative permeability of a non-wetting fluid (i.e. air) is given by:

$$K_r = (1-S_e)^2\left(1-S_e^{\frac{2+\lambda}{\lambda}}\right) \tag{4}$$

where S_e denotes the effective saturation, and λ is a pore distribution parameter.

The effective saturation is given by:

$$S_e = \frac{\left(\frac{\theta}{\epsilon} - S_n\right)}{(1-S_n)} \tag{5}$$

where θ is the volumetric moisture content, ϵ the total porosity, and S_n the residual saturation.

The pore size distribution parameter and residual water content can be estimated using soil–water characteristic curves which relate matric potential to volumetric water content. When initially developing an estimate of relative permeability for a given soil texture and liquid content, values for ϵ, S_n, S_e, and λ can be obtained from the literature. Rawls et al. [5] summarized geometric and arithmetic means for Brook-Corey parameters for various USDA soil textural classes. Figure 3 illustrates relative permeability as a function of volumetric moisture content for clayey soils assuming $\epsilon = 0.475$, $S_n = 0.090$, and $\lambda = 0.131$.

The most effective method of measuring air permeability is by conducting a field pneumatic pump test. Cho and DiGiulio [9] have demonstrated a method for determining pneumatic permeability in the field. Using permeameters or other laboratory measurements provide information on a relatively small scale. Information gained from pneumatic pump tests is vital in determining site-

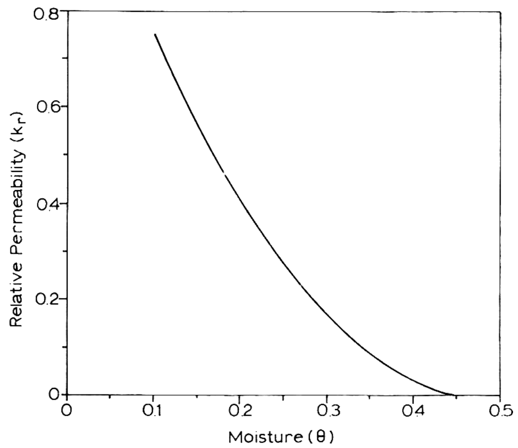

Fig.3. Relative permeability vs. moisture content of clay.

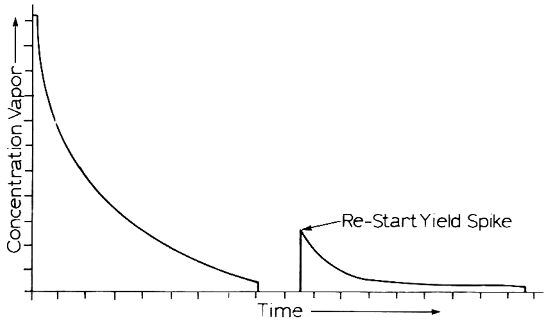

Fig.4. Vapor concentration vs. time plot.

specific design considerations (e.g., spacing of extraction wells). Selecting the placement and screened intervals of extraction and observation wells and applied vacuum rates during a pump test is often based on preliminary mathematical modeling.

Evaluating mass transfer limitations and remediation time

The effects of mass transport limitations are usually manifested by a substantial drop in soil vapor contaminant concentrations as illustrated in Fig. 4 or by an asymptotic increase in total mass removal with operation time. Typically, when venting is terminated, an increase in soil gas concentration is observed over time. Slow mass transfer with respect to advective air flow is most likely caused by diffusive release from porous aggregate structures or lenses of lesser permeability as illustrated in Fig. 5. The time required for the remediation of heterogeneous and fractured soils depends on the proportion of contam-

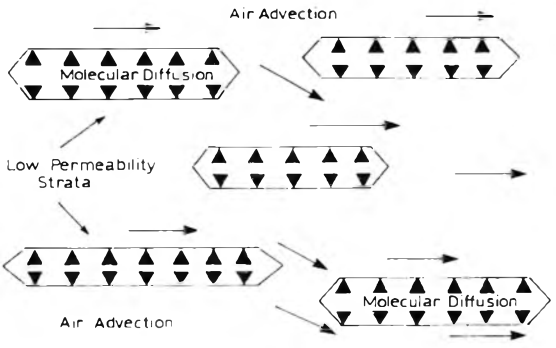

Fig.5. Schematic of soil mass transfer limitations.

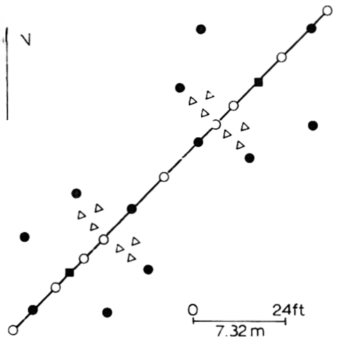

Fig.6. Proposed pilot test design. (○) Venting probe cluster, (●) passive inlet well, (■) vent well, and (△) borehole sampling locations.

inated material exposed to direct bulk airflow. It would be expected that long-term performance of venting will be limited to a large degree by gaseous and liquid diffusion from soil regions not exposed to direct airflow.

Regardless of possible causes, the significance of mass transport limitations should be evaluated during venting field tests. This can be achieved by pneumatically isolating a small area of a site and aggressively applying vacuum extraction until mass transport limitations are realized. Isolation can be achieved by surrounding extraction wells with air injection wells as shown in Fig. 6. Experience has shown that pneumatic isolation is best achieved using air injection wells vs. passive inlet wells. Inability to effectively pneumatically isolate a study area will ruin efforts in studying mass transport because of uncontrolled migration of vapors into the study area. Quantifying the effects of mass transport limitations on remediation time might then be attempted by utilizing models incorporating mass transfer rate coefficients.

The discrepancy frequently observed between mass removal predicted from equilibrium conditions using Henry's Law constants and that observed from laboratory column and field studies is sometimes reconciled by the use of "effective or lumped" soil–air partition coefficients. These parameters are determined from laboratory column tests and are then used for model input to determine required remediation times. While this method does indirectly account for mass transport limitations, problems may arise when one attempts to quantitatively describe several processes with lumped parameters. The primary concern is whether the lumped parameter is suitable for use only under the laboratory conditions from which it was determined, or whether it can be transferred for modeling use in the field. Perhaps the most direct method of accounting for mass transport limitations would be to incorporate diffusive transfer directly into convective-dispersive vapor transport models.

Enhanced aerobic biodegradation

With the exception of a few field research projects, soil vacuum extraction has been applied primarily for removal of volatile organic compounds from the vadose zone. However, circulation of air in soils can be expected to enhance the aerobic biodegradation of both volatile and semivolatile organic compounds. One of the most promising uses of this technology is in manipulating subsurface oxygen levels to maximize *in situ* biodegradation. Bioventing can reduce vapor treatment costs and can result in the remediation of semivolatile organic compounds which cannot be removed by physical stripping alone.

Venting circulates air in soils at depths much greater than are possible by tilling, and oxygen transport via the gas phase is much more effective than injecting or flooding soils with oxygen saturated liquid solutions.

Hinchee [6] described the use of soil vacuum extraction at Hill AFB, Utah for oxygenation of the subsurface and the enhancement of biodegradation of petroleum hydrocarbons in soils contaminated with JP-4 jet fuel. Figures 7 and 8 illustrate subsurface oxygen profiles at the Hill site prior to and during venting. It is evident that soil oxygen levels dramatically increased following one

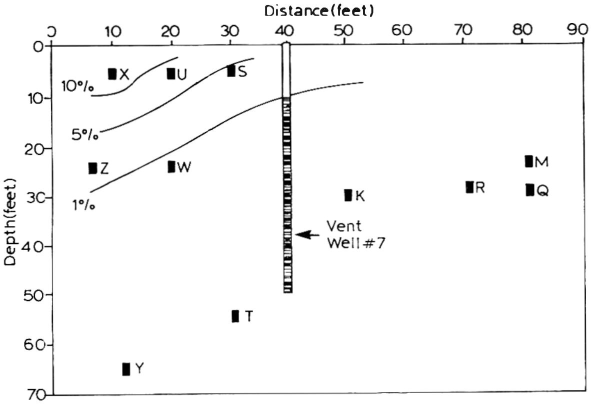

Fig.7. Oxygen concentration in vadose zone before venting.

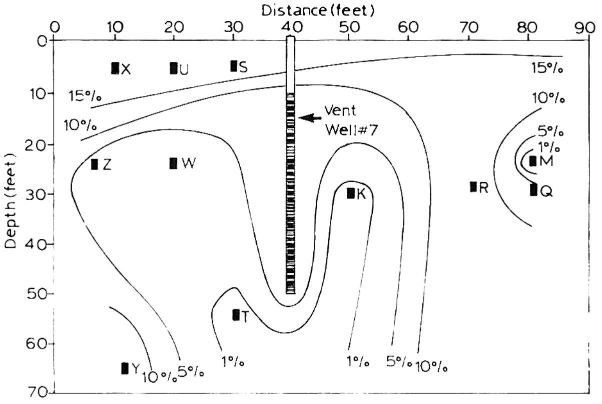

Fig.8. Oxygen concentration in vadose zone after venting.

week of venting. Soil vapor samples collected from observation wells during periodic vent system shutdown revealed rapid decreases in oxygen concentration and corresponding CO_2 production suggesting that aerobic biodegradation was occurring at the site. Laboratory treatability studies using soils from the site demonstrated increased carbon dioxide evolution with increasing moisture content when enriched with nutrients. It is worthwhile to note that soils at Hill AFB were relatively dry at commencement of field vacuum extraction indicating, that the addition of moisture could perhaps stimulate aerobic biodegradation even further under field operating conditions.

When conducting site characterization and field studies, it is recommended that CO_2 and O_2 levels be monitored in soil vapor probes and extraction well offgas to allow the assessment of basal soil respiration and the effects of site management on subsurface biological activity. These measurements are simple and inexpensive to conduct and can yield a wealth of information regarding:

(1) The mass of VOCs and semivolatiles which have undergone biodegradation versus volatilization. This information is crucial if subsurface conditions (e.g., moisture content) are to be manipulated to enhance biodegradation to reduce VOC offgas treatment costs and maximize semivolatile removal.

(2) Factors limiting biodegradation. If O_2 and CO_2 monitoring reveals low O_2 consumption and CO_2 generation while readily biodegradable compounds persist in soils, further characterization studies could be conducted to determine if biodegradation is being limited by insufficient moisture content, toxicity (e.g. metals), or nutrients.

(3) Subsurface air flow characteristics. Observation wells which indicate persistent, low O_2 levels may indicate an insufficient supply of oxygenated air at that location suggesting the need for air injection, higher extraction well vacuum, additional extraction wells, or additional soils characteri-

zation which may indicate high moisture content or the presence of immiscible fluids impeding the flow of air.

Location and number of vapor extraction wells

One of the primary objectives in conducting a venting field test is to evaluate the initial placement of extraction wells to optimize VOC removal from soil. Placement of extraction wells and selected applied vacuum is largely an iterative process requiring continual re-evaluation as additional data are collected during remediation. Vacuum extraction wells produce complex three-dimensional reduced pressure zones in affected soils. The size and configuration of this affected volume depends on the applied vacuum, venting geometry (e.g., depth to water table), soil heterogeneity, and intrinsic (e.g., permeability) and dynamic (e.g., moisture content) properties of the soil. The lateral extent of this reduced pressure zone (beyond which static vacuum is no longer detected) is often termed the radius or zone of influence (ROI). Highly permeable sandy soils typically exhibit large zones of influence and high air flow rates whereas less permeable soils, such as silts and clays, exhibit smaller zones of influence and low air flows.

Measured or anticipated radii of influence are often used to space extraction wells. For instance, if a ROI is measured at 10 feet, extraction wells are placed 20 feet apart. However, this strategy is questionable since vacuum propagation and air velocity decrease substantially with distance from an extraction well. Thus, only a limited volume of soil near an extraction well will be effectively ventilated regardless of the ROI. Johnson [7] describes how the addition of 13 extraction wells within the ROI of other extraction wells increased blower VOC concentration by 4000 ppmv and mass removal by 40 kg/day. They concluded that the radius of influence was not an effective parameter for locating extraction wells and that operation costs could be reduced by increasing the number of extraction wells as opposed to pumping at higher rates with fewer wells. Cho and DiGiulio [9] discuss limitations to using the ROI as a design parameter.

Determining the propagation of induced vacuum requires conducting pneumatic pump tests in which variation in static vacuum is measured in vapor observation wells at depth and distance from extraction wells. Locating extraction and observation wells along transects as illustrated in Fig. 4 minimizes the number of observation wells necessary to evaluate vacuum propagation at linear distances from extraction wells. Pressure differential can be observed at greater distances than would otherwise be possible in other configurations.

Propagation of vacuum in soils as a function of applied vacuum can be determined by conducting pneumatic pump tests with incrementally increasing flow or applied vacuum. Vacuum is increased after steady state conditions (relatively constant static vacuum measurements in observation wells) exist in soils from the previously applied vacuum. A step pump test will indicate a significant increase in static vacuum or air velocity with increasing applied vacuum near an extraction well. However, at distance from an extraction well, a significant increase in static vacuum will not be observed with an increase in applied vacuum. Pneumatic pump tests allow determination of radial distances from extraction wells in which air velocity is sufficient to ensure remediation.

After the initial placement of extraction wells has been established based on the physics of air flow, an initial applied vacuum must be selected to ensure optimal VOC removal. In regard to mass transfer considerations, the vent rate should be increased if a significant corresponding mass flux is observed. Even though an increased venting rate may not substantially increase the propagation of vacuum with distance, air velocity will increase near the extraction well. If most contaminants are in more permeable deposits, an increase in applied vacuum will increase mass removal eventually to a point of diminishing returns or until the system is limited by diffusion. Note that this strategy is for optimization of volatilization not biodegradation. Optimizing *in situ* biodegradation often necessitates reducing air velocity in soil. As a result, vapor treatment costs are minimized but overall mass flux decreases. Thus, *in situ* biodegradation of VOCs minimizes overall costs but may extend venting operation time.

During a field test, it is desirable to operate until mass transport limitations are realized in order to evaluate the long term performance of the technology. This can be achieved by isolating small selected areas of a site by the use of air injection wells. When attempting to evaluate diffusion limited mass removal in isolated areas, applied vacuum should remain high and the distance between passive inlet and extraction wells should be minimized. Too often, venting field tests are conducted for relatively short periods of time (e.g., 2–21 days) which only results in assessment of air permeability and initial mass removal. Longer field studies (e.g., 6–12 months) enable better insight into mass transfer limitations which eventually govern venting effectiveness.

Screened interval

The screened interval of extraction wells will play a significant role in directing air flow through contaminated soils. Minimum depths are recommended by some practitioners for venting operation to avoid short-circuiting of air flow. However, the application of venting need not be limited by depth to water table since horizontal vents can be used in lieu of vertically screened extraction wells to remediate soils with shallow contamination. Often, it is desirable to dewater contaminated shallow aquifer sediments for venting application. For remediation of more permeable soils with deep contamination, an extraction well should be screened at the maximum depth of contamination or to the seasonal low water table, whichever is shallowest, to direct air flow and reduce short-circuiting. For less permeable soils, or for more continuous vertical contamination, a higher and longer screened interval may be useful.

In stratified systems, such as in the presence of clay layers between more permeable deposits, more than one well will be required, each venting a distinct strata. Screening an extraction well over two strata of significantly different permeability will result in most air flow being directed only in the strata of greater permeability. It is important to screen extraction wells over the interval of highest soil contamination to avoid extracting higher volumes of air at lower vapor concentration.

During venting, the reduced pressure in the soil will cause an upwelling of the water table. The change in water table elevation can be determined from the predicted radial pressure distribution. Johnson et al. [8] indicated that upwelling can be significant under typical venting conditions. Water table rise will cause contaminated soil lying above the water table to become saturated, resulting in decreased mass removal rates. Ground water upwelling due to venting system operation can be minimized with concurrent water table dewatering.

Placement of observation wells

Observation wells are essential in determining whether contaminated soils are being effectively ventilated and in the evaluation of interactions among extraction wells. The more homogeneous and isotropic the unsaturated medium, the fewer the number of vapor monitoring probes required. To adequately describe vacuum propagation during a field test, usually at least three observation well clusters are needed. At least one of these clusters should be placed near an extraction well because of the logarithmic decrease in vacuum with distance. The depth and number of vapor probes within a cluster depends on the screened intervals of extraction wells and soil stratigraphy. However, vertical placement of vapor probes might logically be near the soil–water table interface, soil horizon interfaces, and near the soil surface. As previously mentioned, the use of air flow modeling can assist in optimizing the depth and placement of vapor observation wells and in the interpretation of data collected from these monitoring points.

When constructing observation wells it is desirable to minimize vapor storage volume in the screened interval and sample transfer line. This will minimize purging volumes and ensure a representative vapor sample in the vicinity of each observation well. Analysis of soil gas in an on-site field laboratory is preferred to provide real time data for implementation of engineering controls and process modifications. It is recommended that steel canisters, sorbent tubes, or direct GC injection be used in lieu of Tedlar bags when possible because of potential VOC loss through bag leakage or diffusion within the teflon material itself. This problem may lead to erroneous analytical results and the potential of a false negative indication of soil remediation at low soil gas concentrations.

Summary and conclusions

While the application of soil vacuum extraction is conceptually simple, its success depends on understanding complex subsurface physical, chemical, and biological processes which provide insight into factors limiting venting performance. Optimizing venting performance is critical when attempting to meet stipulated soil-based clean-up levels required by regulators. The first step in evaluating a venting application is to assess contaminant volatility. Volatility is a function of a contaminant's soil–water partition coefficient and Henry's constant if present in a three-phase system, and a contaminant's vapor pressure and mole fraction in an immiscible fluid, if present in a four phase system. Volatility is greatly decreased when soils are extremely dry. As vacuum extraction proceeds, lower molecular weight organic compounds preferentially volatilize and biodegrade. Decreasing mole fractions of lighter compounds and increasing mole fractions of heavier compounds affect observed offgas concentrations. Understanding contaminant volatility is necessary when attempting to utilize offgas vapor concentrations as an indication of venting progress.

The significance of mass transport limitations should be evaluated during venting field tests. Long term performance of venting will most likely be limited by diffusion from soil regions of lesser permeability which are not exposed to direct airflow. Mass transport limitations can be assessed by isolating a small area of a site and aggressively applying vacuum extraction. Simplistic methods to evaluate remediation time should be avoided. One of the most promising uses of vacuum extraction is in manipulating subsurface oxygen levels to enhance biodegradation. When conducting field studies, it is recommended that CO_2 and O_2 levels be monitored in vapor probes to evaluate the feasibility of VOC and semivolatile contaminant biodegradation.

Air permeability in soil is a function of a soil's intrinsic permeability and liquid content. Relative permeability of air can be estimated using relationships developed by Brooks and Corey [3] and Van Genuchten [4]. The most effective method of measuring air permeability is by conducting pneumatic pump tests. Information gained from pneumatic pump tests can be used to determine site-specific design considerations such as the spacing of extraction wells. Measured or anticipated zones of influence are not particularly useful in spacing extraction wells. Extraction wells should be located to maximize air velocity in contaminated soils. Pneumatic pump tests with increasing applied vacuum may be useful in determining radial distances from extraction wells in which air velocity is sufficient to ensure remediation. Screened intervals should be located at or below the depth of contamination. In stratified soils, more than one well is necessary to ventilate each strata. At least three observation well clusters are usually necessary to observe vacuum propagation within the radius of influence of an extraction well. Logical vertical placement of vapor probes might be near the soil–water table interface, soil horizon interfaces, and near the soil surface.

Disclaimer

This paper does not necessarily reflect the views of the U.S. Environmental Protection Agency.

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Modeling contaminant transport through subsurface systems*

R.J. Charbeneau[a] and J.W. Weaver[b]

[a]*Center for Research in Water Resources, Balcones Research Center #119, University of Texas, Austin, TX 78712 (USA)*
[b]*Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA)*

Abstract

Modeling of contaminant transport through soil to groundwater to a receptor requires that consideration be given to the many processes which control the transport and fate of chemical constituents in the subsurface environment. These processes include volatilization, degradation, sorption and multiphase partitioning, leaching, advection and dispersion. Mathematical models for simulation of these processes may require significant data inputs. This paper reviews the important factors involved in modeling of subsurface transport as well as the data requirements and uncertainties. An application of a hydrocarbon spill screening model is presented.

Introduction

An understanding of the factors that affect the fate and transport of contaminants in the unsaturated soil and in groundwater, and the ability to develop and apply mathematical models which include these factors, is important for many applications. This understanding is necessary for determining the assimilative capacity of a soil and whether chemicals are likely to accumulate within the soil profile or leach to contaminate groundwater. An understanding of these factors will help identify suitable remediation methods and proper land disposal sites. The factors determine what happens to chemicals under closure conditions and how to avoid groundwater contamination. The models may be used to determine the type and quantity of air emissions that may occur, the necessity and immediacy of remedial action, and potential exposure concentrations at receptor points. The factors and processes that are important include those that affect losses, retardation, solubility, and transport. For

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Correspondence to: R.J. Charbeneau, Center for Research in Water Resources, Balcones Research Center #119, University of Texas, Austin, TX 78712 (USA).

protection of public health and the environment, particularly groundwater, it is desirable to enhance losses and retardation.

The objective of this manuscript is to review the important factors involved in modeling of contaminant transport through soil to groundwater to a receptor. The important processes are discussed, as are the uncertainties and the data that one needs to know or have. In addition, the application of models, and their value and limitations are discussed with reference to a screening model for hydrocarbon spills.

Factors and processes that affect transport

Figure 1 shows a schematic view of the processes that affect the subsurface fate and transport of chemical constituents. The figure shows a near-surface source of contamination such as a spill, landfill, or storage tank. Some of the chemical may be immobilized within the source zone. The remainder is free for transport through one of the mobile phases. Multiphase partitioning determines how much of the chemical constituent will reside in each phase. From the vapor phase the chemical is lost to the atmosphere by the process of volatilization. The soluble components may be leached from the source zone by infiltrating water. The rate of movement of the chemicals during leaching may be significantly less than the rate of water movement if the chemicals are significantly sorbed on the soil, or partitioned into an immobile hydrocarbon phase which may be present. In the source zone and during transport, some of the chemical may be lost due to degradation, either of biotic or abiotic origin. If the losses and retardation are not sufficient, then some of the chemical will reach the water table and be transported with groundwater flow to potential points of exposure. The goals of modeling subsurface transport include prediction of exposure concentrations and evaluation of the relative importance of the various processes and parameters which control this subsurface transport and fate.

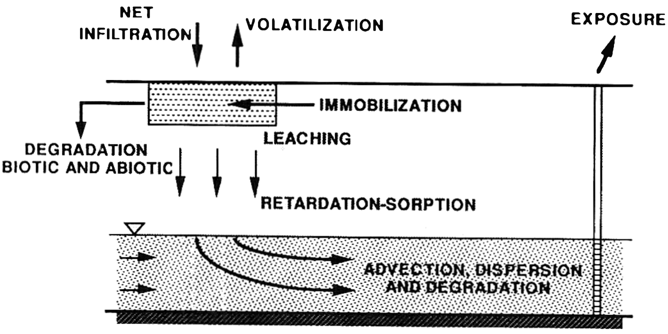

Fig. 1. Processes which influence the subsurface fate and transport of chemicals.

Multiphase partitioning

Investigations of fate and transport of chemicals in the unsaturated zone must inherently deal with a multiphase system consisting of water, air, and soil. In addition, for certain applications such as spills, leaking tanks, or land treatment of petroleum hydrocarbons, there also is a separate non-aqueous phase present. The pore space must be filled by the sum of the fluids present so

$$n=\theta_w+\theta_a+\theta_o \tag{1}$$

where n is the porosity, θ_i is the ith phase volumetric content, and the subscripts refer to water, air, and non-aqueous phase liquid (NAPL) or "oil". Individual chemical constituents will partition themselves amongst the various phases according to thermodynamic equilibrium principles (same activity in each phase) and kinetic factors. The majority of the models in use are based on the assumption of local equilibrium and/or solubility controls. The concentrations of a constituent in the three fluid phases are designated c_w, c_a, and c_o, all on a mass per unit volume basis. The soil phase concentration is specified as mass sorbed per mass of soil and is designated c_s. The bulk concentration, m, which is the mass of constituent per bulk volume is then given by

$$m=\theta_w c_w+\theta_a c_a+\theta_o c_o+\rho_b c_s \tag{2}$$

where ρ_b is the soil bulk density. Equation (2) is perfectly general. When considering the transport of the constituent within the multiphase system, a fundamental question concerns how the concentrations within the various phases relate to each other. The simplest and most common approach assumes that the rate of mass transport within a phase is slow compared with the rate of mass transfer between phases in contact locally. If this is the case, then the concentrations remain in thermodynamic equilibrium, and the assumption that such conditions hold is called the local equilibrium assumption. The local equilibrium assumption appears to be valid for many situations of practical interest. There are exceptions, however, where mass transfer kinetics is important and equilibrium assumptions do not apply. Examples include cases where intra-particle diffusion or dissolution of droplets is important. Nevertheless, in the vast majority of applications, equilibrium partitioning is assumed. To reiterate, the local equilibrium assumption says that the concentration in any phase can be related to that in any other through the thermodynamic partition coefficient. This is shown schematically in Fig. 2.

For the analysis of solute transport in a multiphase system in local equilibrium, it is convenient to refer all concentrations to the water concentration; while for analysis of volatilization the air phase concentration is more appropriate. This allows one to express the bulk concentration in terms of the concentration in a particular phase alone. The linear partitioning relationships are also shown in Fig. 2. In these equations, K_H is the Henry's Law constant

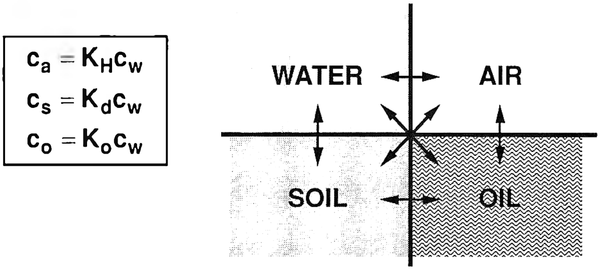

Fig. 2. Partitioning in a multiphase system.

while K_o and K_d are the oil–water and soil–water partition coefficients, respectively. Both K_H and K_o are dimensionless, while K_d has units of volume per mass. Substituting these equilibrium relations in eq. (2) gives

$$m = (\theta_w + \theta_a K_H + \theta_o K_o + \rho_b K_d) c_w = B_w c_w \tag{3}$$

B_w is called the bulk water partition coefficient. Equation (3) shows the relation between the bulk concentration and the aqueous concentration. If one determines the bulk concentration of a soil by chemical extraction, then this equation may be used to estimate the aqueous concentration. Similar relations may be written for each of the other phase concentrations, and one may introduce bulk air, soil, and oil partition coefficients. The important parameters include the volumetric fluid contents and the partition coefficients.

The Henry's Law constant, K_H, is dimensionless. This constant may also be written as the ratio of the vapor density (ρ_{vp}) to the solubility (S), where the vapor density is related to the vapor pressure through the ideal gas law, $\rho_{vp} = P_{vp}/RT$, where R is the gas constant and T is the temperature in degrees Kelvin. The vapor pressure, solubility, and Henry's law constant for many chemicals have been tabulated. See, for example, Mercer et al. [14].

Non-polar organic compounds in the subsurface are found to be sorbed by the medium on existing solid organic matter present in the porous medium [2]. This sorption is due primarily to hydrophobic interactions resulting in weak, non-specific sorption forces. When the organic compounds are present in trace concentrations, linear sorption isotherms are often observed. The distribution coefficient (K_d) is found to be a function of the hydrophobic character of the organic compound and the amount of organic matter present, and may be written [3–5]

$$K_d = K_{oc} f_{oc} \tag{4}$$

where K_{oc} is the organic carbon partition coefficient and f_{oc} is the fraction of organic carbon within the soil matrix. Sorption partition coefficients, indexed to organic carbon (K_{oc}) are relatively invariant for natural sorbents, and K_{oc}'s can be estimated from other physical properties of pollutants such as aqueous solubility or octanol-water partition coefficients (K_{ow}). Equation (4) is valid only for $f_{oc} > 0.001$. Otherwise, sorption of organic compounds on nonorganic solids (clays and mineral surfaces) can become significant. Also, the linear isotherm model is valid only if the solute concentration remains below one-half of the solubility limit of the compound. Use of the hydrophobic theory to estimate the distribution coefficient in equations for modeling subsurface pollutant transport assumes that the sorbed concentration is in equilibrium with the concentration in solution.

Very little is known in detail about the magnitude of K_o, except that it is not a constant but rather depends on the composition of the "oil" phase. Since this composition changes with time as the pollutant ages, one may anticipate that K_o will change with time also. Compositional models are required for estimating how K_o evolves over time. For the partitioning between the water and oil phases Corapcioglu and Baehr [6] apply Raoult's Law which states that the aqueous phase concentration is equal to the aqueous phase solubility of the constituent in equilibrium with the pure constituent phase multiplied by the mole fraction of the constituent in the oil phase. The resulting compositional model leads to

$$K_o = \frac{\omega_k \sum_{j=1} c_{oj}/\omega_j}{S_k \gamma_k} \qquad (5)$$

Equation (5) is written for a species k which is one out of N species which make up the oil phase. ω_j is the molecular weight of the jth constituent (g/mol), c_{oj} is the concentration of the jth constituent in the oil phase (g/L), S_k is the solubility of species k in water (g/L), and γ_k is the activity coefficient of the kth species (which equals 1 for ideal solutions). Equation (5) makes it apparent that K_o changes as the composition of the oil phase changes (because of dissolution, volatilization, and degradation of constituents). Ultimately, one might expect that the value of K_o will approach that of K_{oc} for the constituent.

Volatilization

Volatilization from the soil is a process which involves mass transfer from the soil, aqueous, and air phases that are present in the porous medium to the atmosphere, which serves as the ultimate sink. Since the mass must enter the atmosphere within the air phase, it is often assumed that gaseous transfer must dominate the mass transfer process. However, if the mass transfer between phases is sufficiently fast so that local equilibrium conditions are achieved, the concentration gradient in the air phase follows that in the other phases. This means that one can model the volatile flux in terms either the air concentration, the bulk concentration, the water concentration, etc., whichever is most convenient. In any case, the mass transfer in all phases may be important.

Volatilization is mass transfer associated with diffusion. The rate of volatilization is affected by many factors, such as soil properties, chemical properties, and environmental conditions. Its rate is ultimately limited by the chemical vapor concentration which is maintained at the soil surface and by the rate at which this vapor is carried away from the soil surface to the atmosphere. In this regard, the mechanisms of volatilization are similar to those of evaporation of soil water, with volatilization being the 'evaporation' of a chemical constituent. The factors which control the rate of volatilization are discussed in the literature primarily in terms of their effects on evaporation of pesticides, because most previous studies of volatilization rates have concentrated on these chemicals. However, there is little that distinguishes pesticides from other organic chemicals and one may assume that the observations based on pesticides are applicable to organic chemicals in general. For reviews see [7–11].

Volatilization may be modeled using Fick's Law of diffusion. A simple model gives the cumulative volatile loss (mass per unit surface area) as

$$Q_{\mathrm{loss}} = m_{\mathrm{o}} \sqrt{\frac{4D_{\mathrm{s}}t}{\pi}} \tag{6}$$

where m_{o} is the soil's initial bulk concentration of the volatile constituent, and the parameter D_{s} is the effective soil diffusion coefficient. Equation (6) is essentially the model presented by Hamaker [12] except that it accounts for partitioning and diffusive transfer in all of the phases. The effective soil diffusion coefficient may be estimated using an extension of the model presented by Millington [13]:

$$D_{\mathrm{s}} = \frac{1}{n^2 B_{\mathrm{w}}} \left(\theta_{\mathrm{w}}^{10/3} D_{\mathrm{w}} + \theta_{\mathrm{a}}^{10/3} K_{\mathrm{H}} D_{\mathrm{a}} + \theta_{\mathrm{o}}^{10/3} K_{\mathrm{o}} D_{\mathrm{o}}\right) \tag{7}$$

In eq. (7), D_{w}, D_{a}, and D_{o} are the bulk phase molecular diffusion coefficients

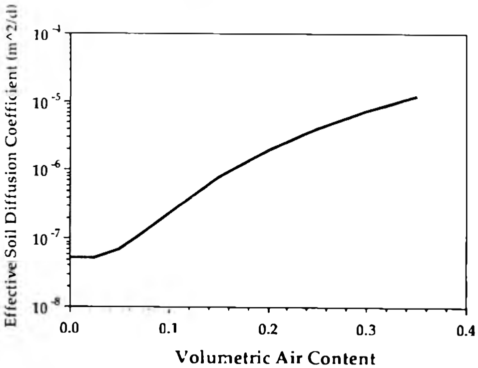

Fig. 3. Effective soil diffusion coefficent as a function of air content for a fixed volumetric oil content of 0.05.

for water, air, and oil. Typically, D_a is four orders of magnitude larger than either D_w or D_o, suggesting that the vapor phase is the major contributor to soil diffusion, except for a very wet soil where θ_a becomes small. For example, Fig. 3 shows the effective soil diffusion coefficient for xylene as a function of volumetric air content. Note that the effective diffusion coefficient increases by nearly two orders of magnitude as one goes from a fairly wet soil with $\theta_a < 0.1$ to a dry soil with $\theta_a > 0.3$.

Immobilization

Chemicals may be immobilized within the source zone due to at least two different types of mechanisms. First, individual constituents may be immobilized because of their chemical nature. This is especially true for heavy metals. The major factors affecting the immobilization of metal are the pH and redox potential of the environment, as well as the metal's solubility and speciation. Under a range of pH and E_h (redox half-wave potential), certain metals may become immobilized as precipitates. For example, uranium forms an oxide precipitate under reducing conditions. However, under oxidizing conditions, uranium forms a mobile complex with carbonates which are usually present. Different metals have different "windows" of mobility based on the pH and E_h of their environment, and especially for metals, redox kinetics may be important in designing remedial systems for contaminated sites.

There is another type of immobilization which is especially important for sites contaminated by NAPL's. An immiscible hydrocarbon phase is free to migrate under force of gravity or other induced energy gradients only so long as its saturation is sufficiently high. At lower NAPL saturation, surface tension causes the hydrocarbon phase to break down into individual "blobs". Since these blobs are no longer continuous, the NAPL is no longer free to migrate as a separate phase. One then refers to the immobilized residual saturation. Perhaps the most important point is that a NAPL may become immobilized as a separate phase, but its individual constituents are not immobilized. Any species which is soluble in water can be leached from the immobilized NAPL which serves as a reservoir of contaminants. In fate and transport models for NAPL's, one needs to be able to estimate their residual saturations both above and below the water table. Field experience has shown that typical hydrocarbon residual saturation varies from 0.10 to 0.20 in the vadose zone, and from 0.15 to 0.50 in the saturated zone [1]. These values correspond more closely to "specific retentions", as the term is used in groundwater hydrology, rather than true residuals at large capillary pressure values.

Degradation

Degradation refers to the *in situ* loss of a chemical constituent in the subsurface. It may be due to abiotic transformations, such as hydrolysis, or it may be due to a biotic origin. Biodegradation is an important environmental process that causes the breakdown of organic chemicals in soil. The chemical transformations are mediated through the activities of microorganisms which are naturally present. The transformation of organic carbon to inorganic carbon (CO_2) is accomplished through enzymatic oxidation. Under aerobic conditions, molecular oxygen is involved as the terminal electron acceptor; while under anaerobic conditions, the final electron acceptor is something other than molecular oxygen such as sulfate or nitrate. Mineralization refers to the complete degradation of an organic chemical to inorganic products such as carbon dioxide, water, sulfate, nitrate, or ammonia. Partial degradation is commonly used to describe a level of degradation less than complete mineralization. The degradation products may be more or less toxic than their parent compounds. Chemical compounds that are not easily degraded are said to be recalcitrant and persistent in the environment.

The rate of biodegradation is a complex function determined by the number and type of microorganisms present, the toxicity of the parent compound or its daughter products to the microorganism population, the water content and temperature of the soil, the presence of electron acceptors and the redox potential, the soil pH, the availability of other nutrients for microbial metabolism, the water solubility of the chemical, and possibly other factors. Various models for the rate of biodegradation are reviewed by Alexander and Scow [15]. For most investigations it is assumed that degradation can be described by first-order rate reactions in which the rate of loss of a chemical is proportional to the chemical concentration

$$\frac{dm}{dt} = -\lambda m \tag{8}$$

In eq. (8), λ ($time^{-1}$) is the first-order rate constant which is related to the half-life, $T_{1/2}$, by

$$T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \tag{9}$$

Measured values of $T_{1/2}$ are quite variable between the laboratory and the field, and from site to site in the field. Laboratory values tend to be measured under optimal conditions so as to assess the potential for biodegradation given the chemical characteristics, geochemistry and bacterial populations. Laboratory half-lives are not necessarily applicable to the field due to limitations in the factors described above. For a well-managed land treatment or contaminated soil bioremediation site, representative half-lives for toluene, naphthalene, and anthracene range from 1–10 days, 30–60 days, and 100–200 days, respectively.

Leaching

Chemical contaminants can be carried from the source zone to the water table through leaching by infiltrating rainwater, and directly with a NAPL which is released at sufficient rates so that it is mobile. Perhaps one of the greatest uncertainties in development of leaching models is estimation of the net water infiltration rate. Some of the water which falls on the ground surface does not infiltrate to the subsurface, but rather forms surface runoff. Most of the water that does infiltrate to the subsurface returns to the atmosphere through evaporation and transpiration by plants. Only a relatively small fraction of the yearly rainfall may infiltrate below the root zone and ultimately become groundwater recharge. In development of subsurface solute transport models one is faced with the question of estimation of the net infiltration rate and whether it is necessary to deal with the details caused by individual rainfall events. It is certain that the water content and seepage velocities are quite variable within the upper region of the soil profile containing the root zone. This in turn influences volatilization rates, degradation, and leaching itself. However, below the upper meter or so, the variability in water content and seepage rates is much less, and one might apply an average value for these variables.

The usual approach in development of transport models is to assume steady-state conditions for the net water infiltration rate. In order to estimate the net infiltration rate, one may apply daily water balance models such as CREAMS or HELP, or continuous time water balance models such as PROFIL. Sensitivity studies have suggested that the net infiltration rate may be adequately estimated using either type of model. These models will provide an estimate of the yearly average infiltration rate, which in turn may be used to estimate the water content and seepage velocity. For the latter determinations, parametric models are often used rather than raw data from laboratory determinations. Parametric models relate the soil water retention parameters and relative permeability parameters to the soil texture. The most commonly used soil water retention and relative permeability models are those of Brooks and Corey [16] and Van Genuchten [17]. Using the Brooks and Corey model, one may estimate the average water content from

$$\theta_w = \theta_{wr} + (n - \theta_{wr}) \left(\frac{q_w}{K_{ws}} \right)^{\lambda/3\lambda+2} \tag{10}$$

where q_w is the net water infiltration rate, θ_{wr} is the residual water content, K_{ws} is the soil's vertical hydraulic conductivity for water, and λ is the pore size distribution index. If infiltration is uniform throughout the soil profile, then one may estimate the seepage velocity through

$$v_{\mathrm{w}}=\frac{q_{\mathrm{w}}}{\theta_{\mathrm{w}}}=\frac{q_{\mathrm{w}}}{\theta_{\mathrm{wr}}+(n-\theta_{\mathrm{wr}})\left(\frac{q_{\mathrm{w}}}{K_{\mathrm{ws}}}\right)^{\lambda/3\lambda+2}} \tag{11}$$

Equation (11) may be used to estimate the seepage velocity for a given net infiltration rate and a known set of soil water retention parameters. Table 1 provides estimates of the average seepage velocity from eq. (11) for different soil textures and recharge rates. For each soil texture the average parameters determined by Carsel and Parrish [18] were used. These parameters are based on data obtained from measurements for all soils reported in SCS Soil Survey Information Reports, and were analyzed using a multiple regression equation developed by Rawl and Brakensiek [19]. It is important to note that the velocities reported in Table 1 are quite small. This suggests that the average residence time for solutes in the unsaturated zone can be very long, especially at locations where the water table is found at great depths. It also should be noted that eq. (11) and Table 1 provide a rough guide only. They are based on the assumption of steady recharge and uniform flow in a homogeneous soil profile. Rainfall events, which produce recharge, create water fluxes much higher than the average velocities. Since recharge occurs through discrete events, rather than due to average recharge rates, higher fluxes occurring over short time periods result in significantly more rapid transport through the root zone and possibly all the way to the water table. Models which rely on average monthly or annual recharge rates may adequately represent the vadose zone moisture content, but may significantly overestimate the vadose zone reten-

TABLE 1

Average solute velocities (m/year)

Soil type	Average annual recharge (m)			
	0.05	0.10	0.25	0.50
Clay	0.16	0.31	0.75	1.48
Clay loam	0.19	0.37	0.86	1.64
Loam	0.26	0.49	1.13	2.11
Loamy sand	0.53	0.99	2.25	4.16
Silt	0.21	0.39	0.88	1.64
Silt loam	0.22	0.41	0.93	1.74
Silty clay	0.16	0.30	0.74	1.45
Silty clay loam	0.16	0.30	0.72	1.37
Sand	0.68	1.27	2.86	5.27
Sandy clay	0.18	0.35	0.82	1.58
Sandy clay loam	0.25	0.48	1.12	2.12
Sandy loam	0.39	0.73	1.67	3.08

tion time. The effects of solute mixing or dispersion, macropores, and spatial variability are not included, and these affects can be very dramatic.

In recent years, it has become recognized that the effects of preferential flow are very significant in determining the residence time for solutes in the vadose zone. Even for homogeneous soil layers, experiments and theory have shown that when flow proceeds from a layer of lower permeability to one of higher permeability, then fingering will naturally occur causing preferential flow paths which channel the water through the higher permeability layer. This is shown schematically in Fig. 4. Since the same total discharge is channeled through a much smaller area, the corresponding velocities will be greater and the travel times less. In the field, naturally occuring macropores, decayed root openings, and heterogeneities will also trigger channeling of subsurface flow through the unsaturated zone.

Advection, dispersion, and degradation

The aquifer processes of advection and dispersion have been greatly studied over the past few decades. As presently understood, advection refers to the average rate of advance of a solute in the aquifer; and dispersion refers to the deviation about the mean. The advection velocity is proportional to both the hydraulic conductivity and the hydraulic gradient, and inversely proportional to the porosity. Dispersion includes both the processes of molecular diffusion and mechanical disperion. The latter process is associated with the non-uniform motion of a solute caused by the flow through the complicated pore structure of the media. For most problems of contamination of shallow aquifers, molecular diffusion plays a negligible role. On the pore scale seen in laboratory experiments, the influence of mechanical dispersion is also small. However, in the field, dispersion is used to account for the effects of aquifer heterogeneities on the transport. The solute will move faster through regions of higher permeability than through regions of lower permeability. The models recognize only the average advection velocity and account for these deviations with the dispersion term. This results in dispersion playing a much more significant role for field scale problems then for laboratory experiments. In addition, the greater the scale of the problem under investigation, the greater the range of hetero-

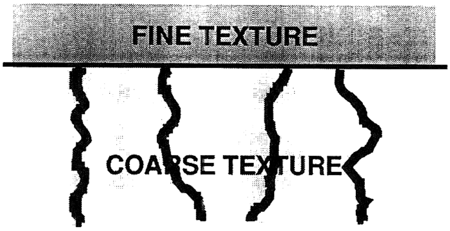

Fig. 4. Preferential flow through porous media.

geneities experienced by the solute and the larger the apparent magnitude of the dispersion coefficient.

Degradation processes are less rapid in the saturated zone than they are within the upper few feet near the ground surface, though they are not any less important. Groundwater transport is very slow, so that even a small degradation rate can result in a significant reduction in solute concentration before the constituent of interest reaches a potential exposure point.

Screening models

Subsurface fate and transport models may be classified as either generic models or site specific models. Generic models are based on a simplified interpretation of the hydrogeology, including generally the assumption of uniform flow in a specified direction and homogeneous conditions for other parameters. These assumptions allow the use of analytic solutions to the transport problem. Analytic solutions have the advantage of simplicity and ease of computation. Site specific models are flexible enough to deal with the individual complexity of a given hydrogeologic setting and can include almost any level of detail in the simulation of important fate and transport processes. This flexibility and ability to address great levels of complexity comes at a price. Site specific models require numerical methods and may come at a great computational expense.

Screening models are generic models in the sense that they cannot be adapted to deal with many site specific conditions. They may be used to evaluate the behavior of large numbers of chemicals in the environment. For example, the pesticide screening model of Jury et al. [20] was used to classify pesticides based on persistence categories in terms of mass remaining in the soil after 30 days [21]. The RITZ model [22] was developed as a screening model for evaluation of the fate of petroleum wastes applied at land treatment sites. EPACML [23] is an exposure assessment screening model for landfill waste. While each of these models is fundamentally different, they are similar in that they incorporate mathematical models of many important processes which affect the fate and transport of chemicals under the particular scenario for which the model was developed.

Hydrocarbon spill screening model

As an example of a model and its application, we consider the Hydrocarbon Spill Screening Model (HSSM), which is a hydrocarbon spill screening model. Hydrocarbon spills impact drinking water supplies at down gradient locations. Conventional numerical models of multiphase, multicomponent flow have extreme requirements for both computer time and site data. Site data and the intent of the modeling often do not warrant the application of such models. An alternative approach is HSSM which is based on semi-analytic models for vertical product infiltration, radial spreading on the water table, and transport of aqueous phase contaminants in the aquifer. The models for these processes are linked to estimate exposure at a down gradient well. The basic set-up of the model is shown in Fig. 5.

HSSM is to be used as a screening tool. For example, the model can be used to estimate the effects of light low density non-aqueous phase liquid (L-NAPL) loadings, partition coefficients, groundwater flow velocities, etc., on pollutant transport. Since approximations are used for developing the model, the model results must be viewed as approximations. If simulation of complex heterogeneous sites is needed, or other approximations made in the model are unacceptable, then a more inclusive model should be used instead of, or in addition to, HSSM.

Complex models, however, may not always be the most desirable tool for a given problem. Such models require large amounts of computer time and available memory. Further, there may be a significant investment in training the users to set up the model and run it properly. Additionally, a large amount of field data is required to run such a model because the expense of running the model is not warranted if adequate site data are not available. In addition to the parameters for aqueous phase solute transport (such as hydraulic conductivity, dispersivity, sorption parameters), multiphase transport parameters are needed (interphase partition coefficients, capillary pressures and relative permeabilities) for each different zone or material present in the field. The latter properties are not well understood and are difficult to obtain for field problems. Site data is usually incomplete because of monetary, safety and regulatory limitations. Historical records of pollutant releases are often non-existent, although such knowledge should be precisely defined in a model. Sampling limitations often result in situations where the total mass of contaminants cannot be defined. These limitations are likely to require approximations to be made even when running a complex model. Certain problems may warrant the use of alternative simplified models.

HSSM has an advantage in some of these areas; the model executes rapidly

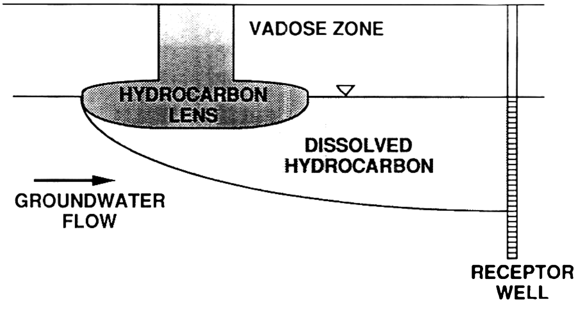

Fig. 5. Hydrocarbon spill screening model (HSSM).

on small computers, requires little memory and is designed to be run easily. The advantage is that HSSM is based on semi-analytic approaches, which do not require discretization of the domain nor iterative solution of the non-linear governing equations. These advantages are achieved at the cost of flexibility in accommodating heterogeneities and other phenomena. Clear recognition should be made that for the sake of efficiency and robustness, accuracy and/or the ability to simulate various situations is sacrificed. At some point, there is a limit to the phenomena that can be treated in a simplified context; beyond that limit, the complex models must be used.

A detailed discussion of the model assumptions is presented by Weaver and Charbeneau [24], and only a brief description is given here. The spill or release of the L-NAPL phase may be simulated in three ways. First is a release of a known L-NAPL flux for a specified duration. The release occurs at the ground surface. Based on an approximate capillary suction relationship, some of the L-NAPL may run off at the surface if the flux exceeds the maximum effective L-NAPL conductivity. Second, a constant depth of ponded L-NAPL, for a known duration, may also be specified. This case represents a slowly leaking tank, or a leaking tank within an embankment. Lastly, a known volume of L-NAPL may be placed over a specified depth of the soil. This last scenario represents either a land treatment operation or a landfill containing a known amount of contaminants at the beginning of the simulation.

Transport of the NAPL through the unsaturated zone is assumed to be one-dimensional. Capillary pressure gradients are neglected except as they influence the infiltration of NAPL into the soil. The resulting equations for NAPL flow are hyperbolic and are solved by the generalized method of characteristics. When relatively large amounts of L-NAPL are released, downward transport of the L-NAPL (say gasoline) is the primary mechanism for downward transport of hydrophobic chemicals (e.g., benzene, toluene, and xylene). Assumptions concerning aquifer recharge are relatively unimportant in this case. If a large enough volume is supplied, the L-NAPL reaches the water table. If sufficient head is available, the water table is displaced downward, lateral spreading begins, and the oil lens part of the model is triggered. Spreading is assumed to be radial, and the thickness of the lens is determined by buoyancy only (Ghyben–Herzberg relations). The shape of the lens is given by the Dupuit assumptions, where the flow is assumed horizontal and the gradient is independent of depth.

The L-NAPL is treated as a two-component mixture. The L-NAPL itself is assumed to be soluble in water and sorbing. Due to the effects of the recharge water and contact with the groundwater, the L-NAPL may be dissolved. The L-NAPL's transport properties (density, viscosity, capillary pressure, relative permeability), however, are assumed to be unchanging. The second component is a chemical constituent which can partition between the L-NAPL phase, water phase and the soil. This constituent of the L-NAPL is considered the primary contaminant of interest. The mass flux of the second constituent into the aquifer comes from recharge water being contaminated by contact with the lens and from dissolution occuring as groundwater flows under the lens. The concentration of the chemical in the aquifer is limited by its water solubility.

The aquifer transport of the dissolved contaminant is simulated by using a two-dimensional, vertically averaged analytic solution of the advection–dispersion equation. The vertical extent of the contaminant is estimated from the recharge rate, groundwater seepage velocity and vertical dispersivity, rather than assuming the contaminant is distributed over the entire aquifer thickness. The boundary conditions are placed at the down gradient edge of the lens and take the form of a Gaussian distribution with the peak directly down gradient of the center of the lens. The peak concentration of the Gaussian distribution adjusts through time so that the simulated mass flux from the lens equals that into the aquifer. Although the size of the lens varies with time, a constant representative lens size is used for the aquifer source condition. In many cases the lens reaches its maximum size rather rapidly compared with the transport in the aquifer, so that the use of the maximum lens size will not introduce large errors.

The required input parameters include parameters specifying the type, extent and magnitude of the L-NAPL release, the residual oil contents for the unsaturated and saturated zones, the residual water content of the oil lens, the transport properties of the water and L-NAPL (density, viscosity, surface tension), the aquifer and soil water retention characteristics (vertical and horizontal hydraulic conductivities, porosity, irreducible water content, pore size distribution index, and air entry head), the dissolved constituent characteristics (initial concentration within the L-NAPL, aqueous solubility, and the soil–water and oil–water partition coefficients), and the aquifer transport charcteristics (vertical, longitudinal and transverse dispersivities, hydraulic gradient, half-life of the constituent within the aquifer). Other parameters control the simulation characterisitcs and locations where exposure concentrations are calculated.

To show the type of output one can obtain, a spill of 1,500 gallons (5400 L) of gasoline over a sandy aquifer was simulated. The area of the the release has a radius of 2 m and the duration of the release is 1 day. The water table is at a depth of 5 m and the aquifer has a seepage velocity of 0.9 m/day. The simulation results show that the gasoline first reaches the water table at a time of 2.6 days, and after 4.3 days sufficient gasoline has accumulated in the capillary fringe to cause the lens to start to spread. Spreading occurs over a period of 68 days with a final lens radius of 3.6 m.

Benzene, toluene, and xylene were separately considered as constituents within the gasoline. Benzene is assumed to have a concentration of 8.2 g/L (1.14% bymass) in the gasoline. Toluene is assumed to have a concentration of 43.6 g/L (6.07% by mass). Xylene is assumed to have a concentration of

71.8 g/L which is 10% of the gasoline. Partition coefficients are based on an assumed fraction of organic carbon in the soil and aquifer of $f_{oc}=0.005$ and with gasoline having a molar concentration of 7 mol/L. With eq. (4), the soil–water distribution coefficients for benzene, toluene, and xylene are 0.415, 1.50, and 4.15 L/kg, respectively. The corresponding aquifer retardation factors for these chemicals are 2.66, 7.0, and 17.6 for benzene, toluene, and xylene. Equation (5) gives oil–water partition coefficients of 312, 1200, and 4240 for benzene, toluene, and xylene, respectively, by using the idealized gasoline mixture presented by Corapcioglu and Baehr [6].

Figure 6 shows the calculated benzene concentrations at the receptor wells located at distances of 50, 100, 200, and 500 m from the spill location. The peak concentration at 50 m is about 3.7 mg/L and occurs 0.7 years after the spill. At 500 m, the peak concentration is 0.7 mg/L and occurs at a time of 4.5 years after the spill. This decrease in peak concentration with distance is associated with mixing in the aquifer since the biodegradation of benzene was neglected in the model. Figure 7 compares the concentrations of benzene, toluene and xylene at the 50 m receptor well. The peak concentrations of these chemicals are similar (3.7, 5.8, and 2.5 mg/L for benzene, toluene, and xylene, respectively) even though they were present in far different concentrations in the

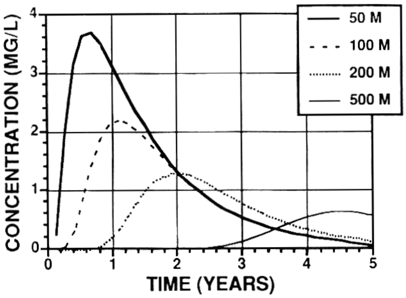

Fig. 6. Benzene concentrations mg/L at receptor wells located 50, 100, 200, and 500 m from the spill.

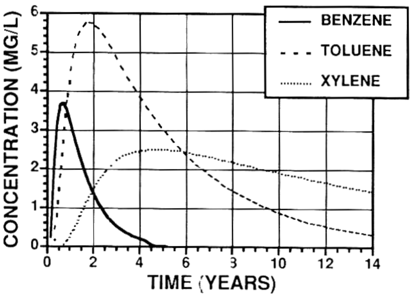

Fig. 7. Benzene, toluene and xylene concentrations (mg/L) at a distance of 50 m from the spill.

gasoline. This behavior is due primarily to the oil–water partition coefficients. Benzene is leached most rapidly from the oil lens. Toluene is leached less rapidly than benzene, but because it was present at much higher concentrations in the gasoline, the receptor concentration is higher. Xylene, which is present in gasoline at the highest concentrations, is leached so slowly from the lens that its concentrations are diluted due to mixing with the groundwater and the resulting exposure concentrations are less.

Discussion

This article has provided an overview of the important processes which affect the subsurface fate and transport of chemicals. Significant parameters have been noted and discussed. Unfortunately, the uncertainties in parameter estimation for model applications are very great. Even for the flow of water, the uncertainties are large. In the unsaturated zone one may anticipate that preferential flow may play an important role, though it is unlikely that one will be able to locate the flow paths (a particularly important point for vadose zone monitoring). In groundwater aquifers, one rarely knows the hydraulic conductivity to within an order of magnitude. This implies that estimates of seepage velocities are often good only to within an order of magnitude unless they are determined directly through use of tracers. The mixing parameters will also remain elusive, though the importance of dispersion is probably less important for many applications.

The parameters which determine the partitioning of chemicals in a multiphase system can in principle be estimated with greater accuracy. Use of hydrophobic theory should lead to estimates of the soil–water distribution coefficient which are good to within plus or minus fifty percent. A similar level of accuracy could be achieved for the oil–water partition coefficient except that the composition of the NAPL phase is generally poorly known and varies with location. Henry's law constants can probably be estimated with the greatest accuracy. Estimation of degradation parameters may also be expected to face considerable uncertainty both because of the first-order rate equation may not be appropriate and because the controls are poorly known and vary with location in the subsurface.

In light of these uncertainties, one may question the use of mathematical models for subsurface fate and transport. One should not expect that models can predict actual concentrations to be found at a field site with any great level of accuracy. However, models can show the relative importance of the various processes which affect fate and transport, and identify the most significant parameters upon which attention may then be focused. Such uses of models highlights the role of models in developing a conceptualization of contaminant behavior at a site. Of ultimate value is the understanding of contaminate behavior developed by the engineer or geologist from regional and local scale hydrology, contaminant properties and distribution, model use, etc. Properly calibrated models then become useful in analysis and design of alternate remedial systems. In general, models play an especially important educational role in training and developing our intuition as to how to interpret and understand field observations from complex environmental systems, and in classification of chemicals in terms of their general fate and transport behavior.

Disclaimer

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EPA's Superfund technical support project*

Marion R. Scalf

Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA)

Abstract

Remediation of hazardous waste sites, especially the subsurface component, is a relatively new, extremely complex, interdisciplinary science. Success is determined more by experience than by hardware. The Technical Support Project of the U.S. Environmental Protection Agency (EPA) has been very successful in minimizing the time between development of the science and application of that scientific knowledge to decision making in the field. The Technical Support Project not only transfers knowledge from research to the field but acts as a critical feedback mechanism for focusing research efforts on the highest priority and most productive areas. Requests for technical support to the Superfund program have increased dramatically through the years as Regional staff have become more familiar with the system and how to access the program. In 1991, EPA's Office of Solid Waste started an effort to extend the Technical Support Project to the RCRA corrective action program. RCRA corrective action may affect almost 4000 facilities and, although administrative efforts may differ, technical questions will be very similar to those addressed by Superfund.

Background

In early 1987, there were several studies conducted by Congress and EPA's Office of Solid Waste and Emergency Response (OSWER) that indicated a number of problems with Superfund site remediation decision making. Regional staff, Regional Project Managers (RPMs) and On-Scene Coordinators (OSCs) who were responsible for selecting and/or approving remediation programs were overloaded and had a high turnover rate. Most had a relatively narrow technical background at a time when managing the cleanup of Superfund sites required state-of-science knowledge of a number of disciplines, in a complex environmental field where the science was (and is) developing rapidly. There was a great deal of inconsistency within and between Regions con-

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Correspondence to: M.R. Scalf, Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA). Fax: (405)332-8800.

cerning site remediation. The OSCs and RPMs needed a source of technical expertise to help resolve technical problems and to evaluate the advice of their contractors.

Also in 1987, there was an *ad hoc* group of Regional ground-water specialists that began a series of meetings to share their experiences in Superfund remediation and investigate methods of obtaining technical support. These meetings led to a formal group called the "Ground Water Forum" which now includes representatives from all ten EPA Regional Offices. EPA's Office of Solid Waste and Emergency Response (OSWER) was exploring ways to make EPA's Office of Research and Development (ORD) scientific expertise more readily available to provide assistance. To this end, OSWER and ORD established the Technical Support Project which provided funding to four ORD laboratories to establish technology support centers. The Centers and specialty areas are:

- Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, Oklahoma (Ground Water Fate and Transport)
- Environmental Monitoring and Support Laboratory (EMSL), Las Vegas, Nevada (Monitoring and Site Characterization)
- Risk Reduction Engineering Laboratory (RREL), Cincinnati, Ohio (Engineering and Treatment)
- Environmental Research Laboratory (ERL), Athens, Georgia (Exposure and Ecorisk Assessment)

The objectives of the Technology Support Centers are to:

- Provide technical support and assistance to Regional staff;
- Improve communications among Regions and ORD laboratories;
- Ensure coordination and consistency in the application of remedial technologies; and,
- Furnish technology workshops and state-of-the-science information for RPMs and OSCs.

Since the establishment of the original four Technology Support Centers, two additional centers have been added to the Technical Support Project. The Environmental Criteria and Assessment Office (ECAO) Laboratory at Cincinnati provides chemical-specific health information and reviews site-specific Superfund risk assessments. The Emergency Response Team in Edison, New Jersey, provides assistance on health and safety and emergency response, remedial and removal program clean-up technologies.

With establishment of the Technical Support Project, a Regional Engineering Forum analogous to the Ground Water Forum was established and both groups provide points of contact between the Centers and the Regional staff.

Centers' mission

The Centers provide technical support in response to formal written Regional requests, in addition to responding to hundreds of telephone inquiries.

The types of assistance provided range from the review of contractor work plans and reports to the development and evaluation of treatability studies and remedial alternatives. The Centers also develop Issue Papers and provide workshops on critical technical topics identified by the Forums. Since the Technical Support Project was initiated in late 1987, the Centers have responded to over 1200 requests for technical assistance in support of remedial activities at Superfund sites.

The Center at the Environmental Monitoring and Support Laboratory (EMSL-Las Vegas) in Las Vegas is most often asked to conduct, oversee, or provide information on portable XRF, soil gas, geophysical surveys, field monitoring and analysis, and radiological analysis.

Requests to the Center at the Environmental Research Laboratory (ERL-Athens) in Athens, Georgia, most frequently involve data and ecorisk analysis, usually by applying mathematical models. They also review reports and work plans.

At the Risk Reduction Engineering Laboratory (RREL) in Cincinnati, requests are generally related to reviewing and overseeing treatability work plans and studies, remedial designs, remedial actions, remedial processes, and traditional and innovative technologies.

The Center at the Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma, regularly reviews and oversees work plans and studies related to bioremediation, soil vapor extraction, treatability studies, ground water modeling, pump-and-treat, and other activities concerned with *in situ* soil and ground water remediation.

RSKERL-ADA technology support center

Each of the Centers operates in a somewhat different manner because of their organizational structure and different research missions. A major area of RSKERL research deals with transport and transformation of contaminants in the subsurface environment, including: use of soil systems in treating waste; characterization of hydrogeologic, abiotic, and biotic processes controlling contaminant transport and fate; and expression of these processes in mathematical models. This in-house program and its extension through extramural research with universities and other research entities is the foundation for the RSKERL Technology Support Center (TSC). The mission of the RSKERL TSC is to make available to site remediation decision makers state-of-the-science information on the transport and fate of contaminants in soils and ground water, along with scientific expertise needed to determine how it may influence remediation selection and performance.

The RSKERL-Ada Technology Support Center is part of the Applications and Assistance Branch, one of the four branches in the Laboratory structure (Fig. 1). The Applications and Assistance Branch was created in 1984 to serve

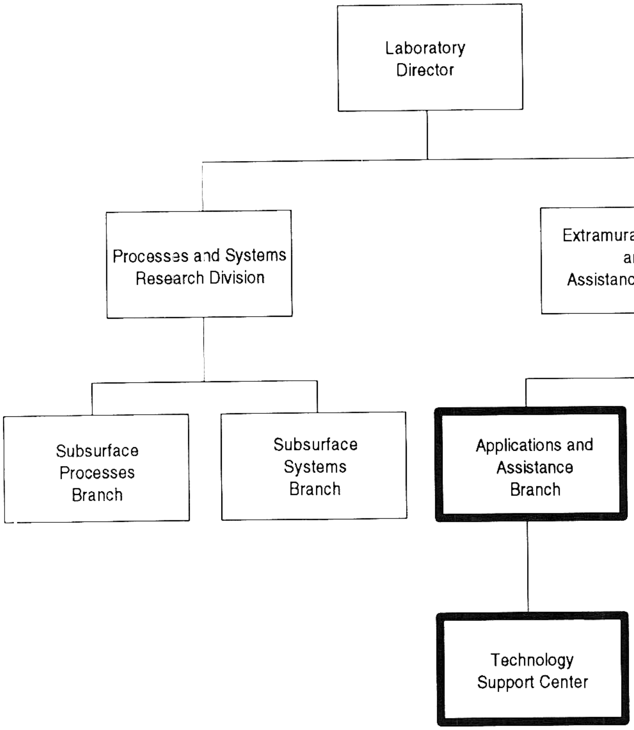

Fig. 1. The TSC in the RSKERL organization.

as the focal point for Laboratory technology transfer and technical assistance. Although many of the Branch staff have research responsibilities, their major responsibility is technology transfer in much the same manner as USDA's extension service. Branch staff make up the TSC Core Team which currently consists of five hydrogeologists, two environmental engineers, two soil scientists, two microbiologists, a biologist, and a chemist. The Core Team is supported by in-house scientists from the Laboratory's Research Division and scientists from the National Center for Ground Water Research (NCGWR), a consortium of Oklahoma, Oklahoma State, Texas and Rice Universities. A contractor with on-site scientific and information transfer personnel, over 100 off-site consultants, and subcontracts with GeoTrans and firms for treatability studies provides additional support to the Core Team (Fig. 2).

With an increasing number of Agency decisions being based on mathematical models as demonstrated by increasing requests for modeling support, RSKERL has established the Center for Subsurface Modeling Support (CSMoS) under the umbrella of the Technology Support Center. CSMoS consists of RSKERL modelers, the NCGWR, the International Ground Water Modeling Center now at the Colorado School of Mines, and an extensive list of ground water modeling consultants available via the on-site technical sup-

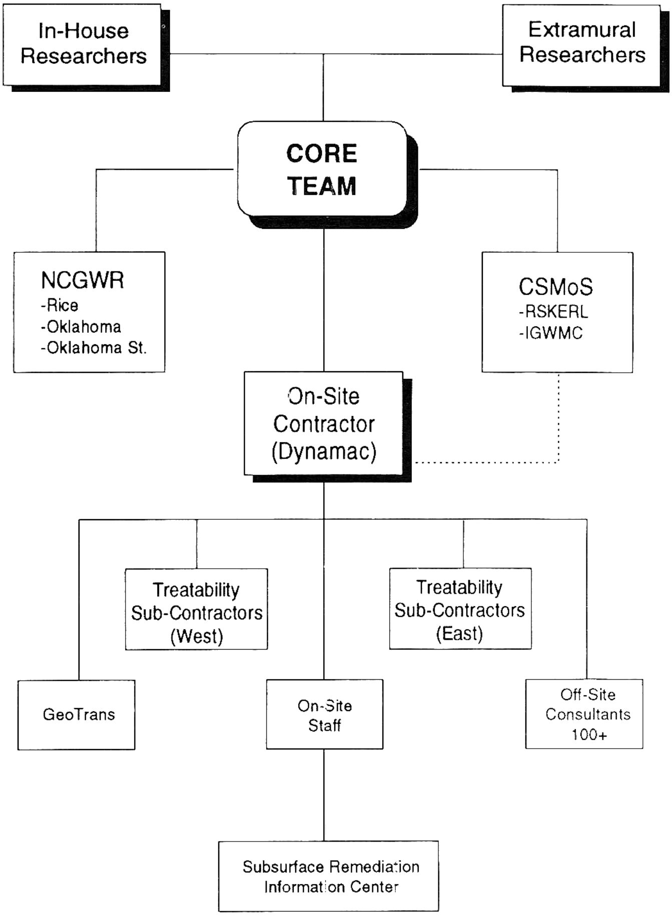

Fig. 2. Position of the Core Team in the project organization.

port contractor. CSMoS distributes and services all models and databases developed by RSKERL, and provides review and assistance to Regional staff on applications of a variety of ground water and vadose zone models.

The RSKERL TSC responds to requests for technical publications with approximately 500 reprints per month and, since its inception in late 1987, has conducted in excess of 60 workshops, seminars, or conferences in all ten EPA Regions; completed 15 issue papers (Fig. 3) with another 10 currently being prepared; and provided site-specific technical support at more than 200 different Superfund sites encompassing all ten Regions (Fig. 4).

The type and duration of site-specific technical support varies greatly among the different sites. Often, the request is for review of a contractor report or workplan for treatability studies or full-scale remediation involving technologies such as pump-and-treat, soil venting, or bioremediation. In many cases,

SF ISSUE PAPERS COMPLETED

- Accuracy of Depth to Water Measurements
- Ground Water Sampling for Metals Analyses
- Colloidal-Facilitated Transport of Inorganic Contaminants in GW: Part 1, Sampling Considerations
- Facilitated Transport
- Contaminant Transport in Fractured Media: Models for Decision-Makers
- Performance Evaluations of Pump-and-Treat Remediations
- Basics of Pump-and-Treat GW Remediation Technology
- Dense Non-Aqueous Phase Liquids
- Basic Concepts of Organic Contaminant Sorption at Hazardous Waste Sites
- Characterizing Soil for Hazardous Waste Site Assessments
- Bioremediation of Contaminated Surface Soils
- Reductive Dehalogenation of Organic Halogenated Pollutants in Soil and GW

Fig. 3. RSKERL TSC project papers completed since 1987.

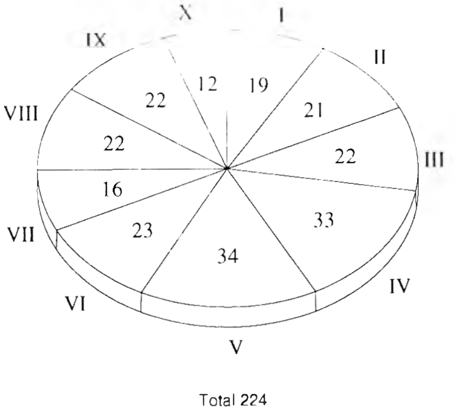

Fig. 4. Distribution of site-specific support given by RSKERL TSC to all ten regional EPA offices.

involvement is much more extensive. RSKERL has been providing intermittent technical support at some Superfund sites for more than four years. Such support has sometimes involved extensive field investigations to better define site characteristics, treatability studies to determine technology applicability, and/or extensive modeling efforts to evaluate the performance of existing remediation efforts.

Conclusions

Remediation of hazardous waste sites, especially the subsurface component, is a relatively new, extremely complex, interdisciplinary science. Success is determined more by experience than by hardware. The Technical Support Project has been very successful in minimizing the time between development of the science and application of that scientific knowledge to decision making in the field. The Technical Support Project not only transfers knowledge from the research to the field but acts as a critical feedback mechanism for focusing research efforts on the highest priority and most productive areas.

Requests for technical support to the Superfund program have increased dramatically through the years as Regional staff have become more familiar with the system and how to access the program. In 1991, EPA's Office of Solid Waste started an effort to extend the Technical Support Project to the RCRA corrective action program. RCRA corrective action may affect almost 4000 facilities and, although administrative efforts may differ, technical questions will be very similar to those addressed by Superfund.

Poster Abstracts

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In situ remediation through contaminant mobilization by vacuum stripping combined with biodegradation*

Aydin Akgerman[a], Robin Autenrieth[b] and James Bonner[b]

Departments of [a]Chemical and [b]Civil Engineering, Texas A & M University, College Station, TX 77843-3136 (USA)

Abstract – Project number 041TAM0203

This project focuses on a *in situ* remediation technique for contaminated soil. The technique combines vacuum stripping for mobilization of the contaminants together with biodegradation in a reactor at the site. The project comprises two major tasks: studies on adsorption of contaminants and studies on biodegradation of contaminants.

The engineering data needed for vacuum stripping, include the adsorption rate and equilibrium parameters, and are not readily available. The first objective of this project concentrates on the determination of adsorption equilibrium and rate parameters for a variety of contaminants on soil and soil constituents. It is shown that soil moisture has a significant effect on these parameters, the nature of which is yet to be determined. Thus our second objective is to quantify the effect of soil moisture and determine the mechanism by which it affects contaminant adsorption/desorption and transport. This project will provide the necessary data base needed for the design of vacuum stripping processes for *in situ* remediation. In addition the data will be extremely useful in relating soil–gas analysis to the extent of soil contamination and for modeling of subsurface contaminant dispersion.

The second task of this project is to understand the fundamentals of the biodegradation of complex chemical mixtures using acclimated mixed microbial cultures. These studies will approach the degradation of selected environmentally significant chemicals from several directions. Specific growth responses and kinetic parameters will be evaluated for mixed microbial cultures from an activated sludge facility acclimated to phenol in a batch-fed apparatus at inhibitory concentrations. These studies will evaluate starvation effects and initial substrate to biomass concentration. A feasibility evaluation will be conducted for TEE degradation introduced via a gas stream with propane and air to the propanotroph, *Mycobacterium spp.* , grown under pseudo-continuous

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*Posters presented at the GCHSRC Fourth Annual Symposium on Groundwater — The Problem and Some Solutions, Lamar University, Beaumont, TX, U.S.A., April 2-3, 1992.

batch-fed conditions. From this study we will determine growth kinetics, loading rates and degradation efficiencies. Simultaneous studies will be conducted to determine the degradation kinetics of multiple substrate combinations of phenol, 2,4-dichlorophenol (DCP) and pentachlorophenol (PCP) fed to acclimated mixed microbial cultures in completely mixed reactors with recycle. To link the air stripping studies to the biodegradation work, we will conduct a series of experiments to quantify the transport of phenol from a soil column to the aqueous phase with and without microorganisms present. Mathematical models will be developed for all phases of this research to evaluate mechanisms of degradation and facilitate interpretation of the results.

Remediation of contaminated soils, sediments, and/or sludges by supercritical fluid extraction combined with adsorption

Aydin Akgerman and Can Erkey

Department of Chemical Engineering, Texas A & M University, College Station, TX 77843-3136 (USA)

Abstract – Project number 100TAM0087

In this project, we are proposing to develop at laboratory scale a novel process which can be used for remediation of soils, sediments and/or sludges contaminated with organic pollutants (e.g. pesticides, herbicides, polyaromatic hydrocarbons, solvents, PCBs, phenols). In this process, the organics are continuously extracted using supercritical carbon dioxide ($SCCO_2$) and then deposited on activated carbon. Since activated carbon has high affinity for organics and the soil contamination is in ppm levels, larger volumes of soil can be treated using small volumes of activated carbon which can either be regenerated or incinerated for complete destruction of organics. The existence of a similar process on an industrial scale for decaffeniation of coffee beans, based on the same principles, provides proof on the technical and economical feasibility of the proposed process.

The work comprises design and construction of the process on a laboratory scale and initial feasibility studies by determination of adsorption isotherms, kinetic and hydrodynamic parameters, extent of decontamination of soil samples, optimum operating conditions, cycle times and the loading capacity of

adsorbents. The experiments will initially be conducted with artificial soil mixtures (0% and 2% organic content) contaminated with known amounts of model organics. The organics will be phenol, pentachlorophenol, a PCB and anthracene. As soil constituents sand, silt, clay (montmorillonite and bentonite), dolomite and soil humic material will be employed. Synthetic soil will be mixtures of these soil constituents at various proportions.

Soil remediation and waste oil treatment by agglomeration with coal

David W. Arnold

Department of Chemical Engineering, University of Alabama, P.O. Box 870203, Tuscaloosa, AL 35487-0203 (USA)

Abstract – project number 100UAL0075

Recovery, transportation, and processing of petroleum and other hydrocarbon fuels generate soil and water contaminated with oil, tar, and other heavy organics. This project will treat oily soil and oily waste water with fine coal. The bridging liquid (oil) will be supplied by the contaminated soil or water. The agglomerated fine coal and contaminant oil will be floated and removed, leaving an oil free water or soil.

The coals processing industry first used oil agglomeration to commercially clean and recover coal in 1922 in Alexandria, Virginia. Agglomeration never enjoyed popularity due to the prohibitively high cost of oil. Due to the demand for higher quality coal, there is renewed interest in this technique because of it's ability to clean fine coal. Very simply, agglomeration works by sticking the finely ground organic coal particles together with the oil in a dilute coal–water slurry after intense mixing. The agglomerates (organic+oil) float to the top and are skimmed off, while the organic free ash sinks and is rejected.

To date, our studies have shown recoveries of combustibles (organics) to be as high as 96.2 percent. Our laboratory has been working on oil agglomeration since 1989 and has received continuous funding from the Alabama Department of Economic and Community Affairs (ADECA) and the School of Mines and Energy Development (SOMED). Our work has focused on recovery of waste coal from impoundment ponds, coal washing plant reject streams and from in-plant fine coal that is not recovered by present day coal preparation plants.

This ongoing work has also investigated low-cost oils for recovery of coal.

The work will also investigate the fate of metals from used lubricating oils in the agglomeration process. There is a potential that waste coal and used oil can be combined to form a clean fuel by rejecting metals with the ash.

Deep well oxidation of aqueous hazardous wastes in supercritical water: modeling and experimental studies

Vemuri Balakotaiah

Department of Chemical Engineering, University of Houston, Houston, TX 77204 (USA)

Abstract – Project number 100UHH3007

The development of supercritical oxidation technology is still in its infancy. The scientific principles needed for the safe design and scale-up of the supercritical water oxidation reactors have not been studied and well understood. In addition, very little experimental data is available on the kinetic and thermodynamic behavior of important hazardous substances in supercritical water. Thus, a major goal of our research is to understand through a combined program of modeling and experimental efforts, the physical and chemical processes that dictate the behavior of supercritical water oxidation reactors. These fundamental principles will then be applied for the safe design scale-up and control of various supercritical combustion systems.

The goal of the proposed theoretical studies is to extend our work on the modeling of the subcritical reactor to supercritical conditions. We plan to develop mathematical models of the supercritical deep well oxidation reactor that will incorporate the experimentally determined kinetics of oxidation of various organic and inorganic compounds that may be present in the waste, the thermodynamics of the reactions as well as the phase behavior, the heat transfer between the reactor tubes, the heat losses to the surrounding earth, the fluid flow and the change of physical properties with temperature and pressure. These models will be used to simulate the steady-state and dynamic behavior of the deep well oxidation process and for predicting the destruction efficiencies of the various organic compounds, temperature and pressure profiles in the reactor up and down tubes, in the casing annulus, and in the earth around the reactor well assembly, as a function of position and time.

Chemical characterization of pore water of a solidified hazardous waste

Bill Batchelor and Susan Trussell

Department of Civil Engineering, Texas A & M University, College Station, TX 77843-3136 (USA)

Abstract – Project number 10TAM3142

The goal of solidification/stabilization is to limit the ability of disposed hazardous wastes to migrate in the environment via leaching mechanisms. The pore water components of a solidified waste constitute the leachable fraction of the waste form. Chemical characterization of the pore water will provide information about the fraction of the waste available for leaching. In this study, synthetic portland cement-based waste forms were prepared by varying heavy metal concentration at constant water cement ratio and varying water cement ratio at constant heavy metal concentration. Pore water was expressed and analyzed for heavy metals, major cations, major anions and alkalinity. Analytical results were used to calculate the fraction of the original contaminant mass present in the pore water. The results varied with original contaminant concentration and alkalinity. Minimum pore water concentrations of each heavy metal showed a significant decrease from the original concentrations. The results can also be used to calibrate a chemical equilibrium model for use in conjunction with a leach model.

Using a modified TCLP to determine the leaching characteristics of stabilized/solidified wastes

Bill Batchelor and Indratjahja Sofjan

Department of Civil Engineering, Texas A & M University, College Station, TX 77843-3136 (USA)

Abstract – Project number 100TAM3142

Solidification and stabilization using portland cement is an established procedure in the management of hazardous wastes. The technology is relatively

simple, cheap, and highly reliable in prohibiting the migration of the hazardous contaminants into the groundwater.

The success of this technology is measured by the amount of contaminants retained in the solidified matrix system. The most prominent procedures to measure the amount that can leach out of the solidified waste were developed by the EPA: the Extraction Procedure (EP) and, its successor, the Toxicity Characteristics Leaching Procedure (TCLP).

However, because of the lack of control on the shape and dimensions of the tested samples, as well as the pH at which the test takes place, the TCLP can be further improved by keeping the pH at a constant value and using samples with fixed dimensions. This will allow most of the leachate to leach out of the matrix at controlled conditions. Thus, the characteristics of the leaching process can be measured more accurately.

The proposed procedure, the Constant pH leaching Test (CPLT), is a modification of the TCLP. It is designed to measure the leaching rates of a fixed-dimension sample at a constant pH.

A mathematical model to predict the leaching of hazardous inorganic wastes from solidified/stabilized waste forms

Bill Batchelor and Krishan Sabharwal

Department of Civil Engineering, Texas A & M University, College Station, TX 77843-3136 (USA)

Abstract – Project number 100TAM3142

Solidification/Stabilization (S/S) technology is an important best demonstrated available technology (BDAT) for treating hazardous wastes. The method focuses on trapping the waste in a confined area and preventing it from disrupting the environment in the future. This is achieved through various mechanisms which solidify the waste by removing free water, decreasing the surface area to minimize loss of waste, limiting solubility and therefor mobility of the contaminants, converting the waste to less toxic form, reducing partic-

ulate or organic air emissions, and improving handling characteristics of the waste. Immobilization of the wastes is achieved with binders which can be inorganics, organics or a mixture. They need to be selected judiciously to obtain the desired solid waste characteristics. Inorganic binders are used in this research project and are predominantly portland cement with varying combinations of additives. Effectiveness of the S/S process can be established by different leaching and physical tests like the TCLP, EP, equilibrium batch, and sequential. However, the results from these tests are specific to the solidifed/stabilized waste being tested and give little indication of the long-term behavior of the wastes. Leach models are an effective means for predicting leaching of the contaminants, describing the immobilization and binding mechanisms, predicting performance of the waste in the TCLP test, and aiding in the understanding of S/S.

A mathematical model has been developed to predict leaching of contaminants from solidified/stabilized waste forms. It assumes local chemical equilibrium, Fickian diffusion as the only means of transport of the mobile contaminants, and homogeneous distribution of the waste at the start of the leaching period. Other assumptions include: rectangular geometry of the waste form, conditions at the solid bath interface being similar to those in the bath, and no sorption phenomena. The model is set-up for an infinite bath (no change in component concentrations in the bath) and can be easily modified for finite bath conditions. These assumptions are used in solving the mass balance equations. The equations are developed in terms of the total concentration of contaminants and their mobile fraction. As non-linear, multicomponent interactions are being considered, a modified Crank-Nicholson technique is developed to solve the stiff set of equations. The solid is divided into nodes of decreasing size from the center to the interface because the leaching rate is not the same throughout the solid. Each node is treated as a homogeneous unit. Thus, accuracy in the computations increases as the nodal size is reduced. The chemical interactions occurring in the solid are solved by the chemical speciation model, SOLTEQ (modified form of MINTEQ version 3.1 developed by EPA). SOLTEQ computes the mobile phase concentration of each contaminant a node at a time starting from the node closest to the interface. To prevent superfluous computations and lower the execution time, SOLTEQ is called for the interfacial node onwards, until the node at which a minimum prescribed component concentration change has occurred compared to the previous time step. Mobile component concentrations at nodes beyond this one are assumed to remain unchanged. To reduce oscillations in the numerical solution technique, small time steps are required. An adaptive time step approach is employed which computes the maximum time step possible while remaining within a user specified error criteria. To increase accuracy, the error criteria can be made more stringent and/or the number of nodes in the solid can be raised which would reduce the individual node sizes. However, both of these lead to an increase in execution time and the latter could cause memory space problems in the computing facility being used. Enhanced accuracy without increasing the total number of nodes is achieved by increasing the number of nodes only in the portion of the solid which requires SOLTEQ computations. The number of nodes in the portion which is not undergoing any significant chemical changes is made use of to achieve the above. The model makes use of the extensive database of MINTEQ modified to SOLTEQ requirements. Therefore, it is capable of modeling waste forms containing a vast array of inorganics.

The model has been tested for a four component system containing Ca^{2+}, Pb^{2+}, H^+, and Ac^-. The results of the model have been found to agree with in 2% of the analytical solution.

Development of a rapid technique for measurement of effective diffusivity of contaminants in solidified hazardous wastes

Bill Batchelor and Declan O'Cleirigh

Department of Civil Engineering, Texas A & M University, College Station, TX 77843-3136 (USA)

Abstract – Project number 100TAM3142

Solidification/Stabilization (S/S) is an effective treatment process in hazardous waste management. As with any technology, it is necessary to be able to predict the performance of the S/S end-products. To do this, an understanding of the binding and leaching mechanisms involved in solidified hazardous wastes is needed. The effectiveness of this process is determined by the degree to which contaminants will leach from the waste end-product.

The physical and chemical factors that determine this leaching rate need to be evaluated separately, and then described. Using a mechanistic model approach, the observed diffusivity can be related to a physical factor (effective diffusivity coefficient) and to a chemical factor. To describe the effective diffusivity the MacMullin number approach is used. The MacMullin number can be defined as the ratio of molecular diffusivity times porosity divided by a tortuosity factor. The MacMullin number can then be shown to be equal to the tortuosity factor divided by the porosity.

An electrical conductivity approach is used to measure the MacMullin num-

ber. Substantially all of the conductivity of the bulk solid is due to the conductivity of the pore water. The conductance of the solid therefore, is the conductivity of the pore water times the cross-sectional area of the pores. From this a relationship between the ration of pore water conductivity to solid conductivity and the MacMullin number can be established.

The proposed procedure involves the development of a rapid technique for measurement of the effective diffusivity of contaminants in solidified hazardous wastes. Thus there now is a way to independently, separate from any leach test, measure in a matter of minutes the effective diffusivity of a material through the pores. This is the basis of the physical characterization of the solid being tested.

The use of in-vessel composting as a treatment technology for hazardous waste minimization

K.W. Brown

Soil and Crop Sciences Department, Texas A & M University, College Station, TX 77843-3122 (USA)

Abstract – Project number 100UTA0065

Increasingly stringent governmental regulations regulating the land disposal of hazardous wastes have created a need to develop new technologies for waste stream treatment to minimize the concentrations of hazardous constituents prior to disposal. Concurrently, advances in composting of municipal sewage sludge have resulted in the development of the in-vessel composting technology. The proposed study will investigate the use of in-vessel composting for the treatment of hazardous waste. Information is available from past studies on the optimum operating conditions for in-vessel composting (type of bulking agent, C:N:P ration, moisture content, and oxygen supply). Other researchers have documented the biodegradability of many of the hazardous organic components of oily and other wastes. What is missing is clear documentation of the fate of these waste components as the waste is treated by in-vessel composting.

The present study is designed to provide a comprehensive database on the fate of selected volatile organic compounds as a hazardous waste stream undergoes in-vessel composting. During the first year we have developed, constructed, and tested our laboratory composters which will be used in the re-

mainder of this study. Preliminary experiments using motor oil are being run to test the sampling and analytical techniques after which experiments will be run in which API separator sludge will be composted. A mass balance of selected organic constituents will be maintained to document the quantities which are degraded, volatilized, or remain after treatment. In the second and third years the experiments will be repeated for waste streams contaminated with pesticide (100 mg kg^{-1} Endrin on adsorbent as from a spill cleanup), PNAs (100 mg kg^{-1} dimethylnaphthalene in API waste), and 100 mg kg^{-1} pentachlorophenol (PCP) in a pond sediment/sludge.

Successful completion of this study will provide data which can be used by the petroleum industry, those faced with cleaning up Superfund sites, and others to design and operate in-vessel composting systems for hazardous waste treatment.

Field study of mineral precipitation associated with biodegradation

Regina M. Capuano and Sarah K. Liehr

Department of Geosciences, University of Houston, Houston, TX 77204-5503 (USA)

Abstract – Project number 100UHH0111

Although biodegradation is the most effective method for subsurface transformation of hazardous organic compounds, the inorganic and organic chemical changes associated with this activity have not been well documented. In this study we propose to conduct a field experiment in which an organic solution is injected into a shallow aquifer. After a quiescent period adequate to permit microbial degradation to proceed, a nearby well that is in hydraulic communication will be pumped. Samples will be collected from the pumped well and analyzed for all major and minor organic compounds and for gases that may have been produced by the microbial activity. In addition, microbial populations will be characterized. Data from these chemical and microbial analyses will be used to document degradation processes, chemical changes resulting from microbial activity, and mineral precipitation or dissolution reactions. The thermochemical reaction progress code EQ3/6 will be used to quantify the mineral-waste reactions that have taken place, and to study the chemical controls on the degradation process.

Solidification of salts of As, Cr and Pb using cement and various additives

Frank K. Cartledge, Harvill C. Eaton, Marty E. Tittlebaum

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804

Abstract – Project number 100LSU3015

Solidification/stabilization (S/S) is a valuable technology for the treatment of certain waste streams; e.g., metal plating wastes, incinerator ashes, etc., and has great potential for use in treatment of contaminated soils arising out of historical malpractice or inadvertant spills. While the technology is relatively cheap to apply, significant questions remain about the range of its applicability. The first broad aim of the present project is to survey solidification/stabilization binding agents and additives with respect to their abilities to immobilize As, Cr and Pb, three species which are known to give problems in S/S practice. These wastes are being studied individually as well as in combinations with themselves and with water-soluble organics, particularly the very common phenolic wastes. The most basic information being obtained is metal concentration in TCLP leachates from solidified samples prepared with cementitious and pozzolanic binders and a variety of additives.

The second goal of the project is to understand the interactions between waste and matrix with the eventual intention of predicting performance and designing effective mixes. That work employs sophisticated characterization techniques, including solid-state nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared spectroscopy, and is being carried out in collaboration with the group at Lamar University.

Results to date include the following:

- Type 1 portland cement (OPC) has broad effectiveness for immobilizing metal ions, and certain deficiencies of OPC can be corrected using additives.
- Matrix changes that take place over long periods of time (1 year or more curing time) have serious consequences for the prediction of leachability. For instance, almost all of our metal waste samples, regardless of binder, show increased leachability after one year compared with after 28 days.

- Particularly large matrix composition changes take place in cement–fly-ash mixtures after long times of cure (> 1 y), and the changes are catalyzed by arsenic salts.
- Alterations in the matrix due to one metal, such as Cr(III), result in enhanced leachability of a second metal, such as arsenic.
- Leaching with a pH 5 buffer produces a predictable effect of degradation of the cement matrix, while TCLP leaching produces a very variable effect on the matrix depending upon which metal has been solidified and also the age of the sample being leached.
- Phenolic wastes are present in either an ionized or non-ionized form, and sometimes both, depending upon the specific phenol, other wastes present, and curing time. Up to 28 days, the phenol, in whatever form, is largely dissolved in pore waters and not present as a solid Ca salt.

Advanced oxidation for the simultaneous removal of NO_x and SO_2 from flue gas in a multi-phase system

Liang Li, D.H. Chen and K.-Y. Li

Department of Chemical Engineering, Lamar University, P.O. Box 10053, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB0083

Nitrogenous oxides (NO_x) and SO_2 emission control is needed for incinerators, industrial furnaces, and boilers to comply with the Clean Air Act Amendment of 1990 and state regulations. In many areas of the USA, NO_x emission control is a more effective alternative that VOC emission control for curbing urban ozone. The preliminary results from our laboratory using a bubbling reactor show that the rate of ozonation for NO is increased by a factor of 10 with UV photolysis. The O_3/NO ratio is 0.5 which is half of the stoichiometric ratio required in a gas phase reaction. Work is under way to set up a new bubble reactor in order to run UV-assisted ozonation for NO/NO_2 system with longer contact time under different pH and temperature conditions and to test synergistic effect of NO_x and SO_2 removal.

Biosurfactant enhanced bioremediation of hazardous substances

Perry F. Churchill and Robert A. Griffin

Department of Chemical Engineering, University of Alabama, Tuscaloosa, AL 35487 (USA)

Abstract – Project number 100UAL0069

The purpose of this project is to study the influence of biodegradable surfactants on the rate of petroleum hydrocarbon waste internalization in bacteria and mineralization in aqueous environments. Biodegradation of hazardous hydrocarbons is being evaluated as a function of surfactant type and concentration, hydrocarbon loading rate, contaminant hydrophobicity, nutrient concentration, dissolved oxygen concentration and temperature. For the currently funded portion of this research program, multiple sealed model bioreactors have been employed to examine hydrocarbon contaminant phase partitioning and microbial cell mineralization in the absence or presence of varying concentrations of biodegradable surfactants.

The multiphase study employed in the research program utilizes bioreactor systems having several levels of complexity with respect to the number of phases, microbes and test hydrocarbons present. The early project phases have been devoted to study of simple pure compound and commercial consortia or single microbial species in aqueous phase bioreactor systems. These systems model aquatic or soil bulk water phase biodegradation environments. Bioreactor studies have demonstrated the action of surfactants to enhance hydrophobic contaminant mineralization by soil microbiota. Surface desorption, aqueous dispersion and enhanced hydrocarbons uptake by microbes can be facilitated by system amendment with biodegradable surfactants, either synthetic or biosynthetic.

Project year 1 has focused on extensively testing several biodegradable surfactant products for their ability to accelerate mineralization of test compounds in aqueous solution. The test surfactants include mixed rhamnolipids, which are biosynthesized surfactants produced by a *Pseudomonas* species, and Inipol EAP-22, the oleophilic fertilizer tested by the U.S. EPA in beach bioremediation of the Valdez oil spill in Prince William Sound, Alaska. Both products have been shown to accelerate the biodegradation of aliphatic hydrocarbons by both microbial consortium and pure bacterial strains in a concentration dependent manner similar to that observed for other synthetic surfactants ex-

amined (Bioversal and Biosolve). With the exception of one known case, aliphatic substrates are chromosome-encoded; when specific metabolic pathways were not induced, the primary enhancement effects observed were attributable to decreased degradation lag phase with respect to non-amended controls.

Other surfactant enhanced biodegradation experiments have targeted selected hydrophobic aromatic pollutants. Dispersion and accelerated cell barrier transport effects promoted the degradation of benzene, toluene, *p*-cresol and naphthalene by pure *Pseudomonas* microbial strains. The oxidation of the later three compounds was carried out by specific *Pseudomonas* strains known to contain plasmids which encode metabolic pathways responsible for the primary metabolism of these aromatic compounds. Mineralization of *p*-cresol, benzene and toluene was considerably accelerated by Biosolve, Inipol EAP-22 and rhamnolipids when the catabolic plasmid enzymes were induced. Enhancement was attributed to (1) reduction in degradation lag phases (in most cases), and (2) increased rate andextent of mineralization. The mineralization rate of naphthalene increased only slightly. The possibility that the *Pseudomonas* spp. responsible for naphthalene degradation produces cell wall biosurfactants is a point of current investigation.

All surfactant preparations utilized, including Inipol EAP-22, were shown to substantially lower surface tension of the aqueous systems tested. Although the level of the rate enhancement was specific for individual surfactant, compound and microbe combinations tested, the maximum rate acceleration per preparation was achieved when the concentration exceeded the critical micellar concentration (cmc) of the surfactant of interest for all combinations tested. Increasing the surfactant concentration beyond the cmc had little additional effect on rate enhancement. This observation supports a micellar-mediated aqueous phase dispersion and transport model.

Feasibility of recovering metals from soil, ash, and sludges using anhydrous ammonia

Dennis A. Clifford

Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204-5503

Abstract – Project number 100UHH3165

We propose to continue the development of an anhydrous ammonia extraction process for the removal of toxic metals from soils using ammonia alone or

in combination with enhancing ligands such as acetate or EDTA. In the commercial process that we envision, finely divided soil containing toxic metals ranging from 0.1% to 50% will be extracted in a closed system at ambient temperature at the saturation pressure of ammonia – 110 psig. The metals extracted under these conditions will be collected for reuse in a separator where the ammonia will be flashed off prior to recompression and recycling.

Experimental results obtained during the last six months indicate that cadmium, mercury, copper, and zinc can be extracted from contaminated soil using anhydrous ammonia alone. Lead can be removed using anhydrous ammonia in conjunction with extraction-enhancing anionic ligands such as acetate and EDTA.

Extensive screening tests were performed at a slightly elevated temperature of 43 °C and 250 psig using a pressurized stainless steel Soxhlet extractor to rapidly evaluate the anhydrous ammonia extraction concept. A typical test involved soil spiking and aging prior to Soxhlet extraction for 2-hours with 30 extraction/siphon cycles. When extracting soils that were soaked with metal nitrate solutions prior to drying and aging, the metal removals were 73% for copper and cadmium, 64% for zinc, and 26% for mercury when the metal-nitrate spiking concentrations ranged from 20,000 to 50,000 mg/kg. Only 8% lead removal was observed using ammonia under these conditions. Furthermore, poor extraction efficiency was uniformly observed for all metals when extracting soil samples with spiking concentration below 2,000 mg/kg.

When enhancing ligands were added prior to ammonia extraction, lead removals greatly improved. For example, 95% removal was achieved from $Pb(NO_3)_2$-spiked soil previously soaked in disodium EDTA solution and dried prior to extraction. When using dry-mixed enhancing ligands such as powdered sodium acetate or disodium EDTA, 75% to 87% lead removal was achieved on $PbSO_4^-$, $PbCO_3^-$, PbO- or Pb°-spiked soil samples during ammonia extraction. Similar extraction results were obtained for lead-contaminated Superfund soil treated with solution-mixed or dry-mixed enhancing ligands prior to ammonia extraction.

A commercially available Supercritical Fluid Extraction (SCE) Screening System has been purchased and used under subcritical conditions (110 psig, 23 °C) to further evaluate the anhydrous ammonia extraction concept. The limited SCE experimental results obtained to date are confirming the Soxhlet extraction data for copper removal from $Cu(NO_3)_2$-spiked soil. Eventually the SCE will be modified to incorporate a mechanically-stirred extraction reactor in place of the fixed-bed extractor now in use. The modified SCE will more closely simulate the extraction mixing conditions in a full-scale soil extractor. The general objectives of the continuing research are to (1) determine the effects of soil parameters such as size and composition on the rate and extent of metal – cadmium, copper, or mercury – extraction by pure ammonia in a stirred reactor, and (2) to determine the effects of the form – oxide, carbonate, sulfate or nitrate – of metal on the rate and extent of extraction.

Feasibility of removing lead and other toxic metals from contaminated soil by volatilization in nitrogen

Dennis A. Clifford

Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204-5503 (USA)

Abstract – Project number 100UHH2092

We propose to continue the development of an inert-atmosphere thermal process for the removal of lead from soil, particularly at battery waste sites and lead reclaiming operations. In the commercial soil treatment process that we envision, finely divided, surface soil containing up to 30 wt% lead will be heated above 850°C in an inert atmosphere furnace such as a rotary kiln purged with nitrogen. lead volatilized under these conditions will be collected in a scrubber containing pure-lead-metal pellets which will grow in size as lead vapor condenses on them.

Bench-scale tests completed during the last year have proven that lead in essentially any form can be removed from contaminated soil with greater than 90% efficiency by heating in reducing (hydrogen) or inert (nitrogen) atmospheres. For example, heating a Texas Superfund soil from a lead–acid battery waste site for 20 minutes in nitrogen at 900°C reduced the lead content from 8,220 mg/kg to less than 560 mg/kg, i.e. a 93.2% removal. Similar percent lead removal was achieved using hydrogen while only 73% removal was attained in air under the same conditions.

The lead volatilized from soil in these tests appeared to condense on the cool surfaces of the clear vycor glass heating tube near its exit. No attempt was made in these tests to quantitatively measure the lead recovered because the apparatus was not designed to do so. The continuation work will address the recovery issue by continuing the study of lead collection on small glass beads in a modified apparatus using pure lead compounds and lead spiked soils. The effects of purge gas oxygen content, soil particle size, and soil clay and organic content will also be studied. One goal of the continuing research is to establish the design parameters for a larger bench-scale apparatus which will be used to determine the quantity and quality of lead recovered from 100-fold larger (50 g) samples.

Development of new environmental analytical methods with high performance planar liquid chromatography

David L. Cocke

Department of Chemistry, Lamar University, P.O. Box 10022, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB0091

Many environmentally important chemical substances are not amenable to analysis by convenient methods such as gas chromatography (GC). Carbamate pesticides, for example, are not stable at the high temperatures that exist in the injection port of a GC. Compounds such as these are often analyzed by high pressure liquid chromatography (HPLC). HPLC, however, is an expensive and very time consuming technique, and requires a highly skilled technician in order to obtain reliable measurements. High Performance Planar Liquid Chromatography (HPPLC) provides a potentially excellent alternative to HPLC. HPPLC has sensitivity comparable to HPLC, but samples can be analyzed in a fraction of the time and for a fraction of the cost of HPLC. If funded, we intend to develop analytical methods using HPPLC for the analysis of environmentally important chemical substances. Under the direction of Dr. Rudolf Kaiser, a pioneer in the field of HPPLC, we plan to utilize equipment already in his possession to develop these new methodologies for the rapid, inexpensive, and reliable measurement of selected hazardous substances. In addition we plan to utilize a fast atom bombardment (FAB) mass spectrometer to investigate the process of HPPLC at the molecular level to make optimal use of the technique for donated to the Environmental Chemistry Laboratory will be used to investigate decomposition, adsorption-desorption, and diffusion phenomena which are the key phenomena of the HPPLC process. The FAB will also serve as an extremely sensitive detector for HPPLC, especially important in the detection of compounds which do not absorb or emit light. The successful development of HPPLC methodology in this project will result in faster and more economical hazardous substance analyses.

Binding chemistry and leaching mechanisms in solidified hazardous wastes

David L. Cocke

Department of Chemistry, Lamar University, P.O. Box 10022, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB3142

This continuation proposal requests funding to further examine the binding chemistry and leaching mechanisms of priority metal pollutants and selected organic hazardous substances with cement and other pozzolanic materials. It can be divided into three main tasks: (a) to determine the nature of the bound states, (b) to determine the mechanism of leaching, and (c) to develop concepts and models that will improve the stabilization/solidification process. The present proposal includes plans to extend this work to mixed metals and to mixed metals and organics to explore the possible synergistic effects in these more complicated systems. Considerable progress is continuing to be made as to the chemical nature of the fixation of Pb, Cr, Ba, Zn, Cd and Hg in the cement solidification medium. These metals strongly affect the hydration chemistry of the cement. Models for these effects have been developed. This work is also leading to a better understanding off the leaching mechanisms. The chemical changes induced by leaching are being explored by surface analysis of XPS, ISS, AES and RBS and bulk techniques of XRD, SEM-EDS, and optical spectroscopies. Leaching substantially removes surface and subsurface calcium. In addition, the material structure as to pore volume, pore area, bulk density and pore diameter are being probed before and after metal doping and before and after leaching with mercury porosimetry. These results that show the original trimodal pore distribution (i.e., three size regions) off the cement is substantially altered by the presence of the metal and the leaching process.

Enhancement of the kinetics of incineration of dilute hazardous organic vapors – phase III

David Cooper and Christian A. Clausen, III

Department of Civil and Environmental Engineering and Chemistry, University of Central Florida, P.O. Box 25000, Orlando, FL 32816-0450

Abstract – Project number 100UCF3149

The destruction of dilute hazardous organic compounds (HOC) in air often is accomplished by oxidation in an incinerator. Many organic pollutants have been combusted at temperatures from 1200 to 2200°F. High temperatures are needed for the high efficiency (99.99%) destruction of odors, paint solvents, chlorinated hydrocarbons and other hazardous organics. Addition of a material that enhances the kinetics of the oxidation reactions in the post-flame zone could result in lower temperatures and more complete destruction of all HOCs of industrial significance. Experiments are being conducted on the enhanced destruction of HOCs by hydrogen peroxide in an externally heated, plug flow quartz tube reactor, and state-of-the-art analytical equipment.

Development of screening tools to estimate the performance of free product recovery

Yavuz Corapcioglu, Rajasekhar Lingam and Kiran Reddy Kambham

Department of Civil Engineering, Texas A&M University, College Station, TX 77843-3136 (USA)

Abstract – Project number 100TAM0093

The success of recovery of the hydrocarbon spill depends on the accurate placement of the recovery well at the spill site. This research obtains analytical expressions for the recovery of a light immiscible fluid on the groudwater table

following an oil spill. Using conservation of mass principles of the oil phase, incorporating boundary conditions and averaging the vertical direction, a governing equation in terms of the oil thickness is derived. By combining the governing equation, boundary conditions and an initial profile, the gasoline thickness at any radial distance from the oil source and at any time can be calculated. The resulting equation is solved analytically by imposing a variety of boundary conditions for a multi-level, two pump recovery technique.

Electrokinetic detoxification of soil

David E. Daniel

Department of Civil Engineering, University of Texas at Austin, Austin, TX 78712 (USA)

Abstract – Project number 100UTA3158

For the past two years, we have been studying electrokinetic decontamination of soil. We have been able to move metals in soils and electric currents but have found that several complicating factors can "make or break" electrokinetic treatment of contaminated soil. The intent of our research is to characterize the complex system of soils treated electrokinetically and to identify an optimal technique.

The single most critical factor in removal of metals from contaminated soil with electrokinetic treatment has been found to be pH. In low pH environments, most metals tend to be quite mobile. However, in high pH environments, most metals adsorb and precipitate to solid surfaces and are extremely difficult to remove from the soil. During electrokinetic treatment, the pH of the soil solution near the anode is low, and near the cathode it is high. With time, the acid front generated near the anode may migrate through the soil and "flush out" the sorbed metal accumulated near the cathode. However, this migration of the acid front depends significantly on the flow rate, boundary fluxes, and internal buffering of the soil solution. For instance, the tendency of alumina to be dissolved from the soil at low pH appears to determine the lower limit of pH in the soil and, ultimately, the migration of the acid front toward the cathode. Thus, we have found that electrokinetic treatment may or may not work, depending largely upon the complex relations that control pH.

We have developed a multicomponent transport model that will predict the changes in pH and associated migration of inorganic chemicals in soil during electrokinetic treatment. Model results have been compared to measured be-

havior. The model has shown the same trends as the experiments: the pH gradients that develop in the soil dominate contaminent transport during electrokinetic treatment.

An experimental study of treated waste/soil interactions and the long term fate of heavy metals in the vadose zone

Rona J. Donahoe

Department of Geology, University of Alabama, P.O. Box 870338, Tuscaloosa, AL 35487-0338 (USA)

Abstract – Project number 100UAL3004

Knowledge of soil–heavy metal sorption-desorption processes is incomplete and experimentally obtained data for heavy metal behavior in soil often fails to accurately predict the behavior of these toxic contaminants in natural systems. We believe that this failure is due in part to the complexity of vadose zone processes, but also to the fact that much of the heavy metal–soil interaction data was collected using overly simplified experimental systems. In addition, the fate of heavy metal elements attenuated by soil during recharge conditions has not been adequately examined, particularly for acid rainwater leaching conditions. In this GCHSRC-funded project, the attenuation and mobility of heavy metal micropollutants in soils is being studied in column flow-through experiments. Treated municipal waste effluent has been reacted with two sandy loam and two silty loam soil samples to study soil–waste interactions characteristic of this waste matrix in the absence of high concentrations of heavy metals. These experiments have been performed in duplicate with very good reproducibility. The mobility of soil-attenuated metals has been studied by subjecting one of the reacted columns for each soil sample to aggressive leaching conditions using a synthetic acid rain solution. These experiments have characterized the interactions occurring between the treated municipal waste effluent and the four soil samples, and examined the response of the reacted soil columns to acid rainwater leaching conditions. In the second half of the project, treated municipal waste effluent spiked with heavy metal elements (Ba, Cd, Cr, Cu, Zn, Mo, Pb) will be reacted with each of the soil samples in column flow-through experiments. One set of reacted soil columns will be leached with the synthetic acid rainwater solution to determine the mobility of soil-attenuated heavy metals. Through the use of a complex waste matrix,

these experiments will increase our knowledge of heavy metal attenuation mechanisms in soil, and will provide basic data needed to more accurately model the behavior of heavy metals in the vadose zone. The data obtained in this study will have application to land disposal of treated waste, the accidental discharge of waste materials containing heavy metals, and the establishment of soil heavy metal accumulation regulation criteria.

Application of microwave heating techniques to the detoxification of contaminated soils

Clifford E. George and Jiayi Fan

Department of Chemical Engineering, Mississippi State University, P.O. Drawer CN, Mississippi State, MS 39762 (USA)

Abstract – Project number 100MSU3107

Investigations have continued to determine the effectiveness of microwave heating techniques to remove the volatile compounds of benzene and xylene from contaminated sand and clay soils. Studies indicate that 99.99% Destruction and Removal Efficiency (DRE) can be obtained when 3% water is added to the soil and the system is operated under vacuum conditions. Additionally, it was found that clay soils were much more amenable to treatment by this method than sandy soils.

The work was expanded to study the removal of semi-volatile compounds such as those found in oil refinery API separator sludges (APISS). Phenanthrene was used as the base representative was used as the base representative semi-volatile compound found in a typical APISS. Near 100% DRE was obtained when synthetic sludge was treated in a modified microwave apparatus with carbon black added to the mixture.

Additional work has been done using soils contaminated with pentachlorophenol (PCP). To date, the results with PCP have been poor (60%)-DRE. However, results from the work with the APISS highlights the necessity of adding an additional liquid in order that co-volatilization might take place. Since the normal boiling point (NBP of PCP is 340 °C, water with its NBP of 100 °C is not able to act as an effective carrier. The phenanthrene studies indicate that the addition of a light oil may be necessary for complete removal of PCP.

Equipment which has been purchased during the course of this research now includes a 1.5 kW Gerling Laboratories microwave power supply and research center. Funds from both GCHSRC and Mississippi were used for this latest acquisition.

Biodegradation of PCBs by the white rot fungus *Phanerochaete chrysosporium*

George Georgiou
Department of Civil Engineering, University of Texas at Austin, Austin, TX 78712 (USA)

Abstract – Project number 100UTA3168

White rot fungi are able to attack and degrade a wide variety of recalcitrant organic pollutants including polyaromatic hydrocarbons and chlorinated compounds. However, the unique degradative potential of these organisms has not yet been exploited for commercial waste treatment processes. *Phanerochaete chrysosporium*, the best studied white rot fungus, synthesizes a variety of oxidizing enzymes, such as ligninases and Mn-dependent peroxidases, that catalyze the initial rate limiting step in the degradation of recalcitrant compounds. While the production of these enzymes is essential for biodegradation, it occurs only when the mycelia are grown under very specific conditions that cannot be easily reproduced in bioreactors. We have examined the production of ligninases in batch cultures of *P. chrysosporium*. High levels of enzymes were obtained reproducibly using mycelia grown at 33 °C in optimized growth medium. The effects of concentration and degree of chlorination on biodegradation of biphenyl and PCBs is being investigated. The compounds degraded include biphenyl, 2-chlorobiphenyl, and 2,2″,4,4′-tetrachlorobiphenyl at concentrations up to 500 to 1000 nmoles. Using uniformly ^{14}C labeled biphenyl, we have shown that as much as 20% of the initial amounts can be mineralized to $^{14}CO_2$, and another 60% converted to water soluble by-products. These studies have demonstrated that *P. chrysosporium* holds great promise for future waste treatment applications. Currently, the use of calcium alginate immobilized cells is being studied for scale up to laboratory scale bioreactors.

Destruction of toxic organic materials and sludges by supercritical water oxidation

Earnest F. Gloyna

Department of Civil Engineering, University of Texas at Austin, Austin, TX 78712-1076 (USA)

Abstract – Project number 100UTA3155

Super Critical Water Oxidation (SCWO) has demonstrated its capability to treat toxic organic compounds. However, the data base that incorporates the destruction performance on a wide variety of compounds does not exist. Since design data are critical to the development of the SCWO process, it is very important to develop batch and continuous-flow apparatus capable of providing the information. In addition, solving engineering problems such as charring, encrustation, and corrosion is also critical to the overall success of SCWO process. Therefore, the objectives of this continuing project are to: (a) obtain supercritical water oxidation data on a wide variety of toxic organic compounds such as heptachlor, γ-BHC, anthracene, 1,2,4-trichlorobenzene, and dimethy phthalate; and (b) evaluate pyrolysis, hydrolysis, charring, and oxidation for biological sludge.

The two unique batch-microreactor systems that have been developed in the previous period will be used to accomplish the research objectives. One (UT Mark I) will be used to collect destruction data and the other (UT Mark II) will be used to investigate hydrolysis and charring phenomena with/without oxygen.

Chemical degradation of unsaturated priority pollutants by oxidation with aqueous sodium perborate

John T. Gupton[a] and John P. Idoux[b]

[a]*Department of Chemistry, University of Florida, Orlando, FL (USA)*
[b]*Department of Chemistry, Lamar University, P.O. Box 10002, Beaumont, TX 77710 (USA)*

Abstract – Project number 100LUB3140

Oxidative degradation has long been an important procedure used both by nature (i.e., various living organisms) and by man (e.g., waste treatment fa-

cilities) to treat and/or effect the decomposition of many substances which pose a significant risk to human health or to the environment. Unfortunately, some of the most common oxidizing agents used by man (e.g., chlorine, hypochlorites and related substances) produce undesirable by-products such as chlorinated hydrocarbons. In addition, such agents are, of course, not effective against certain classes of priority pollutants such as the unsaturated chlorinated hydrocarbons. Thus, the development of safe, inexpensive and efficient alternative oxidative degradation agents and procedures remain a challenge. A material which holds great potential as such an agent is sodium perborate. It is a cheap non-toxic, large scale industrial chemical that serves as a ready source of the "active oxygen" required for oxidative processes. For example, it is used as an oxidative degradation agent in a variety of human, oral hygiene products (e.g., antiseptics, mouthwashes and toothpastes) and has even replaced chlorine as the agent of choice used in fiber bleaching. The objective of the studies outlined in this proposal is to determine if sodium perborate can be used to effect a chemical, oxidative degradation of a variety of EPA priority pollutants which are members of the unsaturated chlorinated hydrocarbon class. Specifically, the ability of sodium perborate to degrade the chloroethylenes, styrene, heptachlor, chlordane, pentachlorophenol, polychlorobiphenyls (PCBs) and other similar priority pollutants will be investigated. The chemical methodology to be used will be based on several previously reported successful studies of sodium perborate's ability to act as an oxidative, degradation agent – i.e., our report of the degradation of 1-methylstyrene, a compound related to the priority pollutants listed above, and the reports by other workers on the oxidation of sulfides, anilines, phenols and ketones. The proposed methodology of the former report, which involves reaction in a water environment at temperatures of 25–50 °C., is a model of simplicity and efficiency. This method will be applied to the priority pollutants listed above with the aim of optimizing the characterization of the degradation products and the concentration, pH and time parameters required for the degradation process. These studies are the initial phase of what is envisioned as a long-term project aimed at eventually developing degradation processes for virtually every class of priority pollutants.

The clam *Rangia cuneata* as a standard biomonitor of hazardous substances in gulf coast and southern atlantic estuaries and inland waters

Richard C. Harrel and Marc A. McConnell

Department of Biology, Lamar University, P.O. Box 10037, Beaumont, TX 77710 (USA)

Abstract – Project number 100MSU3144

The emphasis on hazardous substances, and knowledge that very low concentrations of some substances can cause adverse effects due to bio-accumulation, has caused an increased interest in biomonitoring. The ability of bivalve mollusks to accumulate some toxic materials is well documented. The U.S. Mussel Watch Program uses *Mytilus edulis* as a standard biomonitor species in cold temperate waters along the Pacific and Northern Atlantic coast. No single species is used as a biomonitor along the Gulf Coast and Southern Atlantic estuaries and inland waters. This project is investigating the use of the clam, *Rangia cuneata*, as a standard biomonitor for hazardous substances for southern Atlantic and Gulf Coast estuaries and inland waters.

Accumulation of the metals cadmium, copper, chromium, and lead are being studied under laboratory and field conditions. Bio-accumulation rates and concentrations of the metals in *Rangia* tissues and in the media are being determined in the laboratory for determination of bioconcentration factors (BCF). Specimens from a control population are being placed below industrial effluents that receives some of the metals. After 5, 10, 20, and 40 day exposure periods clams are removed and water, sediments, and clam tissues are analyzed for metal concentrations. Metal concentrations and accumulation rates from the laboratory and field exposures will be compared. Results from laboratory tests on exposure to copper resulted in BCF ratios between 41 and 149, with a correlation coefficient of 0.82. Exposures to chromium resulted in BCF ratios between 12 and 534, with a correlation coefficient of 0.92. Laboratory exposures to cadmium and lead are currently being conducted. Field exposures have been conducted at two sites in the Neches River estuary and the metal analyses have been completed from one site. These data revealed low concentrations of metals in the water, very high concentrations in the sediments, and intermediate concentrations in *Rangia* tissues. No linear relationship was found to exist between exposure time and concentration for any of the metals.

Academic partnerships for minority participation in environmental education, environmental careers, and the EPA Superfund program

J. Paul Hartman

College of Engineering, University of Central Florida, P.O. Box 25000, Orlando, FL 32816-0450 (USA)

Abstract – Project number 1050UCF0062

Using the Environmental Protection Agency's Intergovernmental Personnel Act, the EPA will cooperate with a majority institution, the University of Central Florida, to develop a Florida statewide pilot program with historically black colleges and universities with emphasis on: (1) the prevention of pollution through increased environmental education awareness, (2) informing, stimulating, and preparing minorities for increasing environmental career opportunities, and (3) mentorship programs for minority faculty in Superfund research projects to help solve environmental pollution problems. This pilot program also will study increased statewide networking with respect to EPA Superfund–industry–university–elementary and secondary education linkages for future activities.

Metal capture and partitioning during fluidized bed incineration of solid wastes

Tho-Ching Ho

Department of Chemical Engineering, Lamar University, P.O. Box 10053, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB3114

The U.S. EPA has reported that metals account for almost all of the identified risks from waste incineration systems. However, current incineration technology does not control metal emissions effectively. The proposed project is to develop an alternative control technology for heavy metal emissions via the capture of metals during fluidized bed incineration. The objectives of the project are to demonstrate the technology and to investigate the characteristics

of the metal capture process. Experiments have been carried out in a 7.62 cm laboratory-scale fluidized bed of various sorbents, including limestone, bentonite, aluminum oxide and sand. Artificial test materials contaminated with lead nitrate and lead chloride were utilized. The results from the first two years of investigation have demonstrated that the proposed technology is highly practical. The capture efficiency has been observed to range from 19 to 96% depending on operating conditions. In this continuation application for the third year, two phases of investigation are proposed. Phase I is to continue the current experimental investigation to quantitatively and systematically characterize the metal capture process with emphasis on wastes contaminated with mixed metals. Phase II is to construct and test a novel two-stage fluidized bed incinerator which has a great potential to further enhance the metal capture process.

Waste minimization by process modification

Jack R. Hopper and Carl L. Yaws

Department of Chemical Engineering, Lamar University, P.O. Box 10053, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB3139

This research involves a continuation of development of examples of waste minimization by process modifications including reaction and separation parameters. Such examples can be used as guidelines for process and environmental engineers to minimize waste generation.

In the first phase of the research, waste minimization by process modification was investigated for the production of allyl chloride. The investigation focused on modification of reaction and separation parameters to minimize the generation of 1,2-DCP (1,2-dichloropropane) by-product while maintaining the production of allyl chloride (3-chloro-1-propene) product. For the two-reaction model, specific condition (temperature, propylene/chlorine mole ratio, residence time, pressure, distillate/feed mole ratio, reflux ratio, etc.) were specified for minimum generation of 1,2-DCP by-product.

In the present study of waste minimization by process modification is being conducted for the production of acrylonitrile. Acrylonitrile (propanenitrile) is one of the largest volume chemicals produced in the U.S. It is used in acrylic fibers, copolymers, nitrile rubber and many other applications. It is produced by gas-phase catalytic air oxidation of propylene and ammonia. Several by-products are generated in the process.

The present study will focus on minimization of generation of the by-products by conducting the following primary activities:

(1) Develop an analysis of the effect of modification of reaction parameters on the waste minimization for the process.
(2) Develop an analysis of the effect of modification of separation parameters on the waste minimization for the process.

An electronic bulletin board system for the Gulf Coast Environmental Library

Donald Jordan

Department of Computer Science, Lamar University, P.O. Box 10056, Beaumont, TX 77710 (USA)

Abstract – Project number 031CWP0190

Disposal of the ever-increasing amounts of hazardous substances is a critical concern in our society. Vast amounts of resources are necessary to conduct research into the most efficient and effective means to treat these wastes. Officials of the Federal Government, State Governments, and in Industry are involved in the planning, allocation of resources and exchanging technical information to combat this problem.

An important element in this process is the rapid transfer and exchange of information concerning new technology, existing and proposed research efforts, current literature, and scientific conference information exchange. Sharing of data and information among agencies can reduce cost and eliminate unnecessary redundancy. Storage of this information in a central repository for expeditious retrieval and transmittal can result in timely decisions in situations dealing with hazardous materials and substances.

The Gulf Coast Environmental Library is designed to assist and share this current, state-of-the-art information and/or technology with requesting researchers, scientists, government officials, and individuals.

High-pressure solvent extraction and catalytic oxidation of hazardous wastes from aqueous streams

F. Carl Knopf and Kerry M. Dooley

Department of Chemical Engineering, Louisiana State University, 3418 CEBA, Baton Rouge, LA 70803 (USA)

Abstract – Project number 100LSU3101

Our aim is to develop a comprehensive understanding of the supercritical fluid (SCF) extraction of contaminants from aqueous streams, and subsequent catalytic oxidation of the high pressure solvent/contaminant mixture. We want to use this knowledge to aid in the commercialization of SCF-based waste treatment processes.

We are investigating a new treatment process for contaminated streams – the application of non-toxic SCF (high pressure, moderate temperature) solvents to effect contaminant extraction. In particular, advantage can be taken of the unique properties which exist when a solvent becomes supercritical. In supercritical fluid (SCF) extraction, a solvent gas such as carbon dioxide, at high pressure and moderate temperature, is contacted with a solid or liquid phase. Slight changes in the system temperature or pressure can cause large changes in solvent density and consequently in its ability to solubilize relatively nonvolatile components. Thus, manipulation of system temperature and pressure can be useful in extraction and separation of organic contaminants. We are examining both CO_2 and propane as candidate SCF solvents, with a current focus on cleanup of priority pollutants from contaminated streams. Results for the removal of benzene, *m*-cresol, *p*-chlorophenol and phenol from water have been reported. To help demonstrate the utility of SCF technology, we have also reported on our cleanup studies of industrial waste streams.

Removal of toxic heavy metal ions from industrial effluent by membrane separation technology

Sefa Koseoglu and Bill Batchelor

Departments of Food Protein R&D and Civil Engineering, Texas A&M University, College Station, TX 77843-2476 (USA)

Abstract – Project number 100TAM2036

Waste streams of toxic and hazardous substances usually are dilute solutions. Removal of hazardous substances from effluent by conventional methods (liquid-liquid extractions, floculations, adsorptive separations and distillation) often are not economical due to the large volumes that need to be handled. Even if the treatment is based on oxidation or reducing agents in mole-to-mole basis, reductions in volume can drastically reduce capital costs of waste treatment facilities. Many treatments are energy intensive or produce secondary waste materials that can create environmental problems.

The proposed research will combine advantages of both aqueous Micellar Enhanced Ultrafiltration (MEUF) and ultrafiltration/reverse osmosis to develop a non-aqueous MEUF technique to separate organics and dissolved metal complexes in waste waters, oils and solvents from metal finishing industries by using biodegradable natural surfactants such as phospholipids. The retentate from this process containing concentrated hazardous and toxic organics and heavy metals attached to surfactant or phospholipids could be treated economically due to its low volume by various processes including electrochemical, chemical, thermal and physical methods.

The first phase of the project that was funded last year includes the study of the binding of pollutant and five dissolved metals (Cd, Cu, Pb, Ni, and Zn) to phospholipids (micellas) using ultrafiltration (diafiltration) method to obtain binding parameters to prepare binding curves showing the molar binding ratio vs. the free dissolved toxic metal complexes/organics concentration to determine the number of binding sites available within the micelle structure and intrinsic association constants. In addition, the stability of the membranes was determined by examining UF membranes (ceramic, metallic and polymer) before and after separation trials to evaluate effects of solvents on membrane structure, using scanning electron microscopy as needed.

The proposed second phase will evaluate the commercial membranes identified during the first phase of the project in pilot scale and determine permea-

tion rates at various system pressures, operating temperatures, and critical micella concentrations and to correlate data with removal of toxic substances. Effects of surfactant concentration and permeate/feed concentration ratio, critical micella concentration (CMC) and on permeate flux, membrane pore size and selectivity will be determined. Also, opportunities for separating phospholipids from the pollutants by chemical methods for reuse and easy disposal will be examined. As time permits, in-field applicability of the process with samples of electron-plating wastes will be determined and finally a feasibility report on construction of small a portable non-aqueous MEUF system will be prepared.

Detoxification of pentachlorophenol and cresols in woodtreating waste

Chiang-Hai Kuo

Department of Chemical Engineering, Mississippi State University, P.O. Drawer CN, Mississippi State, MS 39762 (USA)

Abstract – Project number 100MSU3104

The present research concerns the detoxification of woodtreating wastes containing pentachlorophenol and/or cresols by chemical oxidation. A stopped-flow spectrophotometer system and several stirred-tank reactors were applied to study kinetics of the oxidation reactions. Treatment of the pollutants by hydrogen peroxide may not be feasible because of slow rates of oxidation. The ozonation process can be an effective mean for the detoxification; the half-life of the pollutants in the ozonation reactions is only a few milliseconds. The kinetics of reaction is second order overall with first order in the concentrations of the dissolved ozone and pollutant. For complete conversion of one mole of a cresol isomer, three moles of ozone are required. On the other hand, the stoichiometric ratio is five moles of ozone per mole of pentachlorophenol.

In distilled water at 25 °C, the second order rate constant for the pentachlorophenol–ozone reaction is 4,860,000 L/mol s. For the ozonation of cresols, the rate constants are 32,240, 60,870 and 45,460 L/mol s, respectively, for *o*-, *m*- and *p*-cresol at the same condition. In the temperature range of 10 to 40 °C investigated in this work, the ozonation rate of *m*-cresol is faster than that of the other isomers. The experimental results indicated that the ozonation rate of a pollutant increases with the temperature and pH value of an aqueous solution.

Characteristics of MSW incinerator fly ash promoting the formation of polychlorinated dioxins

Alan Lane and W.S. Hinton

Department of Chemical Engineering, University of Alabama, Box 870203-255 MIB, Tuscaloosa, AL 35487-0203 (USA)

Abstract – Project number 100UAL3106

Polychlorinated dioxins are known to be formed on municipal waste incinerator fly ash by catalytic activity of the fly ash itself. However, it is unknown what characteristics of the fly ash are responsible for the dioxin formation. The study is aimed at correlating specific fly ash characteristics to dioxin content of fly ash samples from various MSW incinerators across the United States. Several elemental species exhibited positive correlatability to dioxin formation. Laboratory experiments were performed to confirm the reactivity of several of the noted elemental species.

Systematic approach for the selection of the least-cost treatment technology for aqueous organic hazardous wastes

Desmond F. Lawler and Gerald E. Speitel, Jr

Department of Civil Engineering, University of Texas at Austin, Austin, TX 78712 (USA)

Abstract – Project number 100UTA0098

Decisions concerning the technologies to be used to treat waters contaminated by hazardous organic chemicals are complex. The complexity stems from the mixture of chemicals in contaminated waters, the range of concentrations encountered, the variety of available treatment technologies, the maze of reg-

ulatory constraints, and the multitude of process configurations that give technically feasible solutions. Faced with this complexity, designers aim for a reasonable design, but not necessarily a least-cost design. The proposed research is designed with two objectives:

(1) to create a unified decision tool, a computer-based system, that will allow designers to investigate systematically a wide variety of technically-feasible solutions and arrive at the least cost option, and

(2) to increase our understanding of one treatment option, simultaneous biodegradation and liquid-phase adsorption.

The two objectives are linked because understanding of the biodegradation/ adsorption technology is poor and designers ignore the biodegradation that can occur in an activated carbon adsorption bed. This omission leads to choosing an entirely different technology. The results of our previous research indicate that, when technically feasible, air stripping with off-gas adsorption is cheaper than liquid phase adsorption. For liquid phase adsorption to be a reasonable option, understanding the biodegradation/adsorption process is critical.

The accomplishment of both objectives requires a large amount of computer work; the second also necessitates laboratory experimentation. To accomplish the first objective, the framework for the computer-based system for the decision analysis and optimization will be created first, using expert system software and several programs to guide the user. Then, simulation models for each treatment process will be written (or improved), and set into the unified framework. Six treatment processes are to be included: air stripping, air stripping with gas phase adsorption, liquid phase adsorption, combined biodegradation and adsorption, steam stripping, and biodegradation. Finally, results of many hypothetical cases will be analyzed and the results synthesized into general guidelines; these guidelines will be incorporated back into the expert system frame work in the final package. For the second objective, a rapid screening model for the applicability of biodegradation/adsorption systems will be developed first. A refinement of an existing detailed model will then be undertaken. As noted above, these models will be inserted into the unified decision analysis framework established in accomplishing the first objective. Finally, laboratory experimentation will be undertaken to verify the biodegradation/ adsorption models.

Treatment of chloro-hydrocarbon contaminated ground water by bio-degradation

Ku-Yen Li

Department of Chemical Engineering, Lamar University, P.O. Box 10053, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB3136

Air stripping of trichloroethylene, dichloromethane, 1,2-dichloroethylene, 1,2-dichloroethane, chlorobenzene, and 2-chloroethyl ether from groundwater has been demonstrated in a pilot scale packing column unit with a granular activated carbon (GAC) adsorber in the air stream. This study has shown that these compounds can be stripped but that the removal efficiency of 2-dichloroethyl ether (DCEE) needs to be improved. This can be accomplished by using a stripping system of multiple columns in series instead of one single stripping column.

Although air stripping is cost effective, it is still a separation method which leaves a hazardous residue. This residue must be collected from the air stream and treated to reduce its toxicity before it can be safely sent to final disposal.

The previous work on this project has established basic data on the air stripping approach coupled with collection on carbon for biological treatment. it is now proposed to examine the direct treatment of the original waste by an anaerobic aerobic treatment train to provide data to permit evaluation of the comparative advantages of the two approaches.

The biodegradation method proposed here will degrade the chloro-hydrocarbons to methane, carbon dioxide and water or at minimum to an effluent suitable for discharge under an NPDES (National Pollutant Discharge Elimination System) permit.

The objectives of this research proposal are:

(1) To develop a microbial community acclimated to the following chloro-hydrocarbons :
  1,2-dichloroethane,
  1,1,2-trichloroethane,
  1,1,2,2-tetrachloroethane, and
  2-chloroethyl ether

(2) To design and demonstrate a continuous flow bioreactor to treat the chloro-hydrocarbon contaminated ground water.

Optimum operating conditions such as temperature, pH value, hydraulic retention time and fluidized velocity in the reactor will be examined. Important parameters such as biodegradation rate constant, microbes yield coefficient, and endogenous rate constant will be estimated.

Analysis of post-combustion products from waste derived fuel by FTIR spectroscopy

Jeffrey S. Lindner and Robert L. Cook

Mississippi State University, DIAL, P.O. Box MM, Mississippi State, MS 39762-5932 (USA)

Abstract – Project number 100MSU0137

Many cement manufacturers now employ waste-derived fuel as an energy source. The use of this fuel either alone or in combination with coal is attractive as fuel costs are reduced and large quantities of waste are used in energy recovery. Some studies of the environmental impact of cement clinker formation using supplemental fuel have been reported. In most cases, the quantitative determination of the products of incomplete combustion and gases like CO, NO_x and SO_2 has been accomplished by sampling followed by gas chromatography with or without a mass spectrometer. In this work we are evaluating the use of a Fourier Transform Infrared (FTIR) spectroscopy as an on-line, near-real-time diagnostic instrument for the analysis of products of incomplete combustion, particulates and combustion gases. Optics development, laboratory experiments and initial studies on DIAL's existing 500 kW oil-fired test facility will be discussed. Laboratory work has centered on the quantitative analysis of CO, CO_2 and Freon 22 (chlorodifluoromethane, a species which does not contribute to depletion of the ozone layer). Additionally, qualitative scattering measurements are reported for SiO_2 particles. The test facility experiments have been aimed at the determination of CO and CO_2 concentrations. Such data provides a measure of the stoichiometry (fuel-to-air ratio) of the combustion process. At present, no limiting factors have been observed in using the FTIR spectrometer as an on-line diagnostic instrument.

Fate of volatile organics in soil

Raymond Loehr

Department of Civil Engineering, University of Texas at Austin, Austin, TX 77843-3136 (USA)

Abstract – Project number 100UTA3006

This research: (a) is providing fundamental data on removal of volatile organics in soil, (b) is identifying the significant mechanisms causing such re-

moval, (c) will improve existing unsaturated soil contaminant transport models to reflect volatile organic removal processes, and (d) will provide unsaturated soil model output estimating air emissions and leachate concentrations when vapor removal in the soil is accounted for properly. This knowledge will benefit both industries and regulatory agencies as decisions are made about the use of soil as a waste management alternative, particularly for disposal of hazardous wastes and for contaminated soil bioremediation.

The research has several phases. Batch laboratory studies are underway to evaluate the sorption, degradation and gaseous losses using radio-labeled and other volatile organics. The kinetic coefficients from these studies will be utilized in an unsaturated zone contaminant transport model (RITZ-UT) to quantify the effect of volatile organic removal in the soil on volatile emissions from the soil.

To date, extensive protocol development has been completed, sorption data have been collected, and degradation rates have been determined. Batch sorption studies have been conducted in unsaturated soil with benzene, trichloroethylene (TCE) and *o*-xylene. Results indicate VOCs are attenuated as they pass through the soil in the vapor phase.

Laboratory degradation studies have been conducted with the same three compounds and with radio-labeled benzene. The results indicate that degradation of benzene and *o*-xylene does occur and thats the degradation rates increase rapidly as the volatile compounds sorb and the bacteria in the unsaturated soil become acclimated to the compounds.

The sorption coefficients and degradation rates have begun to be used with the unsaturated zone contaminant transport model noted earlier. This component of the research will have increased activity during the rest of 1990 and in 1991.

The initial studies have been conducted with single compounds. However, rarely are there only single compounds in unsaturated contaminated soils. Therefore, laboratory sorption and degradation studies with mixtures of volatile compounds are beginning. The resultant kinetic constraints also will be used with the unsaturated zone contaminant transport model.

Hazardous waste site cleanup design: Pump-and-treat systems

Daene C. McKinney

Department of Civil Engineering, University of Texas at Austin, Austin, TX 78712 (USA)

Abstract – Project number 110UTA0172

Remediating sites where hazardous substances have contaminated groundwater is an urgent and important task for environmental regulators, responsible parties, and consultants. In a pump-and-treat system, contaminated groundwater is pumped from the aquifer to the surface where it is transported, usually via pipeline, to a groundwater treatment system. The treatment system removes contaminants using a combination of wastewater treatment processes. Once the water has been treated it is either reinjected into the aquifer or discharged to a surface water body. Currently, pump-and-treat systems are designed in a piece-meal fashion. First, a pumping well field is configured to approximately contain and remove a contaminant plume which exists in an aquifer, then a groundwater treatment system is designed to remove enough of the contaminants to meet required effluent standards for reinjection or discharge. Treatment systems used to remove contaminants form the extracted groundwater are designed independently of the extraction and reinjection well fields. However, these systems are intimately related to each other in that the flow rate of the extraction wells and the contaminant concentrations in the aquifer affect the treatment process design, scale and size, and, in addition, the removal efficiencies of the unit processes of the treatment system affect the concentration and flow rate of the reinjected or discharged effluent.

A new pump-and-treat system design methodology is needed which integrates both well field and treatment process design to provide an overall optimal system design. In addition to this integrated design methodology, a technique is needed to assess the reliability of remedial designs in light of the uncertainty present in the aquifer property estimates used in the design process. This reliability analysis will help to estimate the likelihood that the remedial actions will actually achieve cleanup goals in a reasonable length of time.

This research will develop a rational methodology for integrating the optimal design of pumping well fields, groundwater treatment systems, and injection well fields. A second objective is to identify and evaluate the potential effects of deviations from the presumed subsurface conditions (i.e., aquifer property heterogeneity) used in the design of pump-and-treat remediation. The objectives will be accomplished in two steps, first a mathematical optim-

ization model will be developed and used to determine the optimal configuration and operation of the pumping well field and groundwater treatment system, then a sensitivity analysis of the resulting design will be conducted to determine the effects on system performance of the heterogeneity or spatial variability inherent in the aquifer properties that the design is dependent upon. This optimization-sensitivity analysis approach will lead to increased cost-effectiveness of cleanup designs and improved estimates of the reliability of the remedial designs and the time required to achieve cleanup.

Technical feasibility and cost effectiveness of the co-disposal of spent organic solvents and municipal sludges using anaerobic digestion

Joseph F. Malina, Jr.

Department of Civil Engineering, University of Texas at Austin, ECJ 8.6, Austin, TX 78712 (USA)

Abstract – Project number 100UTA0073

Organic solvents used in the electronic industry and other manufacturing facilities in urban-industrial complexes require disposal with minimal impact on human health and the environment. In some cases the solvents can be reprocessed and reused; however, some organic residue remains. In many situations the spent solvents are incinerated with or without the need for auxiliary fuel to sustain combustion. However, public resistance to land disposal or incineration of spent solvents has limited the available sites in Texas for the disposal of spent solvents. One alternative technology is the co-disposal of spent solvents with municipal wastewater sludges using anaerobic digestion. The technical feasibility and the cost effectiveness of this type of co-disposal system has not been established. However, perceived advantages include co-disposal of spent solvents (hazardous wastes) and sludges; elimination or at least reducing hauling cost and energy used in transporting the solvents great distances to disposal sites, conversion of the solvents biologically to methane gas and the recovery of methane gas for other municipal uses, elimination of the need for auxiliary fuel required to incinerate some solvents, and elimination of the potential air pollution resulting from improper incineration of the spent solvents.

The objectives of this proposed engineering investigation are the evaluation of effectiveness of co-disposal of spent organic solvents and municipal sludges by anaerobic digestion; evaluation of the effects of organic solvents on the performance of the anaerobic digestion process; and establishment of the solvent loadings at which efficient co-disposal is energy efficient, cost effective, and with minimal environmental impact.

Laboratory and bench-scale anaerobic digestion systems will be operated. Solvents used will be selected from acetone, benzene, cyclohexane, ethylbenzene, toluene, xylene, furfural, carbon tetrachloride, naphthalene, 2-butanone, nitrobenzene, phenol, chlorobenzene, di- and tri-chloroethane, methylene chloride, chloroform and butyl benzyl phthalate, among others. Continuously fed anaerobic digestion systems will be operated under quasi steady-state conditions to establish engineering design data.

The chemistry of stabilized Cr^{3+}, Hg^{2+} and Pb^{2+} ions in cement

Hylton McWhinney, John R. Williams, Andrea D. Ashley and Washington F. Sereatan

Department of Chemstry, Prairie View A&M University, Prairie View, TX 77445 (USA)

Abstract – Project number 100TAM0067

X-Ray Photoelectron Spectroscopy (XPS) is applied in the elucidation of the chemistry of Cr^{3+}, Hg^{2+} and Pb^{2+} ions stabilized in portland cement. Cement samples tested were aged over periods of approximately twenty eight days, six months and two years. No significant differences in the chemical speciation of the metal ions were observed. There is an observed increase of surface carbonate content in the doped cement over the undoped cement during the earlier periods of aging. In the latter period of aging, the carbonate content of the undoped cement approximates that of the doped cement. There is evidence of Cr^{3+} ion incorporation in the bulk cement grains. Small area analysis of Hg^{2+} doped cement, shows that there are areas of mercury deposits, some of which are lacking in silicon.

Chemical binding and leaching mechanisms of solidified hazardous substances

J. Dale Ortego

Department of Chemisty, Lamar University, P.O. Box 10022, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB3160

Solidification/stabilization (S/S) frequently employs cement and related silicate materials to treat liquid or sludge forms of hazardous materials to produce solids which are suitable for safe land disposal. Key issues in assessing the effectiveness of the treatment concern the durability of the solid produced and its resistance to leaching under various conditions. Important concerns in S/S studies therefore include characterization of the interactions of binding agents with the hazardous material and the effects of leaching solutions on the solidified matrix. Because ground water is usually acidic and since cementitious matrices are adversely affected by acidic aqueous solutions, it is important to define the effects associated with acid leaching. Our recent efforts using spectroscopic techniques (Fourier transform infrared and ^{29}Si solid-state nuclear magnetic resonance) have enabled us to more clearly understand the leaching process. Briefly, we have shown that silicate polymerization is slightly enhanced with lead doping and retarded in the presence of zinc. Leaching studies reveal that silicate polymerization occurs when the samples are exposed to acidic leaching conditions. The degree of cross-linking is directly proportional to the acidity of the leaching solution, being pronounced when pH five buffers are employed. The percentage of solidified metal leached during a buffer extraction is extremely high compared to the TCLP protocol. These results are important in helping to devise guidelines for S/S technologies and environmental protection. In addition to achieving a more fundamental understanding of the chemistry and leaching mechanisms of solidified hazardous systems, we have found that certain additives (phosphates, sulfates, sulfides, arsenites) greatly enhance stabilization of toxic metals when subjected to repeated batch leaching treatments. At the present time, efforts are being directed to studying mixed waste systems containing two or more priority pollutant metals and one or more organic contaminants. In addition, successful solidification of an industrial sludge from a munitions plant containing lead, cadmium and zinc has been achieved.

In a separately funded but related project, interactions of toxic metals, arsenates and organics on montmorillonite interlayer silicate surfaces are being pursued. Initial results indicate promising applications in the field of S/S.

Also during the past summer, we performed lead analysis on a soil sample

taken from a Texas superfund site. Four different extraction methods were used for comparison purposes. Methods studied involved extraction with (1) hydrochloric acid, (2) nitric acid, (3) nitric and hydrochloric acid and (4) nitric acid with hydrogen peroxide. It was obvious from our results that the highly oxidizing mixture of (4) was most efficient in removing lead from contaminated soils.

Our goals for the near future are to complete ongoing studies of the mixed metal systems (lead, chromium, cadmium) with chemical binders and additives (phosphates, sulfates, sulfides, latex) and to investigate mixed waste systems containing both metals and organics. The techniques to be employed include Fourier transform infrared spectroscopy, ^{29}Si and ^{27}Al solid-state nuclearmagnetic resonance, leaching studies, flame and graphite furnace atomic absorption analysis and thermal methods. Results of our studies will lead to a better understanding of the effectiveness and chemical behavior of specific binding agents, the mechanisms of acidic leaching processes and the usefulness of cement based materials and montmorillonite clays in solidifying hazardous organics.

Destruction of chlorinated aromatic olefinic and aliphatic aliphatic molecules using hydride reducing agents together with glycol ether/KOH nucleophilic displacements

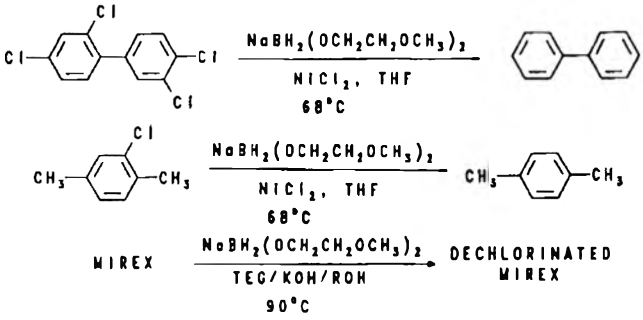
C.U. Pittman, Jr., K.T. Mead and S.M.H. Tabaei

Mississippi State University, P.O. Drawer CN, Mississippi State, MS 39762 (USA)

Abstract – Project number 100MSU3144

The goal of this research is to develop a single decontaminating solution which can dehalogenate all common pesticides, herbicides, chlorinated solvents, PCB's, etc. Hydridepromoted poly(ethylene glycol) PEG/KOH or tetraethylene glycol TEG/KOH dechlorinations of aromatic, aliphatic and olefinic chlorocarbons were conducted at mild conditions. The use of $NaBH_4$, $NaBH(OR)_3$ and $NaBH_2(OR)_2$, alone, or with TEG/KOH began in July 1989 with GCHSRC support. Destruction of PCBs using PEG-KOH (PEG=poly(ethylene glycol), pioneered by General Electric Co., converts highly chlorinated aromatic compounds to arylpolyglycols and phenolic compounds but high temperatures were required. We have discovered that $NaBH_2(OCH_2CH_2OCH_3)_2$ in THF will dehalogenate PCBs. This reason is greately accelerated upon adding $NiCl_2$to the solution at 68 °C. Apparently,

Ni(O) or nickel boride intermediates promote dehalogenation. Thus, Arochlor 1016 is quantitatively converted to biphenyl in a few hours at 68 °C using excess hydride and $NiCl_2$. Model compounds 2-chloro-*p*-xylene and 4-chlorobiphenyl were readily reduced to *p*-xylene and biphenyl, respectively. Many hazardous wastes have aliphatic or olefinic C–Cl bonds not readily destroyed by PEG/KOH. They are, however, dehalogenated by the hydride reagents coupled with PEG (or TEG) plus KOH. Mirex (a very stable aliphatic chlorinated pesticide) is destroyed at <90 °C in $NaBH_4/TEG/KOH/CH_3OCH_2CH_2OH$. The catalytic effects of tin hydrides and transition metals was studied. A key finding was the high activity without the need of catalysts for aliphatic systems. The role of *in situ* conversion of BH_4^- to BH_2^- and the increased dehalogenating power of such reagents is being explored. Some example reactions are given in the scheme depicted below.



Scheme 1. Destruction path of several hazardous chlorinated compounds.

Hydrogen peroxide/ultraviolet irradiation process for treatment of leachates and contaminated groundwater

James M. Symons and H. William Prengle, Jr.

Department of Civil and Environmental Engineering and Department of Chemical Engineering, University of Houston, Houston, TX 77204-4791 (USA)

Abstract – Project number 100UHH3132

Organic contamination of groundwaters from improper disposal of wastes and hazardous waste sites is a national problem. The problem manifests itself

both in production of highly contaminated leachates (mg/L concentrations) and the contamination of groundwaters used as drinking water sources (μg/L concentrations). Currently, each of the two common treatment techniques, air stripping and granular activated carbon (GAC) adsorption have problems, particularly for remote sites and small drinking water utilities. Thus, an alternative, a simple treatment technique for organic contaminant control was sought.

The overall objective of this project is to develop the H_2O_2/Vis–UV Chemical Oxidation Process for the destruction of waterborne hazardous substances that occur primarily in leachates and groundwater. The method is general, and, thus could be applied to municipal and industrial waste streams as well. The work proposed herein, PHASE II, is a flow-reactor study, following the completed batch-reactor study on eight selected chemical compounds. PHASE II is important because the ultimate embodiment of the process will be in a continuous-flow system. The specific objectives of PHASE II are as follows: (1) Use of the mathematical-flow model and ten benzene runs to determine the effect on conversion of benzene of four primary variable as follows: space velocity (contact time), initial oxidant/reactant mole ratio, photon flux, and temperature; (2) Tests on the seven other compounds; (3) Tests on mixtures and real water; (4) Correlation of reaction rates for purposes of a design model; and (5) Development of a predictive model for mixtures and real waters.

A continuous-flow reactor has been constructed in which organic compounds can be exposed to H_2O_2 and visible and ultra-violet (Vis–UV) light. Two major variables of the flow-through reactor (2.56 L of nominal volume) are fluid flow rate and irradiation intensity. To date, each test has a pre-irradiation period (lamps(s) off) for about three detention times, followed by the irradiation period, more than three more detention times to ensure steady-state conditions by the end of the test. Data collected during the pre-irradiation period is used to calculate the diffusion coefficient, and the data collected during the irradiation period is used to calculate the reaction rate constants of the contaminant (initially benzene) and TOC (POC-purgeable organic carbon+NPOC-non-purgeable organic carbon) for several different runs. Variation in the feed water composition, the flow rate, and the irradiation intensity will provide the variable to be studied.

Characteristics of incidents involving transportation of hazardous substances

Essam Radwan and Scot Leftwich

Department of Civil and Environmental Engineering, University of Central Florida, Orlando, FL 32816-0450 (USA)

Abstract – Project number 110UCF0161

A survey conducted by the U.S. Department of Transportation in the mid seventies showed that 5–15% of all the trucks on the road at any time carry hazardous materials or waste. In a recent study, trucks carried 24.9% hazardous materials and were responsible for 57.3% of the property damages. Hazardous material shipments are expected to double every ten years which creates potentially more volatile accident situations.

The main objective of this study is to have a better understanding of the characteristics and causes of highway incidents involving trucks transporting hazardous substances and, if possible, to identify countermeasures to reduce the probability of occurrence and potential risk to public safety.

(1) Review the literature on the U.S. in general, and Florida.

(2) Collect data on highway truck incidents in Florida.

(3) Analyze and provide statistical analysis of the data.

(4) Utilize data to determine the correlation, or lack thereof, between accident rates and measure of highway design.

(5) Identify countermeasures that could reduce accident occurrence and severity of damage.

Active municipal solid waste landfill operation: A biochemical reactor

Debra R. Reinhart

Department of Civil and Environmental Engineering, University of Central Florida, P.O. Box 25000, Orlando, FL 32816-5783 (USA)

Abstract – Project number 100UCF0202

Landfills remain the most frequently used method of municipal solid waste (MSW) disposal. Landfills are designed and constructed to prevent contact between the waste and the environment. Modern designs include hydraulic barriers to collect and control liquids to be treated and disposed. Gas production from MSW landfills also requires collection and control. Landfill management alternatives and options must consider the consider the potential uses of these landfill outputs.

Active Landfill Management (ALM), as used herein, includes management of a waste disposal facility to minimize risk to human health and the environment while optimizing landfill volume by promoting decomposition of landfilled waste, reducing the potential health risks by immobilizing constituents in the waste mass, and optimizing the quality and quantity of decompositional gases, such as methane.

In order to identify design, construction, and operational requirements for ALM, and recognizing the need to avoid duplication of ongoing or past related efforts, the objective of this research is to support sutdies necessary to initiate a full scale demonstration of ALM to optimize solid waste stabilization, leachate control, and gas production.

The principal investigator, Dr. Debra R. Reinhart, as contracted by the Gulf Coast Hazardous Substance Research Center, will provide support to a United States Environmental Protection Agency funded project with the above described objective.

Toxicological and chemical monitoring of microbial degradation of oil-based sludge in liquid–solid contact reactors

B.S. Shane, M.B. Williams, R.J. Portier, M.M. Walsh, P. Iyer, T.R. Irvin and E.B. Overton

Institute for Environmental Studies, Louisiana State University, Baton Rouge, LA 70803 (USA)

Abstract – Project number 100LSU3127

Production of hazardous waste in the United States exceeds the capacity available for storage and treatment of these wastes. While onsite bioremediation of oil-based sludges may be a viable alternative to offsite shipping and storage of wastes, concerns regarding the possible production of more toxic intermediates during degradation have been raised. In this study, bioremediation of oil-based contaminated sludges was conducted in a laboratory reactor in concert with two short term mutagenicity bioassays (Ames assay and Prophage Induction assay) and a mammalian toxicity assay (Chinese hamster ovary cells, CHO) to monitor changes in the waste during degradation. Following eight weeks of bioremediation of contaminated soil, an enhanced mutagenic response in both the Ames and Prophage assays was obtained after 30 days of incubation. The Prophage induction assay was more sensitive than the Ames assay in detecting mutagens. In the Ames assay, an increase in mutagenic compounds causing frameshift mutations was more marked than compounds eliciting base-pair mutations. Only one of the extracts was toxic in the CHO assay. The identification of the active organic components eliciting these responses is being pursued. This approach using biomonitoring concurrently with bioremediation will assist in the determination of the feasibility of this technology in future large scale cleanup procedures.

Preliminary investigation of continuous flow reactor treatment of contaminated soils

Joseph H. Sherrard and Dennis D. Truax

Mississippi State University, P.O. Drawer CN, Mississippi State, MS 39762 (USA)

Abstract – Project number 100MSU0076

Biological treatment of various hazardous substances has been shown to be a viable option. However, when these materials contaminate soils, bioremediation can become prohibitively difficult due to problems in development of needed microorganism populations. *In situ* technologies experience limitation due to nutrient addition while removing the soil for above ground treatment is controlled by an often excessive time for microbial acclimation and an extensive surface area requirement. These limitations area typical off batch-type treatment regimes.

The proposed two-year research project will be an initial study of the feasibility and benefit of developing a continuous flow reactor regime for treating soils contaminated with hazardous materials. During the first year, a series of bench-scale reactors will be used. Pseudo-continuous loading off the rectors will be achieved by daily addition of small portions of silty sand saturated with fuel oil. Removal off treated soil in amounts equal to this addition will be performed to maintain a constant reactor volume. The amounts will be varies between reactors to provide variation in the mean cell age of the microbial population. Moisture content in the reactor will also be varied. Supplemental nutrients will be added and monitored so as to assure that carbon contained in the contaminant is the only limiting nutrient. Upon achieving steady-state removal, the reaction kinetics will be determined and evaluated to define optimum conditions. During the second year, kinetics will be evaluated in similar fashion for different soil types and fuel contaminant levels.

Development of bioreactors for the destruction of chlorinated solvents

Gerald E. Speitel, Jr., Robert L. Segar, Jr. and Shelley L. Dewys

Department of Civil Engineering, University of Texas at Austin, Austin, TX 78712 (USA)

Abstract – Project number 100UTA3131

Biological treatment of groundwaters contaminated with chlorinated solvents is a promising alternative to conventional treatment technologies. Biodegradation is advantageous because the contaminants are destroyed in place rather than transferred to another phase. This project builds on recent observations that many aerobic microorganisms, when grown on substrates that induce nonspecific oxygenase enzymes, can cometabolize chlorinated solvents. The goal of this research is the development of cometabolism based treatment processes for the destruction of compounds such as 1,1,1-trichloroethane, chloroform, and trichloroethylene (TCE) at concentrations below 1 mg/L.

The suitability of several microbial cultures was screened for and evaluated, with emphasis placed on mixed cultures grown with simple aromatic substrates. A consortia of phenol-utilizing organisms was selected for further study based on its rate of trichloroethylene degradation, its reliability of degradation, and its ability to rapidly form cohesive biofilms. In batch studies of a chemostat culture, pseudo first-order TCE degradation rate constants were typically in the range of 10 to 80 $L/g_{TSS}/day$. Greater than 95% removal and 80% mineralization of TCE were obtained in batch incubations lasting a few hours. The culture could transform greater than 12 $\mu g_{TCE}/mg_{TSS}$ at a TCE concentration of 1 mg/L. Phenol at concentrations of 5 to 10 mg/L strongly inhibited TCE degradation.

Continuous-flow column experiments and mathematical modeling of column performance with existing biofilm reactor computer models were conducted. TCE and phenol were fed simultaneously to columns packed with glass beads. TCE removals over time were sporadic and low, ranging from 0% to 20%. In short term continuous-flow tests without phenol present, TCE removals improved to about 40%. When the reactors were continuously fed phenol, they plugged with biofilm in the inlet region after several days of growth.

Modeling indicated that elevated flow rates during phenol feeding would provide more biofilm activity and better distribution of biomass throughout the reactor. However, because the TCE degradation rate is lower that that of

phenol and high TCE removals are desired, feedwater with TCE must be fed at a flow rate about ten times less than the phenol feedwater flow rate. To accommodate this, our recent research has focused on sequencing biofilm reactors, which cycle between growth on phenol followed by removal of TCE. This type of operation provides a practical means of dealing with the differences in kinetics, controls plugging by limiting growth and avoids enzyme competition between phenol and TCE.

With the sequencing biofilm reactor, average TCE removals of greater than 90% at an empty bed contact time of 35 minutes have been sustained for one week. Average TCE removals greater than 70% have been sustained for up to one month. Reactor modeling has determined that initial rate constants greater than 50 L/mg$_{\mathrm{TSS}}$/day are being obtained in the reactors, which are significantly higher that other reports for biofilm reactors. Several combinations of feedingfrequency, duration, and phenol concentration have been examined. Ongoing and future work will address other important factors related to increasing and sustaining the cometabolic activity in sequencing reactors. Bed fluidization during growth, more efficient media, and enzyme competition between several chlorinated solvents will be examined.

The feasibility of *in situ* treatment of soil to promote desorption of hazardous wastes, thus permitting capture and treatment

James M. Symons and Michael W. O'Neil

Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204-4791

Abstract – Project number 100UHH3008

Hazardous wastes are frequently fixed on soil particles by adsorption. Final destruction of these wastes is limited, because they are not available for treatment without removal of the soil itself. If some technique could be found to desorb these materials from the soil particles *in situ*, then they would be mobilized, and could be intercepted, captured, and treated. Treatment alterna-

tives could be either *in situ* biodegradation or "pump and treat" chemical oxidation. Neither of these processes would be effective on adsorbed organics, however. Thus, some method of freeing the organics bound to the soil must be found.

This project has begun by investigating altering, *in situ*, either the surface chemistry of the soil particle or the nature of the sorbed organic compounds, such that the organic compounds will be desorbed and then be ready for transport and treatment. Four approaches will be investigated to alter the soil–sorbate bond; (1) the addition of an oxidant to make the sorbate more oxygenated (more polar), (2) the addition of sodium hydroxide as a source of hydroxide ions, (3) the addition of lime as a source of calcium and hydroxide ions to alter the surface properties of the soil and (4) the addition of surfactants to competitively displace the sorbate.

The study is employing six special flexible-wall permeameters designed and built by the University of Houston. To start a desorption test, a clayey soil, mixed with sand to adjust permeability, is contaminated with the organic to be tested on a batch basis, then is compacted wet of or at optimum liquid content to simulate a saturated condition and placed in a permeameter. As the *in situ* mobilization process is applied, the effluent is examined for the organic compound under study. As this effluent stream is monitored over time, the quantity of material leaving the column is calculated, and the extent of desorption is determined as compared to a control that is flushed with plain deionized water. This allows a comparison of the treatment process to simple flushing. Environmentally contaminated soils will be tested later; however, the batch contamination step above will not be employed. Each test is performed in replicate so that any differences in performance of the treated sample compared to the flushed samples can be tested statically.

Solidification/stabilization of hazardous waste substances in latex modified portland cement matrices and ultrasonic pulse velocity and echo attenuation as a evaluation tool

C. Vipulanandan[a], Saeed Daniali[b] and J. Dale Ortego[c]

[a]*Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204 (USA)*
[b]*Department of Chemistry, Lamar University, P.O. Box 10022, Beaumont, TX 77710 (USA)*
[c]*Department of Civil Engineering, P.O. Box 10028, Beaumont, TX 77710 (USA)*

Abstract – Project number 041LUB3205

Immobilization of hazardous waste substances in a portland cement matrix is considered a major solidification method due to the simplicity of the process and its low cost. However, relatively high porosity of the cement matrix, which could lead to considerable leaching, has created a demand for improving portland cement matrices. The main objectives of this study are twofold:

(1) To develop alternative hybrid materials using portland cement modified with different admixtures to treat inorganic and organic wastes.
(2) To develop a non-destructive test method using ultrasonic pulse velocity and echo attenuation, for evaluating the performance of solidified/stabilized inorganic wastes.

In situ treatment for cracked and contaminated clays and permeable soils: Seapage control and long-term performance

C. Vipulanandan

Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204 (USA)

Abstract – Project number 100UHH3176

The increasing incidence of failure of existing hazardous waste storage and disposal facilities, due to the failure of primary or secondary clay barriers, has drawn much attention recently. There is also growing concern about deep aquifers being contaminated due to the seapage of hazardous organic permeants through confining clay barriers. However, little is known about repairing clay barriers or reducing the hydraulic conductivity of permeable local soils *in situ* to control seapage and satisfy the EPA limit of 10^{-7} cm/s. The hydraulic conductivity of clay is affected by the interactive nature of local defects (desiccation cracks, fissures, faults and fractures), chemical wastes and *in situ* stresses. Since field tests are expensive, time-consuming and, in many instances impractical, reliable laboratory permeability tests have been developed where the field conditions including cracks are closely modeled. These cracked clay samples are being used to evaluate effect of cracks on the hydraulic conductivity of cracked soils *in situ*. Preliminary studies show that the hydraulic conductivity of cracked clay ($>10^{-7}$ cm/s) and contaminated soils ($>10^{-4}$ cm/s) can be reduced to below 10^{-7} cm/s by treating with grouts, but the long-term durability of such treatment has to be verified.

In this study, the long-term performance of treated cracked clays and contaminated soils under various chemical environments will be evaluated. Permeant list will be expanded to include chlorinated organics and actual field leachate and field clays obtained from the Gulf Coast region. The compatibility of grouts with the organic permeants and the soils will also be studied in a fundamental way. performance of various grouts such as sodium silicate, cement, lime, fly ash and bentonite grouts or their mixtures thereof will be evaluated for longer periods of time under various chemical environments. A field study is proposed to demonstrate the laboratory findings. These findings will improve the current repair practice for leaking clay barriers, control seapage through contaminated soils and increase the use of permeable local soils with *in situ* treatment as impermeable barriers at future waste disposal sites.

Leaching mechanisms and performance of solidified/ stabilized organic hazardous waste substances in modified cementitious and polymeric matrices

C. Vipulanandan
Department of Civil and Environmental Engineering, University of Houston, Houston, TX 77204-4791 (USA)

Abstract – Project number 100UHH3160

Solidification/stabilization (S/S) is one of the treatment technologies with the potential to meet the cleanup standard outlined by SARA and, in recent times, it has been used at numerous CERCLA sites to reduce waste toxicity and/or mobility. However, the primary concern of the current S/S technology using cement and pozzolanic systems is the interfering effects of organic contaminants which affect setting, chemical stability and long-term durability. Due to the lack of understanding of treating organic wastes and anticipating problems from using the currently available treatment regulators have used limitations on the amount of organics treatable, which range from 1% to 20%. Hence, alternative binder materials for S/S treatment of non-volatile organic hazardous wastes must be developed to meet the current demand in treating organic wastes and mixed wastes. Recent studies at the University of Houston and Lamar University were limited to cement-phenol and polymer–phenol systems and it was concluded that (1) even 0.1% of phenol concentration will affect the performance of cement and the phenol leached (TCLP test) from the cement matrix exceeds the regulatory level, and (2) the polyester polymer is very effective in rapidly treating much higher concentrations of phenol.

It is being proposed to develop alternative hybrid materials using a combination of additives (sorbents), cement and polymers (organic and inorganic) for effectively S/S phenolic wastes in particular and non-volatile organic hazardous wastes in general. The additives will include sorbents such as organophilic clay, activated carbon, silica fume, fly ash, lime and clay. Organic waste list will be extended to include halogenated phenolic derivatives such as 2-chlorophenol, pentachlorophenol and polychlorinated biphenyls (PCBs). The interaction between the wastes and the modified binders will be studied in a fundamental way from the time of mixing to final solidification and there after (up to 2 years) using chemical analysis, leachate tests and microstructural studies. Using at least two representative industrial organic sludges, the capabilities of the new modified cement–additive–polymer binder systems in solidifying/stabilizing the organic wastes will be demonstrated by bench scale process development.

Resolving the dilemmas of hazardous waste management: The why of NIMBY attitudes

M. Elliot Vittes, Philip H. Pollock and Stuart A. Lilie

Department of Political Science, University of Central Florida, P.O. Box 25000, Orlando, FL 32816-0450 (USA)

Abstract – Project number 100UCF3150

This plan describes our continuing investigation as to why people and communities oppose the siting of hazardous waste management facilities. Our preliminary research suggests that people may be more receptive to the idea of such facilities than is generally recognized, and that concerns of proximity and political cultural beliefs play a significant force in producing opposition attitudes and behavior. A majority of people appear to support hazardous waste facility siting, and only minorities see them as either health and safety or general environmental threats. The problem in understanding NIMBY ("not in my backyard") attitudes remains a central research focus, as does the measurement of political culture attributes. We propose to measure these attitudes in more extensive and complex ways, following on the experience to date. The final result will be an analysis of what factors best explain the resistance to siting, and how those factors relate to conditions that can or cannot be changed. We will utilize a mass public random sample survey of Florida residents to better measure the variables, and give us a longitudinal basis for understanding attitudes. This is unique survey data not available elsewhere that will most likely attract wide interest. It will include measurement of demographic factors; cultural beliefs; attitudinal precepts; and questions concerning proximity, health and safety, environmentalism, and risk.

Application of ultimate Bingham material in hazardous spills

Richard E. Walker

Department of Chemical Engineering, Lamar University, P.O. Box 10053, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB0090F1

This proposal is for a one-year exploratory investigation of adding solid particles to increase the gel strength of an ultimate Bingham material (UBM).

Such a material might be useful to mitigate pollution from hazardous spills on land and water. The material is a gel, and thus has a solid-like structure, but when given sufficient shear will liquify at a shear plane and immediately redevelop the gel when motion stops. Thus, the material can be mixed by a fire truck, pumped through standard hose to a spill and the material exiting the hose can form a dike to contain the spill. Or, it can be foamed to cover the spill and the foam will not drain. A combination of gel and foam might be used to protect shore lines (with a minimum of wave action) from oil spills. The material is a mixed metal layered hydroxide compound (MMLHC) that is added to a prehydrated bentonite in water mixture. It is not hazardous. As presently used in oil well drilling, the gel strength is too weak to build dikes but is adequate for foam.

The first step is to find how the gel strength varies with the concentration of prehydrated bentoninite (in water) and concentration of MMLCH (in the prehydrated bentonite-water mixture). While high gel strengths can be obtained by high concentrations (and high costs) theory predicts that small particles may be able to produce the needed properties at much lower costs. The second step is to find how the concentration, size distribution, and shape of particles change the gel strength.

Hydrometallurgical treatment of hazardous waste for simultaneous detoxification and metal recovery

R. Hadkar, K. Sreenivasarao, G.W. Warren and M.D. McKinley

Department of Metallurgical and Materials Engineering, Department of Chemical Engineering, University of Alabama Box 870202, Tuscaloosa, AL 35487-0203 (USA)

Abstract – Project number 100UAL3103

Many industrial processes generate hazardous solid wastes containing heavy metals such as lead and cadmium. Flyash from municipal solid waste (MSW) incinerators and waste molding sand from brass foundries are two examples. This material is currently disposed of in hazardous waste landfills. Investigations address a potential hydrometallurgical process for (1) chemical dissolution (leaching) of the metal values from the hazardous waste, and (2) recovery of the dissolved metals from the aqueous leaching solution which can then be recycled. The process is flexible and has been applied here to MSW flyash.

The leaching of metal values from MSW flyash has been compared for var-

ious lixiviants, including HCl, H_2SO_4, acetic acid, NaCl and HCl+NaCl. The maximum extractions observed for Pb, Cd and Zn were 89%, 98% and 74%, respectively in 1 *M* HCl. Chemical dissolution of Pb, Cd and Zn can be accomplished quickly and effectively in both HCl and HCl+NaCl solutions. Optimization of leaching conditions for effective detoxification and subsequent metal recovery can be achieved by controlling the pH of the lixiviant and the ratio of flyash to lixiviant. Significantly, Toxicity Characteristic Leaching Procedure (TCLP) tests have been conducted which show that residues can be produced which meet the toxicity limit for Pb and Cd. Furthermore, lead and cadmium can be recovered from the leaching solution by cementation with zinc dust. Experiments have been performed to determine the effects of pH, particle size of the zinc dust used, quantity of zinc added, and dissolved impurities on the cementation kinetics. The final solution obtained after leaching and cementation yields a dissolved zinc concentration of approximately 15 g/L or higher, a level suitable for direct electrowinning of zinc. Electrochemical experiments have been performed which are aimed at determining the critical parameters which affect the cementation and electrowinning steps.

Many MSW incinerators use lime to reduce SO_2 emissions in the flue gas. The flyash generated by such incinerators cannot be economically treated with acidic leaching solutions, since unreacted lime would consume excessive quantities of acid. Recent experiments have been aimed at determining the feasibility of leaching out Pb, Cd and Zn in basic solutions, pH $>$ 11, using CaO, Na_2CO_3 And NaOH. Results indicate that Pb is much more leachable than the Cd or Zn under these conditions.

The NIMBY syndrome: Exploring the relationship between public education and siting opposition

Stuart A. Wright

Department of Sociology, Lamar University, P.O. Box 10026, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB3135

Studies of NIMBY indicate that opposition to or acceptance of new hazardous waste facilities may be related to the level of public education about the issue. The role of knowledge or information has not been adequately studied. Statements by industry representatives often reveal assumptions that link level of knowledge with support for new sites or facilities. Yet these assumptions

remain untested. Environmentalists also make assumptions that informed persons are more likely to oppose current methods and technologies. These assumptions are untested as well (public opinion polls demonstrating attitudes favorable to environmental issues are measuring opinion not level of knowledge). Neither side is willing to claim the ignorant or uninformed since each party in the siting impasse feel they are allied with better information and the best solution to the waste problem. Therefore, more research is needed to clarify the role of public awareness and knowledge. Two surveys are proposed to evaluate the relationship between public education and siting opposition/acceptance.

Water solubility and Henry's Law constant for crude oil hydrocarbons

Carl L. Yaws

Department of Chemical Engineering, Lamar University, P.O. Box 10053, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB0101

The contamination of water with crude oil hydrocarbons (primary compounds in gasoline, diesel, jet fuel, heating oil, etc.) is an important issue that will intensify in the future. It is especially important to have quantitative data on how such hydrocarbons and related compounds distribute or partition themselves in the environment between air, water and soil.

The solubility (S) of a crude oil hydrocarbon in water is an indication off how much off the hydrocarbon will dissolve in water. Knowledge of the waste solubility is very helpful in environmental studies. As an example, solubility data is very helpful in determining the assessment and distribution of a hydrocarbon spill upon its contact with water. Unfortunately, data for solubility of crude oil hydrocarbons in waste are very limited and nonexistent for many compounds. Additional data are needed.

Henry's Law constant (H) for a compound in water is an indication of how the compound will partition or distribute between air and water. Knowledge of Henry's Law constant (i.e., air–water distribution coefficient) is also very helpful in environmental studies. Unfortunately, data for Henry's Law constant for crude oil hydrocarbons in water are very limited and nonexistent for many compounds. Additional data are needed.

The objective off this research is to provide additional data and expanded results for water solubility and Henry's Law constant for crude oil hydrocarbons:

- Part 1 Paraffins (alkanes) (year 1)

- Part 2 Naphthenes (cycloalkanes) (year 2)
- Part 3 Aromatics (benzenes) (year 3)

The results issuing from this research for water solubility and Henry's Law constant for crude oil hydrocarbons may be used by process and environmental engineers in initial engineering and environmental studies.

Applications of materials handling approaches and systems to remediations on Superfund sites

Victor Zaloom and Hsing-wei Chu

Department of Industrial Engineering, Lamar University, P.O. Box 10026, Beaumont, TX 77710 (USA)

Abstract – Project number 100LUB0102M1

Very few Superfund project managers have a particular expertise in the technologies available for materials handling in general or hazardous materials handling in particular. This study will result in a manual and user friendly software package which will provide Superfund site managers the information necessary to make materials handling decisions which are cost effective, in compliance with applicable regulations and utilize "current best" technologies.

A case study approach will be utilized in the first year of this project. It will involve inspection, documentation, analysis and improvement of materials handling technologies at Superfund sites in Region VI. Approximately six sites will be visited by members of the research team. Process flow analyses will be performed and documented. Special emphasis will be placed on the movement and handling of hazardous materials. Documentation may include videotape process flow charts and narrative explanations.

A survey of superfund sites outside of Region VI will be conducted by telephone or written survey form in order to gather additional information regarding materials handling technologies and problems at Superfund sites. This survey data will be used to decide on whether or not to visit sites outside the region which may present special problems or opportunities.

A review of the documentation on all six sites visited as well as survey information will be conducted and three sites will be revisited in order to gather more indepth and quantitative data and measurements regarding materials flows and materials handling problems and/or bottlenecks. A report will be prepared outlining the status of materials handling technologies at Superfund sites visited. This report will provide a baseline of knowledge from which additional research land development tasks will be defined.

The second year of the project will involve development of a taxonomy of materials handling technologies and a database system for analyzing the hazardous materials handling requirements of Superfund sites and relating those

requirements to existing technologies. This analysis will form the basis for two major research thrusts: the first being the development of a quality function deployment (QFD) model for hazardous materials handling systems design and the second being the development of a knowledge based expert system for hazardous materials handling system selection. The third year of the project will involve completion of the QFD model and further development of the expert systems model. Additionally, a handbook to aid Superfund site managers in making material handling decisions will be developed in year three of this project.

Potential new technologies such as robotics, artificial intelligence and artificial vision will also be examined. Finally, a taxonomy of the myriad types of material handling equipment categories will be developed.

Removal of hazardous organic contaminants to purify water

Albert Zlatkis and Henry Shanfield

Department of Chemistry, University of Houston, Houston, TX 77204 (USA)

Abstract – Project number 100UHH2011

Experiments done to date on water deliberately contaminated with organic compounds, widely accepted as environmentally dangerous, have resulted in a promising method for reducing such pollutants to acceptable levels from a health hazard viewpoint. The method appears to offer simplicity, low cost, and ability to be regenerated, thus allowing extended reusability.

We utilize the unusual permeability to many organic compounds we have observed for certain stable, silicone polymers, in the form of tubing, through which the polluted water is pumped.

The data we have accumulated to date has provided us with sufficient engineering parameters to permit the preliminary design of a purification system, comprised of tubing "bundles", each capable of delivering 500 gallons (1900 L) per day of purified water. the influent water is presumed to contain 1–2 parts per million of chloroform, trichloroethylene and benzene (prime targets of pollution control), while the effluent water can be reduced to levels at or below the presently accepted values of 50 parts per billion.

We believe that the additional data we propose to obtain will permit the firm design of units exceeding these quality goals. We propose to make such a module, measure its performance over a range of influent contamination, flow rate (laminar vs. turbulent flow), total water gallonage decontaminate and regeneration procedures, ranging from simple air flushing to more complex approaches.

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Transport in Fluidized Particle Systems

edited by **L.K. Doraiswamy,** *National Chemical Laboratory, Pune, India,* *and* **A.S. Mujumdar,** *McGill University, Montreal, Que., Canada*

(Transport Processes in Engineering, 1)

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