ENVIRONMENTAL PROGRESS

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ENVIRONMENTAL PROGRESS

Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multifaceted aspects of the pollution problem. It will provide through coverage of abatement, control, and containment of effluents and emissions within compliance standards. Papers will cover all aspects including water, air, liquid and solid wastes. Progress and technological advances vital to the environmental engineer will be reported.

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Cover: Installation of groundwater monitoring wells in Del Mar, CA (See Environmental Shorts on page F4.) Photo courtesy of TorStan Inc., Cardiff, CA.

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Evolving a Science/Engineering Mind-set for the Environment

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With the explosive expansion of the environmental marketplace in recent years, there is an increasing demand for new technologies, approaches and management styles. Putting aside the opportunities for new technologies, the approaches, and management techniques for dealing with environmental problems, specifically the remediation of soil and water, require a melding of science and engineering. The traditional view of engineering is to develop an engineering solution to a fixed problem (e.g., the right size beam, the right size and system for a wastewater treatment plant, or an appropriate piping network for fluid distribution). The traditional view of science is to answer questions divorced from application (e.g., how and where will rainfall develop, what do microbes "eat", or what is the grain size distribution of glacial till).

There is a major component in developing solutions for environmental problems for which traditional engineering or science approaches have failed and will continue to fail. This component of the problem-solving process isn't the very basic characterization of the site, or the details for instrumentation and control of a treatment system. The component referred to is the decision-making process, of which technology or a remedial approach is appropriate for a given natural (i.e., valuable and unique) system. This decision depends upon an incomplete, and often inadequate, understanding of the natural system (data collection in soil and ground-water problems is extremely expensive and time-consuming), but requires a sound understanding of the variations and vagaries associated with specific natural systems.

For example, the decision for treating a fluid stream to remove a constant 2% (within narrow tolerances) vinyl chloride at a given flow rate is relatively simple. The range of technologies is generally known, and cost effectiveness and applicability can readily be determined. However, a typical environmental problem may involve the removal from groundwater of a mere 5 parts per billion of vinyl chloride to non-detect. Keep in mind that because the problem involves groundwater, the actual concentration will vary depending upon the exact configuration of the plume of contaminants in the subsurface and where the liquids are derived. In addition, the quality of water will vary seasonally (including "non-contaminants" such as iron and hardness), and the system, if working, will lower concentrations over time and should remain equally effective.

Those who are involved with this key decision-making process are often referred to as Remedial Engineers. Are there schools from which one can graduate as a Remedial Engineer? It is doubtful - these individuals often have strong engineering capabilities (chemical and/or civil) and the experience of applications in natural systems. There are also many talented Remedial Engineers who are more oriented

the sciences (e.g., hydrogeology and/or chemistry) than toward engineering. The challenge is to develop many more individuals skilled at both the engineering and science aspects of solving environmental problems. This will result in *environmental solutions* that are more likely to be appropriate, cost effective, and less prone to failure.

A new mind-set must also develop from a management standpoint. On a project management level, environmental problems must be managed from investigation, through decision-making, through implementation. The divorcing of data collection ("science"), decision making (as described above), and implementation often results in catastrophe, or at a minimum, inefficiency. In fact, many of the environmental problems facing society are relatively small when compared to the construction of multi-million dollar treatment plants. As a result, there is no room for "hand-off" between project tasks (the common transfer of projects between technical disciplines). Thus engineers must learn to manage and staff scientific "expeditions," and scientists must learn to manage the construction of remedial systems in the field. That is, a good manager for an environmental problem must have his/her eye on an appropriate solution from start (collecting the right data) through finish (making the solution work with minimal operation and maintenance).

To support the needs of teams of individuals charged with developing environmental solutions, there must also be a development of a new mind-set in "corporate" management; i.e., staffing projects with the right people and tools, and maintaining the technical skills of a diverse staff. Team management approaches appear to work well, but have their challenges. Management approaches that are overly weighted toward individual skills tend to promote hand-off problems and unsatisfactory results in product and/or process. Whatever approach is devised, it must reflect reaching a solution, not merely the individual components within the process of reaching the solution (e.g., ground-water investigation or civil/design).

Solving environmental problems is a long-term issue worldwide. The marketplace and demand for services is large (projected expenditures of hundreds of billions of dollars for the U.S. Department of Energy alone in the coming years). However, the recognition that traditional approaches are prone to failure must be addressed. Many aspects of science and engineering must become more closely aligned and integrated. In particular, attention must be placed on integrating both management and technical approaches to developing environmental solutions.

Decline in Hazardous Waste Facilities During 1992 Reported

Hazardous waste management facilities reported dramatic increases last year in the types of treatment they provide, but the number of facilities declined, according to an analysis of data in the recently published *1993 EI Environmental Sciences Directory.*

The analysis indicates that hazardous waste facilities are responding to a trend of recent years: generators want to rely on a short list of hazardous waste firms having broad capabilities.

Environmental Information Ltd., found that the number of hazardous waste treatment and disposal facilities (excluding facilities that provide storage only) continues to decline, shrinking from 295 facilities in the 1992 directory to 282 in the 1993 directory. facilities that closed are generally small, poorly capitalized facilities that are unable to shoulder the costs of expanding hazardous waste regulations. Solvent recycling facilities have been unable to shoulder the costs of expanding hazardous waste regulations. Solvent recycling facilities have been particularly hard hit because, in addition to steeper regulatory costs, their most profitable waste streams have declined as generators minimize solvent use in response to CFC phaseouts.

Key findings in the analysis include:

- Twenty-four hazardous waste facilities added metal recovery capabilities.
- Eleven hazardous waste facilities added biological treatment capabilities.
- Dozens of facilities upgraded or expanded services such as oxidation, reduction, neutralization and fuels blending,
- Two new commercial hazardous waste incinerators received RCRA Part B permits in 1992.
- The number of commercial hazardous waste landfills shrunk by one. The U.S. now has 20 commercial hazardous waste landfills.
- The number of boilers and industrial furnaces (excluding cement and lightweight aggregate kilns) commercially burning hazardous waste decreased from 12 to 5, reflecting expensive permitting requirements under the Boiler and Industrial Furnace Rule.
- The number of cement and lightweight kilns burning hazardous waste remained stable at 29.

For more information contact Environmental Information Ltd., 4801 West 81st St., Suite 119, Minneapolis, MN 55437. Telephone: (612) 831-2473.

Environmental Sciences Consulting Firm Assesses Subsurface Soil Contamination at Historic Site

TorStan Inc., an environmental sciences consulting firm in Cardiff, CA was contracted by the city of Del Mar to assess the extent of subsurface soil contamination at Del Mar's historic Powerhouse. TorStan Inc., has completed necessary subsurface soil assessment work and has found that soil contamination is limited.

In order to satisfy regulatory agency requirements and to obtain necessary data on the groundwater condition below the historic structure, TorStan was recently awarded a follow-on contract to install two groundwater monitoring wells (see photo on the cover of this issue).

TorStan will utilize in-house computer modeling capabilities to determine the type of remediation which will be necessary. Computer analyses will model site specific subsurface contaminant migration patterns and evaluate their probable future extent. It is anticipated that significant cost savings will be realized by conducting the current work and related computer modeling studies. The work is expected to require about nine months to complete.

CWRT and DOE to Sponsor Workshop on Waste Reduction and R & D Needs

This workshop jointly sponsored by AIChE's Center for Waste Reduction Technologies and the U.S. Department of Energy's office of Industrial Technologies will be held in mid-1993. It will identify waste reduction technology needs in the manufacturing industries. The goal is to provide CWRT and DOE with expert consensus on R & D priorities that can aid planning activities - and help determine areas likely to yield the greatest overall industry payoff.

For more information please contact Tammy Nilson at the Center for Waste Reduction Technologies, AIChE, 345 East 47 St., New York, N.Y. 10017. Telephone: (212) 705-7424.

Opportunities for Retired Environmental Engineers

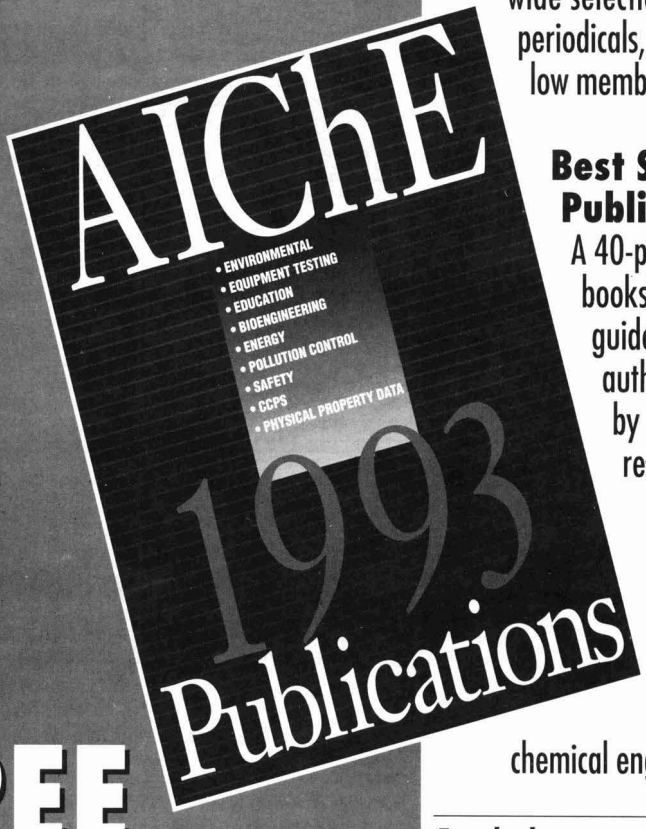
The Environmental Careers Organization is starting a pilot program to place retired engineers and scientists in technical advisor positions with nonprofit groups promoting industrial pollution prevention. The Technical Advisor Program for Toxics Use Reduction is a national program that will recruit, train, and place ten technical advisors in 1993.

Technical advisors work on projects such as researching toxic chemical substitutes in a citizens' laboratory; assisting citizen groups to develop "Good Neighbor Agreements" with local manufacturing facilities; or assisting national environmental groups developing model toxics use reduction legislation.

The Environmental Careers Organization is seeking engineers and scientists to work on six-month projects in Boston, Washington D.C., New York, Chicago, Cleveland, Buffalo, Detroit, Tampa, Seattle, San Francisco (and, possibly, other cities).

Interested individuals should send a resume and a cover letter to Ms.Lori Colombo, The Environmental Careers Organization, 286 Congress St., Third Floor, Boston, MA 02120-1009.

NOW AVAILABLE!



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Washington Environmental Newsletter

National Technology Policy

Perhaps the most significant recent development in U.S. policy is a strong new focus on industrial technology, which emerged by the late 1980s from concerns over the deterioration of the United States' relative economic position. In 1988, Congress articulated this focus clearly by committing itself to support "areas of technological development....essential for long-term security and economic prosperity." [The Omnibus Trade and Competitiveness Act of 1988].

This legislation thus validated the concept that technology, like science, could be seen as a public good. Subsequently, new institutions, such as the Advanced Technology Program in the Department of Commerce, have been created to support civilian technology development. In 1990, the Bush Administration's Technology Policy statement also contained the idea that public support should be directed to "generic" technologies in a"pre-competitive" stage of development [OSTP, 1991].

By early 1991, the concept of "critical" technologies had assumed the central place in technology policy discussions. Variously defined, critical technologies were seen as those that "enable" a wide range of related technical and economic developments, confer a strategic economic lead, augment national security, or dominate the technological future. Lists of critical technologies were issued by the White House Office of Science and Technology Policy, the Commerce Department, and the private Council on Competitiveness.

Critical Technologies and the Environment

The lists of national critical technologies in the United States and other countries were developed primarily out of concern about national security and international economic competitiveness. The OSTP list combined an extremely large, diverse group of technical fields under the general heading of "Energy and Environmental Technology," while recognizing that other technologies also have environmental implications.

If environmental technology is segregated and regarded narrowly as remediation and pollution treatment equipment, environmental concerns will inevitably be neglected in the promotion of critical technologies, and the potential of many emerging technologies for environmental improvement will be overlooked.

Environmentally critical technologies are those that can reduce environmental risk substantially through significant technical advance. because society as a whole will benefit from environmentally critical technologies, they represent appropriate targets for public investment. Technological developments can be considered environmentally critical if

- their use brings about large, cost-effective reduction in environmental risk;
- they embody a significant technical advance;
- they are generically applicable at the pre-competitive stage; and
- their adoption involves favorable ratio of social to private returns.

As for technology's potential to make possible major reductions in environmental risk, the first criterion, environmental risk, must be interpreted broadly to encompass diverse threats over a range of categories: human health, public welfare, and ecology. Technological developments that can avert serious risks to which large populations in the United States and elsewhere are likely to be exposed, or that can markedly reduce the costs of coping with such risks, rank high under this criterion.

Environmental technologies offer a classic example of this problem, since environmental damages typically take the form of unpriced external costs. Typically, those who would benefit from a reduction in environmental damage or risk are not able to express their willingness to pay through a marketplace. Developers of environmentally superior technologies thus depend on incentives created and driven by environmental regulations. Such incentives are uncertain, sporadic, and, often weak. Moreover, the sectors with the most serious pollution problems - energy, agriculture, and transportation, for example - are so highly distorted by environmentally insensitive public policies that the economic incentives facing the developers of new technology are skewed.

As the Clinton Administration takes hold, we will be reporting on progress in these areas - areas that can affect the future for all chemical engineers.

This material was prepared by AIChE's Washington Representative, Siegel • Houston & Associates Inc., Suite 333, 1707 L. Street, N.W., Washington, D.C. 20036. Tel. (202) 223-0650. FAX: (202) 833-3014

Surface and Colloid Chemistry in Natural Waters and Water Treatment by Ron Beckett, Plenum Press, New York, NY, 159 pages [ISBN No:0-306-43802-X] U.S. List Price: 59.50 (1990)

Water resources in Australia have long been precious, not only due to the arid climate but further due to the relatively level topography of the continent. Thus, the quality of raw waters is generally poor, with limited dilution of impurities and relatively high turbidities. At the same time, the concentration of this country's population into a few urban areas has centralized both the facilities and expertise for water treatment, leading to technological capabilities more than commensurate to Australia's population.

Australian expertise in colloid and surface chemistry has also achieved renown in recent decades, attributable in part to the historical importance of mining and mineral extraction industries. Researchers from academic and other research groups in Australia and New Zealand have acquired a particularly strong reputation in the area of aquatic colloid and surface chemistry.

Thus, a book originating in Australia and entitled *Surface and Colloid Chemistry in Natural Waters and Water Treatment*, would be anticipated as an insightful addition to the technical literature on these topics. The volume lives up to these expectations with few exceptions.

The book is described in its front matter as "proceedings based on a symposium on the Role of Surface and Colloid Chemistry in Natural Waters and Water Treatment", held on June 16-17, 1987, in Melbourne, Australia. Unfortunately, several of the chapters suffer from the three-year delay of publication since the symposium. However, some chapters have been more recently completed, referring to publications dated 1988and 1989. The chapters concerning photochemistry of colloids and surfaces, and surface chemistry of humic substances, are among the latter.

The chapters are grouped into two sections, "Processes in Natural Waters" (six papers) and "Water Treatment Processes" (five papers). The first section begins with "The Surface Chemistry of Humic Substances in Aquatic Systems" written by Ron Beckett. This chapter is an insightful review which also includes recent findings from Beckett's laboratory. In spite of the title, the authors deals with humic substances as soluble materials rather than as colloids, but surface chemistry is discussed from the perspective of humic' adsorption and consequent effects on interfaces and surfaces. These effects include surface activity and the air/water microlayer charge and electrophoretic mobility, on aggregation, and on speciation of trace metals and organic compounds.

A brief paper on "Microbial Processes at Surfaces" is followed by a well-written chapter by T. David Waite entitled "Photochemistry of Colloids and Surfaces in Natural Waters and Water Treatment". Aquatic photochemistry is receiving much attention currently with respect to naturally occurring photo-degradation processes and, as a logical extension, engineered processes for photo-degradation of toxic substances. The interesting role of organic substances (such as humic)in enhancing photochemical processes is given consideration, as in the structure of the inorganic catalyzing surface. Although the importance of photochemical reactions in aerosols is covered, its possible relevancy in developing photo-degradation processes is not. Much of the material concerning treatment processes comes from the work of David F. Ollis.

The following chapter on "Kinetics and Mechanisms of Iron Colloid Aggregation in Estuaries" is by Keith A. Hunter (the sole representative of New Zealand in the book). An aggregation model is described which invokes second-order dependency on dissolved iron concentration and appears to fit observations rather well. A succinct explanation of what iron species and colloidal sizes may be included in "dissolved" iron, and why this relates to aggregation in the manner it does, remains to be considered. Although the effects of organic matter are cited as important, this is not related to the kinetic coefficients.

The first section is completed with chapters on "The Generation of Suspended Sediment in Rivers and Streams" (B.L. Finlayson) and "Application of Uranium Decay Series to a Study of Ground Water Colloids" (R.T. Lowson and S.A. Short). The former is of limited relevance to surface and colloid chemistry, but the latter raises some interesting possibilities for determination of colloidal transport in groundwater through radioisotope analysis.

The section on water treatment processes starts out with "Water Treatment Technology in Australia", a review by Brian A. Bolto. Of note in this paper is the material on newer processes including two developed in Australia (Sirotherm and Sirofloc). The former is an ion exchange process for partial demineralization which uses a temperature increase for resin regeneration and magnetic composite resin beads to allow continuous process operation. The subsequent chapter on "The Role of Surface and Colloid Chemistry in the Sirofloc Process", written by David R. Dixon and Luis R. Kolarik, describes the Sirofloc process in more detail (the name stems from the CSIRO acronym indicating involvement of the Commonwealth Scientific and Industrial Research Organization). At the heart of this process is use of magnetite particles as the adsorbent (with polymer aid) followed by their magnetic separation. The surface characteristics of the magnetite are critical in defining process performance both by adsorption and by hetero-coagulation with other particles, and this paper provides a comprehensive discussion of important factors such as inorganic and organic ions, turbidity-causing particles, and coagulants used.

Following these papers is a paper reviewing coagulation and destabilization by Hutchison and Healy. While well-versed in classical theory and containing some new experimental results, this chapter does not review more recent developments from the international literature. Concluding the book are two chapters of limited relevancy to surface and colloid chemistry, which concern biological removal of phosphorus from water, and effects of dam destratification on manganese speciation.

It is rare that a volume seeks to unify fundamental aspects of surface and colloid chemistry with the more complex phenomena occurring in natural waters

and water treatment. This book succeeds in this task to an admirable extent, and is a welcome contribution to the field.

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Wastewater Treatment by Immobilized Cells, R.D. Tyagi and K. Vembu, editors; CRC Press, Inc., Boca Raton, FL, 281 pages [ISBN No: 0-8493-5176-6] U.S. List Price: $ 199.95 (1990)

The use of microbial biomass for wastewater treatment has been a feature of such systems since the introduction of the activated sludge process in the 1920s. Recent developments in the immobilization of cells for increased throughput and efficiency have increased the performance of numerous biological treatment systems. Drs. Tyagi and Vembu have assembled an impressive array of experimental and practical reviews of this area for this volume.

The book consists of ten chapters, each forming a complete review of an area of immobilized biomass. The effect of the combination is to produce a thorough, yet understandable review of the entire field. The opening chapter reviews the basics of microbial adhesion and immobilization ranging far afield from wastewater treatment to include discussions of cellular adhesion from heat exchanger fouling to dental caries. For those not acquainted with the works of Claude Zobell and K.C. Marshall, this chapter provides an admirable overview and a comprehensive bibliography.

The following three chapters focus on the processes of microbial immobilization from adsorption (Chapter 2) to physical entrapment (Chapter 3) and a view through the electron microscope of their structure (Chapter 4). Chapter 2 provides a good general overview of several theories and models of microbial adsorption while detailing some of the chemical mechanisms of adhesion. Chapter 3 details a broad range of entrapment and immobilization methods and carefully compares their relative efficacies and applications. The chapter concludes with a discussion of original research on the use of mixed microbial cells for the treatment of wastewater contaminated with phenol.

Chapter 5 discusses the range of applications for biomass carriers (such as submerged solid surfaces, porous systems, and microcarriers) in the activated sludge process. The authors provide a concise but comprehensive overview of most existing commercial processes, including detailed process diagrams. In addition, a range of research results from experiments utilizing microcarriers is reviewed.

Chapter 6 briefly describes the potential uses for microalgae in the wastewater treatment process. Chapter 7 returns to the pattern of review combined with original research results in the discussion of immobilized cell systems in anaerobic digestion processes. The authors (Samson, Pauss, and Guiot of the National Research Council of Canada) discuss their work in the development of anaerobic bacteria laden granules and their use in upflow anaerobic sludge blanket reactors for the production of methane and the treatment of wastes.

Chapter 8 examines the theory behind the use of microbial biomass for the detoxification of chemical waste and some potential research avenues. Chapter 9 examines the use of the expanded bed reactor for wastewater treatment and provides a theoretical framework for the development of such reactor systems.

The editors conclude the volume with a discussion of the use of fluidized bed reactors for wastewater treatment, including a discussion of design, specification, and application.

In summary, this volume provides an excellent review of the developing area with considerable effort made to develop extensive bibliographies for the reader's future use.

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Air Toxics and Risk Assessment by Edward J. Calabrese and Elaina M. Kenyon, Lewis Publishers, Inc., Chelsea, MI, 480 pages [ISBN No.: 0-87371-165-3] U.S. List Price: $ 89.00 (1991).

The primary premise for writing this textbook, as described by the authors, is that during the 1970's and 1980's, the U.S. EPA neglected the whole environmental regulatory area known as "air toxics". Because of this situation and due to political pressure and increasing information on chemicals measured in the ambient air, state and local (S/L) air pollution control agencies developed separate and distinct air pollution control programs focusing on air toxics. As the authors state correctly, this plethora of regulatory programs, without strong federal involvement, has resulted in the development of a diverse number of acceptable ambient air levels (AALs) for the same chemicals. The authors provide examples where S/L AALs for the identical chemical differ as far as averaging times (i.e., 1 hr, 8 hr, 24 hr, and/or annual) and the method of development (i.e., Threshold Limit Value times a safety factor, quantitative risk assessment, etc.). Such differences in approach can result in AALs for the identical chemical that differ over many orders of magnitude. The text adequately explains why these differences exist, how S/L regulatory agencies are short on proper technical personnel capable of developing technically sound AALs and that AALs, while often only providing guidance for air pollution permit writers, play a key role in decision making (i.e., risk management decisions) at S/L agencies. In summary, this text is essentially about the development of an AAL methodology, and its application, for the formation of guideline health standards for air toxics.

The text is organized into two sections. Part I provides an introduction to the origin of S/L air toxics programs in the U.S., an overview of the basis for the development of AALs, a review of important secondary sources of toxicological data and health assessment data for specific chemical and a description of a new AAL developed by the

authors called an acceptable ambient level guideline (AALG).

Part II includes key information (i.e., toxicity profiles) on over 100 chemicals for which the authors have derived AALGs. These chemicals include a broad range of substances that are important to modern commerce, such as antimony, chromium, copper, cadmium, lead, manganese, nickel, and zinc. Major industrial solvents such as benzene, ethylbenzene, toluene, xylenes, methylethylketone, methylisobutylketone, and a number of chlorinated solvents such as methylchloroform, trichloroethylene, and perchloroethylene. Inorganics such as ammonia, hydrochloric acid, hydrogen cyanide, and nitric acid are also included.

The text was released in 1991, and as such has some overall limitations regarding the implications for the authors' AALG methodology. This is primarily the case due to the enactment of the Clean Air Act Amendments (CAAA) of 1990. The CAAA requires the U.S. EPA to develop Maximum Achievable Control Technology (MACT) standards for some 190 hazardous air pollutants (HAPs), which include many, but not all, air toxics addressed by most S/L air pollution control programs. Under the CAAA, the U.S. EPA must evaluate MACT standard implementation and use a health risk assessment approach, if necessary, to develop so-called residual risk standards (i.e., standards to reduce residual risks that remain after the implementation of MACT controls). Thus, as a result of the CAAA, federal involvement in the regulation of air toxics will be extensive. A real concern, not addressed by the authors, is how such a federal program will interface with the many existing S/L air toxics agencies with delegated authority for the 190 HAPs under the CAAA. Once the federal health risk assessment approach is adopted by most S/L agencies, the AAL approach for air toxics regulation is likely to disappear.

The information provided by the authors is useful to those practicing environmental scientists and engineers who are not actively involved in the area of health risk assessment. However, the overall title of the text is misleading: the title does not address health risk assessment as is currently recommended by the National Research Council (NRC), whose approach has been adopted by the U.S. EPA and many S/L agencies. The four steps of a NRC health risk assessment include:

- Hazard Assessment;
- Dose Response Analysis;
- Exposure Assessment; and
- Risk Estimation

The present text primarily addresses specific aspects of hazard assessment and, to a limited extent, dose response analysis. Exposure assessment is barely discussed and risk estimation cannot be addressed in the absence of real or hypothetical pollution source.

The text is not particularly useful for those scientists and engineers that actively use or conduct health risk assessments. Virtually all of the information sources discussed by the authors are readily available to risk assessors, and in many cases, current original literature is used for a given health risk assessment since secondary literature sources are often out of date. The calculation approaches used to develop the AALGs are essentially variations on a theme from the previous S/L approaches to AALS, and are consistent with specific aspects of the U.S. EPA methodology to develop unit risk factors (URFs) and inhalation reference concentrations (RfCs). Thus, no new ground is broken here. In fact, that is the primary shortcoming of the text. Health risk assessments have been conducted for air toxics for about 11 years. The field has matured and currently there is a wealth of experience, both good and bad, in the application of the NRC health risk assessment principles. Yet there is no dis-

Errata

corrected
10 May 93 AP

In "Use of Risk Assessment Groundwater Model in Installation Restoration Program (IRP) Site Decisions" by David.K. Goldblum, John D. Erving and John M. Clegg [*Environmental Progress* **11**, 91 (1992)] Equation (5) should read:

$$Intake\left(\frac{mg}{kg-day}\right)=\frac{(CW)(SA)(PC)(ET)(EF)(ED)(CF)}{(BW)(AT)} \qquad (5)$$

Equation (6) should read:

$$Intake\left(\frac{mg}{kg-day}\right)=\frac{(CW)(SA)(MF)(ET)(CF)}{(BW)} \qquad (6)$$

On page 96 the *CF* definition should read:

CF = conversion factor (1 liter/100 cm^3 or 1 liter/10^6 mg)

In "Oxygen Membrane Electrode Uses as a Toxicity Biosensor" by David K. Goldblum, Steven E. Holodnick, Khalil H. Mancy and Dale E. Briggs [*Environmental Progress* **10**, 24, (1991)] Equation (6) should read:

$$C=C_s-\frac{kN_o}{k'}\left(e^{k't}-1\right) \qquad (6)$$

cussion by the authors regarding the approaches, information voids, exposure assessment methods, and the uncertainties associated with currently conducted health risk assessments. Uncertainty analysis is an important and evolving component of health risk assessments. Since most health risk assessments involve predicting impacts of future air pollution sources, estimating the uncertainties for a health risk assessment provides important information for the overall risk management decision making process.

To develop a text focusing on AALGs, is to ignore the many analytical steps required by the risk assessor to complete risk assessment study. In fact, the authors have omitted any discussion of key federal decisions regarding air toxics (e.g., arsenic, benzene) which suggested that health risks greater than 1×10^{-5} were acceptable or that previous risk assessments were flawed (i.e., the current controversy concerning 2,3,7,8 - tetrachlorodibenzodioxin).

Health risk assessments are generally conducted for new and/or modified source sources that emit air toxics. Many S/L agencies require mandated health assessment approaches which may include multi-pathway exposure assessments, even for sources that release exclusively air pollutants. Health risk assessment are conducted to evaluate the incremental impact of these new pollution sources. Thus, the diverse technical and practical aspects faced by most risk assessors implies that AALGs are of limited value for these individuals.

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A Review of Two Risk Assessment Computer Programs

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INTRODUCTION

Managing environmental health risk due to the release of pollutants from an industrial complex requires the assessment of environmental dispersion, exposure and health risks. As new health risk based environmental standards and guidelines are introduced, integrated computer programs will be needed to prepare documents for permits to design control equipment and to conduct environmental assessments. Kumar and Rao [*1*] reviewed software for regulatory compliance of chemical hazards and provided a list of available computer programs. The purpose of this review is to look at two computer programs. The first program RISKPRO [*2*] is an integrated environmental health assessment package. The second Program HRA [*3*] is designed to accept the results of an atmospheric dispersion model to compute the risk at a plant in California.

RISKPRO SOFTWARE

The software package is developed by General Science Corporation and is marketed by American Chemical Society (Tele. No. (202) 872-4564). RISKPRO combines selected programs in such a way that the package can be used for releases from air, soil and groundwater systems. The package has good graphical capabilities and a collection of data management programs. It is a user-friendly program, with sufficient help instructions whenever needed. However, some of the modules in RISKPRO should be updated to keep up with the changing regulations/guidelines.

RISKPRO contains environmental programs such as ISCLT, PTPLU, SESOIL, EXAMS-II, and AT123D. The databases on census population (BG/ED), CAS Number/SMILES, windrose (STAR), and chemical properties (AUTOTEST) are included. The graphic programs such as ROSE and GENMAP are used for graphical work. The data management programs CATMGR, EDITINS, EDITFILE, REFORMAT, CENSUS, etc., and estimation programs SMIGET, ATOMLOGP, and AUTOTEST are a part of the package. The communication program MS-KERMIT is also available. The programs and associated data sets available in RISKPRO are briefly described in Table 1.

The RISKPRO package is available in 25 3 1/2″ disks along with a user's guide. Installation instructions are given in the guide. It is easy to install the program following the instructions. The minimum system requirements are:

- IBM XT/AT/PS2, 80386 or compatibles with 640K RAM
- Hard disk and one floppy disk drive
- DOS version 2.2 or higher
- Graphics display adapter
- 540K RAM availability at all times

Optional hardware:

- 8087, 80287, or 80387 Math co-processor to speed up the execution of programs
- Parallel of serial port for use with output device
- Modem for communication with other computers.

It is recommended that the programs are copied in a separate directory and not directly on the hard drive. If more than one hard drive is available, copy onto the drive which has enough memory and has few or no memory resident programs, as RISKPRO is highly memory intensive. Depending upon the memory space and necessity, you have to copy the programs and data sets into appropriate directories. During the installation process, you can select the output options you would like for the graphics output in RISKPRO. The text output of results in RISKPRO is in American Standard Code

Table 1 Available Programs and Associated Data Sets in RISKPRO

Estimation Programs:

SMIGET:	Retrieves the SMILES notations when the CAS number for the chemical is fed by looking through a data set containing 20,000 chemical notations.
ATOMLGOP:	Estimates the octanol/water partition coefficient value for a chemical.
AUTOEST:	Provides access to the AUTOEST data set which contains measured values for over 1,000 chemicals including about 250 chemicals on the EPA's SARA Title III, Section 313 list of highly toxic chemicals. It estimates seven chemical properties of a chemical with least input data.

Environmental Modeling Programs:

ISCLT:	This is an EPA guideline air model which calculates annual ground-level concentration or deposition values.
PTPLU:	The model estimates the location of the maximum short-term concentration in the atmosphere from a single point source.
SESOIL:	The program estimates the rate of vertical chemical transport and transformation in the soil column.
AT123D:	This model predicts the spread of a contaminant plume through groundwater.
EXAMS-11:	The model simulates the fate of organic chemicals in surface water bodies.
ENPART:	This is a multi-media model that estimated equilibrium concentration ratios of a chemical between the environmental components of air, water, and soil.
RISKTAB:	This allows you to create tables of dose, risk, and hazard index estimates for multiple exposure pathways, using environmental concentrations from the results of the various models.

Data Management Programs:

CATMGR:	This multi-task program allows you to organize and list the many output and input files that RISKPRO generates and needs.
EDITINS:	This installs a data editor under RISKPRO environment so that you may manipulate RISKPRO output files.
EDITFILE:	This is used to edit a file under the RISKPRO environment.
REFORMAT:	This allows you to convert ASCII files into two different formats so that the files may be used by other commercial software, including Lotus 1-2-3.
CENSUS:	This retrieves population data from the census population BG/ED data set.

Graphics Programs:

ROSE:	This program allows you to visually represent the distribution and speed of wind patterns.
GENMAP:	This allows you to draw high-quality maps at various spatial scales depicting county, state, and EPA region boundaries.

Communication Programs:

MS-KERMIT:	This runs the MS-KERMIT terminal emulation program.

Utilities:

CRFIG:	This changes RISKPRO configuration file.
XINSTALL:	This allows to install a non-RISKPRO program under the RISKPRO environment.
XRUN:	This runs a non-RISKPRO program under the RISKPRO environment temporarily.
XRUNNPC:	This runs a non-RISKPRO program under the RISKPRO environment after it is installed using XINSTALL.
DXDYCALC:	This program calculates the X- and Y-coordinates in meters relative to a primary location.

Data Sets:

Census Population BG/ED:	Currently is used by ISCLT, CENSUS and the General Geographic Mapping Program.
Reach Trace:	This is used by the Geographic Mapping program to draw river reaches.
CAS Number/ SMILES:	This is used by SMIGET and ATOMLOGP. Contains SMILES notations for 20,000 chemicals.
STAR:	It is used by the ROSE program, the Geographic Mapping Program, and the ISCLT Program.
AUTOEST	Used by the AUTOEST Program.
Chemical Properties Database:	Contains measuring properties for 1,010 chemicals.
Geographic Mapping Boundaries Data Sets:	Used by Geographic Mapping program.
ZIPCODE:	Used by the ISCLT program, ROSE program and Geographical Mapping program.

for Information Interchange (ASCII) format and may be printed on any output device that you may have.

RISKPRO uses four types of menus: navigational menus, parameter editing menus, array editing menus, and table selection menus. The menu designs are explained briefly in Table 2. The menu screens in RISKPRO have been divided into five sections. Each section imparts a different type of information. This helps you to know where to look for system commands or other information, and you will know the kind of information the system is sending you just by where it occurs on the screen. A brief description of various sections is given below:

Title section: This section provides you with the system and the default drive name.

User interaction section: This section is often called as the MAIN WINDOW in the color specification menu. This section is where the main user interaction occurs in all types of menus. The help messages are also shown in this section, appearing in a window whenever you press the help key (F1 key).

Table 2 Types of Menu's in RISKPRO

Menu	Description
Navigational Menu	This menu helps you to navigate through RISKPRO. These present with a list of options from which you may select one by highlighting the selection using the arrow keys and then pressing the ENTER key. When you select an option, you may proceed either to another navigational menu or to a parameter menu.
Parameter Editing Menu	These are used to enter values into RISKPRO for specific parameter needed by a RISKPRO program in its execution.
Array Editing Menu	They are similar to parameter editing menus in that require input necessary for the execution of the program. This input is in the form of tables and they are different from parameter editing menus in that they are arranged in rows of related data values with headings illustrating the type of data values that you must enter.
Table Selection Menu	This is seen when a program like Catalog Manager Program is selected. This lists all the variables, parameters or program names in a tabular form. Instead of entering any data as in other menus, one must select the required item from among the ones that are displayed.

Error message section: This area is meant for the error messages which will appear if you do make an error in entering any input if the program or data set is not located in the specified path. The message will tell you that you made an error and the type of error that you made. It is usually accompanied by bell.

Instruction section: This is meant to be the user message section. It gives the user information about the limitations of interaction. This should be often referred to in order to see how to select items and how to move from that particular menu to the next one.

Command key section: This is the last area of the RISKPRO menu which is the command keys section. It gives a list of the keys and their function in RISKPRO. For information regarding the function keys available, one can look into the user's guide.

The graphic capabilities include giving contour plots, windrose patterns, concentration isopleths, US county, state, EPA boundaries, etc.

A familiarity with menus and the practice to use a menu will help you to do the work efficiently. After loading the computer program, we checked different sections of the program by using dummy input data. More runs were made using ISCLT and PTPLU. There was not enough data to run ISCLT. Therefore, we modified our data on an industrial source and used arbitrary values for few parameters. The program ran and the results were in acceptable range. PTPLU is much easier to run. It did run for several test cases involving point sources. Other programs (SESOIL, AT123D, AUTOEST, etc.) did not create any problems. However, input data to run these programs were limited.

RISKPRO is a very useful tool for conducting a risk assessment. Addition of ISCST model will increase the usefulness of the package. New versions of ISCST and ISCLT are available from the EPA and may be incorporated for regulatory purposes. Since the SCREEN model is being used for screening purposes, it may be a good idea to include SCREEN model along with PTPLU.

HRA1.1 SOFTWARE

This program was developed by the staff of the California Air Resources Board (ARB) and Office of Environmental Health Hazard Assessment (OEHHA). The program facilitates to calculate cancer risk, cancer burden, and hazard indices for non-cancer health effects. Prior to using HRA model, the dispersion modeling results, which provide concentration (χ) over emission rate (Q) must be known. χ/Q gives the site specific dispersion factor. The algorithms and default values of this program are based on information contained in the Multi-Pathway Health Risk Assessment Input Parameters Guidance Document.

HRA program version 1.1 updated its earliest version by incorporating the most current cancer potency values,

Table 3 Required Input Files for HRA Program

Analysis	Input Files
Acute Inhalation Analysis	Maximum one-hour Emissions File
	Background Concentration File
Chronic Inhalation Analysis	Emissions File
	Background Concentration File
Risk Analysis	Emission File
	Route File
Cancer Burden Analysis	Emission File
	Receptor Data File

Acceptable Exposure Levels (AEL) and default values recommended by OEHHA. Few exposure algorithms and the methodology used to evaluate non-cancer effects have been revised in HRA version 1.1.

The requirements of this program are:

- MS-DOS Computer (IBM or IBM clone)
- At least 640K of RAM with hard drive and at least one floppy drive
- Printer port

The program can be run from the hard drive or from the floppy drives. To start the HRA program, copy all the files to a separate directory on the hard drive, and then type HRA92 and press enter key. This is a menu-based program. It asks for the necessary information such as emission rates and routes of exposure through menus and prompts. This information, stored in input files, is a must to calculate cancer risk, cancer burden, and non-cancer effects.

The program is user friendly and it informs whenever errors are made. Errors include items such as wrong file specification, inputting out of the permitted range value, or inappropriate response.

Input files are created by selecting "create input files" option from the main menu. Once you finish creating an input file/s select "R" to return to main menu. Input files required and the analysis done using them are listed in Table 3. The program will ask to create a file name while creating an input file. From the "create input file" menu the emission file, the maximum one-hour file and a background file can be created. The process of entering data into three different types of files is the same. A list of the pollutants in alphabetical order, beginning with chemicals with numerical characters, will appear on the screen once you provide a name for the emission file. List of chemicals the HRA program can evaluate and the applicable types of analysis for that chemical are given in software documentation [3].

The program evaluates the following routes of exposure: inhalation, dermal adsorption, mother's milk, soil ingestion, crop ingestion, milk ingestion, meat/egg ingestion, surface water ingestion and fish ingestion. Select "Route Files" from the "Create Input Files" sub-menu to create a route file. Provide a name for the file and provide the necessary information when asked. In preparing the route file, if you are asked for a χ/Q and you do not provide a value, the program will assume that the sources are located at the receptor site under evaluation.

The receptor file is created by selecting "Receptor File" from the "Create Input Files" sub-menu and providing the required information. This file is necessary to provide information needed to calculate the cancer burden. The receptor information is entered one receptor site at a time.

The HRA program can be used to calculate the risk analysis, the cancer burden, acute inhalation analysis and chronic inhalation analysis. Risk analysis is calculated by selecting "Risk Analysis" from the "Run Program" sub-menu. You have to provide site specific χ/Q. The program will then calculate the chronic exposure and the individual cancer risk of pollutant and route.

Cancer burden is assessed by selecting "Cancer Burden" from "Run Program" sub-menu. This calculation includes the following routes of exposure: inhalation, dermal, and soil ingestion.

Acute or chronic inhalation hazard index assessments for non-cancer effects can be performed by selecting either "Acute Inhalation" or "Chronic Inhalation" respectively from the "Run Program" sub-menu. If risk analysis is selected, chemical by chemical comparison of chronic ingestion exposures to oral AELs is done.

We did not encounter difficulty in using the program. A number of runs were successfully made to prepare a refined risk assessment for a plant. The program is used by graduate students and in air quality modeling courses. The program is of limited value. Multiple sources cannot be handled in a run. Complete risk contours cannot be obtained and require manual work. However, the program is useful for understanding the concept of risk calculations and for performing quick sensitivity analysis.

CONCLUSIONS

We enjoyed using both the programs. Both the programs are a useful addition to the growing field of risk assessment. With improvements, the programs can meet industrial needs. The programs are also useful for training staff in an industrial environment.

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Biocatalytic Desulfurization of Petroleum and Middle Distillates

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Biocatalytic Desulfurization (BDS) represents an alternative approach to the reduction of sulfur in fossil fuels. The objective is to use bacteria to selectively remove sulfur from petroleum and middle distillate fractions, without the concomitant release of carbon. Recently, bacteria have been developed which have the ability to desulfurize dibenzothiophene (DBT) and other organosulfur molecules. These bacteria are being developed for use in a biocatalyst-based desulfurization process. Analysis of preliminary conceptual engineering designs has shown that this process has the potential to complement conventional technology as a method to temper the sulfur levels in crude oil, or remove the recalcitrant sulfur in middle distillates to achieve the deep desulfurization mandated by State and Federal regulations.

This paper describes the results of initial feasibility studies, sensitivity analyses and conceptual design work. Feasibility studies with various crude oils and middle distillates achieved unoptimized desulfurization levels of 40–80%. Sensitivity analyses indicate that total desulfurization costs of about $3.00 per barrel for crude oil and less than $2.00 per barrel for diesel are possible. Key criteria for commercial success of the process include the cost and half-life of the biocatalyst, residence time in the reactor, oil/water ratios required to extract the sulfur and the disposition of the separated sulfur products.

INTRODUCTION

There have been numerous attempts over the last forty years to develop an enzyme-based process for the desulfurization of fossil fuels. The first U.S. patents on processes for the biocatalytic desulfurization of petroleum date back to the 1950's, and many related patents have been issued in the subsequent years (see reference 7 for a review of the early work in this area). These patents describe methods to combine bacteria with oil and selectively ferment the sulfur-containing compounds, thus removing them from the hydrocarbon. These patents and other publications suggest steady advances in the development of biological desulfurization technology. Despite this apparent progress, none of the inventions have ever been commercialized. The primary reason for the practical and commercial failure of these inventions is that in the process of releasing the sulfur, a significant portion of the hydrocarbon is also destroyed [*4*, *7*]. This lack of specificity limits the usefulness of these inventions, since it is not economical to destroy 10–50% of the hydrocarbon in order to desulfurize the material. A second limitation of these systems is the need for the bacteria to be growing in the presence of the hydrocarbon in order to liberate the sulfur.

In the last two years, new strains of bacteria have been developed which catalyze the selective cleavage of carbon-sulfur linkages in model compounds and petroleum samples while leaving the hydrocarbon portion intact [*5*, *6*]. The best documented example of this phenomenon is the bacteria isolated by J. J. Kilbane at the Institute of Gas Technology which are being developed by Energy BioSystems Corporation (EBC). Recent work at EBC and elsewhere suggests that a biocatalytic process can be developed to remove DBT and DBT-like molecules from middle distillates and thus may be a useful process to augment the existing desulfurization technologies in refineries. The purpose of this paper is to report on the results of this development effort, and to assess the prospects for a commercially viable biocatalytic desulfurization process now that the specificity hurdle has been overcome.

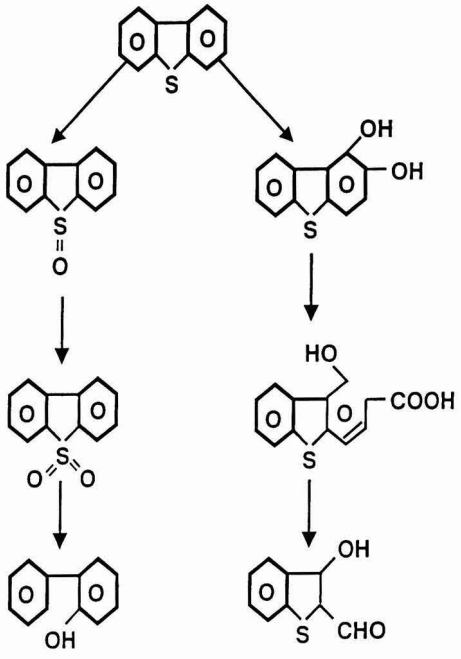

FIGURE 1. Dual pathway of microbial oganosulfur metabolism.

DEVELOPMENT OF THE BIOCATALYST

In 1989, Kilbane reported the isolation of bacteria which could oxidize dibenzothiophene (DBT) to 2-hydroxybiphenyl (2HBP) and liberate sulfur [*5*]. The initial studies were conducted on coal as part of a DOE sponsored "Clean Coal Initiative." The organism, a strain of *Rhodococcus rhodochrous* (dubbed IGTS8), was initially isolated from soil based on its ability to liberate sulfur from pulverized coal in order to obtain sulfur for growth. Subsequently, the potential of the bacteria to desulfurize other molecules was demonstrated, and in 1990 the bacteria were used to desulfurize a variety of petroleum samples, ranging from crude oil to diesel fractions.

THE BIOCHEMISTRY OF BIOCATALYTIC DESULFURIZATION

The biochemistry which underlies the ability of IGTS8 to liberate sulfur is not completely understood. It is clear that the bacteria can catalyze the conversion of DBT to 2HBP, but the intermediate(s) in the conversion have not been identified. The practical implications of this oxidative of DBT are obvious however, especially when compared to the known route of DBT oxidation by bacteria. These alternate pathways are illustrated in Figure 1.

The "traditional" route of DBT oxidation proceeds from the destruction of the aromatic ring structure and eventually leads to the formation of water soluble organosulfur compounds. It was through the use of bacteria employing this mechanism that earlier workers were able to desulfurize oil, but in the process solubilized significant quantities of hydrocarbon into the aqueous phase. This was the primary reason that these bacteria were unacceptable as catalysts for biocatalytic desulfurization systems [*4*]. In contrast, the mechanism which has been proposed for the oxidation of DBT to 2HBP leads to the formation of hydrocarbon-soluble product (2HBP)

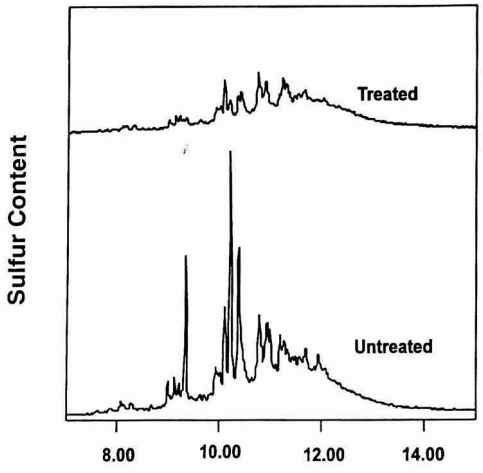

FIGURE 2. Retention time in minutes.

and a water-soluble form of sulfur. Recent experiments with bacteria closely related to IGTS8 have shown that one of the products of this oxidation is sulfate [*8*].

MICROBIAL GROWTH IS NOT REQUIRED FOR ENZYME ACTIVITY

Until recently, it was assumed that it was necessary for bacteria to grow in the presence of the hydrocarbon in order to desulfurize the material. We have found that this is not the case with the biocatalytic system we are developing. The bacteria can be pregrown in conventional fermentors, frozen or dried, shipped to the experimental reactors and utilized as nonviable cells. The bacteria at this point have been converted to "bags of chemicals," unable to grow but still retaining the enzyme(s) which catalyze the desulfurization reactions.

An example of the results of this catalytic approach is illustrated in Figure 2. The diesel sample used in the experiment had 0.22% sulfur by weight. In this experiment, biocatalyst was suspended in buffered water, combined with the diesel and the mixture was processed for several hours in an airlift reactor. The GC/FPD analysis of the diesel samples before and after treatment (Figure 2) shows the significant reduction of the sulfur content of the oil and the reduction of all the sulfur containing molecules. No differences in the GC/FID traces (not shown) of the treated and control sample could be detected, indicating that the overall profile of the sample was essentially unchanged. These data show that the biocatalyst can be used to desulfurize real oil samples as well as the model compounds, that they retain the specificity which is vital to the commercial application of the process, and can catalyze the reaction without the need for microbial growth. This breakthrough has enabled us to separate the production of the catalyst from its use, and to conceptualize a process where the bacteria are used as conventional catalysts in a commercial desulfurization process.

INDUSTRIAL APPLICATIONS OF BIOCATALYSTS

There are many well known precedents in the chemical industry for the use of enzymes on an industrial scale. The best known example of this is the use of amylases and glucose isomerase in the production of high-fructose corn syrup from corn starch. Millions of pounds of this material are produced

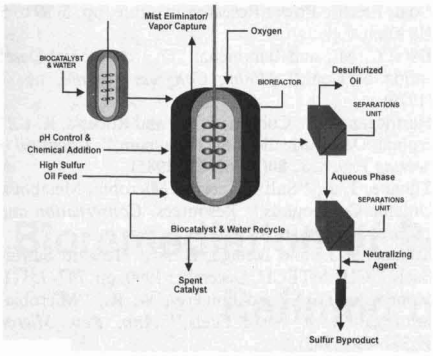

FIGURE 3. Biocatalytic desulfurization.

in the U.S. each year. Enzymes are also used in the production of fuel ethanol, amino acids and laundry detergents. The implication of these large scale uses of enzymes in commodity products is that the economics of biocatalytic processes can compete with non-biological processes, and that many processes which in the past were viewed as amenable only to the use of inorganic catalysts may be benefited by the use of biocatalysts. It appears that biocatalytic desulfurization may be added to this list in the future.

CONCEPTUAL DESIGN OF BDS SYSTEMS

In the past year, we have analyzed a variety of potential process designs. One of these is illustrated in Figure 3. It shows one of the simplest conceptualizations of the technology. In this case, the high sulfur oil is mixed with the biocatalyst to form an emulsion in the continuous stirred tank reactor (CSTR). Following a residence time of about 1 hour, the emulsion is broken and the desulfurized oil is separated from the biocatalyst and sulfur-laden water. The biocatalyst is then separated from the sulfur/water and recycled to the reactor. In this scenario, the sulfur (in the form of sulfate) is precipitated from the system with calcium oxide to form calcium sulfate. There are several alternate methods to convert the soluble sulfate into saleable byproduct, but precipitation as gypsum appears to be the most costly alternative and so is the case we have used in this analysis.

PROCESS ECONOMICS

Previous examinations of the economics of biocatalytic desulfurization have focused on the cost of catalysts and hardware, and the loss of fuel value associated with bacteria which degrade sulfur containing hydrocarbons [*1*, *2*, *3*, *9*]. In 1985, Hartdegan [*4*] concluded that the single most important factor impacting the cost of the biocatalytic desulfurization of residual fuel oil was the lack of specificity of the biocatalyst, which would remove the sulfur from the oil while degrading the carbon fraction. This problem has been overcome with the development of the sulfur-specific organism IGTS8, and our analysis shows that the biocatalytic desulfurization of middle distillate fractions is economically attractive with the use of these sulfur-specific bacteria. Sensitivity analyses of the conceptual BDS system indicate that there are several key factors which dictate process economics. The single biggest cost in this analysis is disposal of the sulfur, followed by cost of the catalyst and finally capital costs associated with the process. The influence of catalyst cost is largest when one assumes limited recycle of the catalyst and is also related to the specific activity of the material. Capital costs are most impacted by the residence time and the oil/water ratio which is required.

These analyses are based on a series of assumptions, which are outlined below:

- The target fuel is a middle distillate which is to be desulfurized from 0.25% to 0.05% sulfur.
- The sulfur containing molecules are in the form of dibenzothiophene (DBT) or similar sulfur heterocyclic molecules.
- The sulfur heterocycles are desulfurized by the biocatalyst according to the "4S" pathway.
- The products of the process are desulfurized oil, hydroxylated oil soluble products and sulfate.
- An oil to water ratio of 1 to 1 is maintained.
- Volatilization of oil in the reactor is insignificant and can be neglected in this analysis.
- The reactor can process 10,000 barrels per day.
- The retention time in the reactor is one hour.
- The biocatalyst is recycled and reused in the reaction.

All the previously published work on the aerobic desulfurization of DBT indicates that the product of the biocatalytic reaction is water-soluble sulfur, in the form of dilute sulfuric acid. Since low pH and high sulfate concentrations can be expected to inhibit the biocatalytic desulfurization processes, the sulfuric acid produced from inorganic sulfur (in coal), or from organic sulfur via the 4S pathway must be neutralized and removed from the process. There are several alternative approaches to removal of the inorganic sulfur from the system. In our analysis we examined several alternatives, including precipitation as gypsum, neutralization with caustic, production of ammonium sulfate and concentration to sulfuric acid. Precipitation as gypsum and subsequent land filling appears to be the least desirable alternative, and so we have used it to illustrate the worst case costs of the process.

Sensitivity analysis of this conceptual design, and more complex systems, indicates that the biocatalytic process should be able to desulfurize middle distillates for between $1.50 and $2.50 per barrel. This cost includes both capital and operating expenses.

PROCESS DEVELOPMENT ISSUES

Energy BioSystems' effort to commercialize a BDS system is in the process development stage. We have established the feasibility of the process in one liter reactors and are scaling the process up to the pilot plant level. There are several issues which must be addressed in order to complete this process. These include:

1. Strain improvement and fermentation development work for the production of the catalyst.
2. Selection and testing of reactor configurations.
3. Selection of appropriate emulsion breaking technology.
4. Determination of the best methods for disposition of the products (sulfur, water, spent catalyst, etc).

Each of these issues has been successfully addressed in other process technologies, and it appears that they can be integrated into novel configurations for the development of an economically attractive technology to augment the desulfurization capabilities of refineries. This development effort over the next few years should lead to the completion of the first commercial scale units in 1996.

CONCLUSIONS

The primary issue which has limited the application of biotechnology to the refining industry has been the lack of a biocatalyst with the appropriate specificity. This problem has

been overcome with the development of new bacteria which can selectively liberate sulfur from DBT and DBT-like molecules. We have found that the bacteria can be used as catalysts, in an environment which does not support microbial growth, to desulfurize middle distillate fractions, thus overcoming one of the other major limitations of the approach. The process development effort from this point, while not trivial, does not require any other "breakthroughs." Based on conceptual process designs and data from our laboratories, it appears that the process will be able to desulfurize middle distillate fractions for a capital and operating expense between $1.50 and $2.50 per barrel.

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Bioremediation of Petroleum Wastes from the Refining of Lubricant Oils

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The results of an initial feasibility study on the bioremediation of sludge are presented. The sludge used in the study was taken from a site containing waste produced during the refining of lubricant oils to which sulfuric acid had been added. The effectiveness of bioremediation was examined using shake flask experiments with indigenous and other bacteria sources and nutrient supplementation. The initial results show limited effectiveness of biological treatment at conditions employing indigenous bacteria and low (2%) sludge concentrations in Bushnell-Haas media. In addition, the indigenous bacteria were seen to degrade the polycyclic aromatic hydrocarbons naphthalene, penanthrene and pyrene which are present at some locations at the site. No apparent degradation of material was seen using conditions of high (30%) sludge concentrations in Bushnell-Haas medium under a variety of conditions. In addition, nutrients were rapidly depleted at these sludge concentrations, with the exception of sulfates which were produced when high sludge concentrations were used.

INTRODUCTION

Petroleum refineries have historically produced large quantities of hydrocarbon sludge as a waste product. It is estimated that petroleum refineries presently generate over one million tons of total waste material per year nationally [*3*]. The form of the waste may include formation waters, crude oils, produced sands and spent chemicals [*18*]. The chemical composition can include a range of organics such as aromatics, polyaromatics and branched hydrocarbons. In addition, there may be a number of inorganics and metals present.

As common past practice, petroleum refinery waste was stored in open impoundments or pits. These waste sites now require remediation to meet current environmental regulations. This report presents the results of an initial feasibility study on the biological treatment at one such site. The goals were to characterize the sludge from this site both physically and chemically, and to determine the potential of biodegradation under a range of environmental conditions. The study was carried out concurrently with an independent examination of stabilization/solidification of the refinery waste [*16, 10*]. The site in question contains 9 sludge lagoons and three spent clay piles on 71 acres.

The petroleum sludge used in this study was obtained from the production of highly refined lubricated oil used in refrigeration processes. Sulfuric acid was added during processing which produced an acidic product. The lubricating oil was filtered through fuller's earth (attapulgite clay) to remove impurities such as waxes. The resulting sludge from the process was stored in open pits and lagoons. Sludge was placed into these lagoons from 1925 through 1971 [*20*].

A number of remediation techniques are possible in treating petroleum wastes. The most commonly considered as physical, chemical, thermal and biological approaches. Physical methods such as extraction simply transfer the wastes from one medium to another without providing a permanent solution. Chemical treatment is generally based on exploiting different chemical properties of the soil and the contaminant such as acidity and precipitation potential. This approach can leave hazardous by-products. Chemical stabilization increases the

volume of toxic material by diluting it with a binding material. In addition, the contaminants are not eliminated but simply entrapped within a matrix. Thermal techniques such as incineration are effective but are frequently costly. Finally, biological treatments seem promising but present unique problems of their own and are still not well established.

Bioremediation is defined as the breakdown of organic compounds by microorganisms. The degree of alteration varies and is typically defined as either mineralization or biotransformation. Mineralization is the complete breakdown of organic molecules into inorganic substances such as carbon dioxide and residuals. Biotransformation is the partial degradation of a parent compound to one or more daughter compounds, which may or may not be less toxic than the original material.

Biological treatment can be a viable and economical technology in treating petroleum wastes. The possible benefits and advantages of bioremediation are extensive. These include *potential* savings of time and money due to a number of factors. Bioremediation provides the ability to treat on site, reducing transportation costs and liability. It provides a permanent elimination of the waste, reducing the long term liability risks. Biodegradation also enjoys a positive public acceptance and can be coupled with other treatment techniques to treat a host of environmental problems.

Bioremediation has been known since 1895, but the technology received little attention until recently. Acceptance of biotechnology has grown with the potential market. The EPA has now approved bioremediation at hazardous waste sites at several locations throughout the country [*1*]. Several investigators have reported successful laboratory and field bioremediation studies on petroleum refinery wastes [*3, 17, 19*]. Christiansen *et al.* [*8*] demonstrated oil and grease reduction of 87% in the treatment of refinery wastes and reduced sludge volume by over 50%. Kuffner *et al.* [*15*] achieved greater than 99% removal of BTEX (benzene, toluene, ethylbenzene and xylene) reducing final levels to 20 ppb in contaminated ground water at an oil refinery site. These studies provide incentives to examine the feasibility of bioremediation at the site currently under investigation.

Effective biological treatment processes depend on a number of environmental conditions. Appropriate microorganisms capable of degrading the desired compounds must be present or supplied. While naturally occurring organisms have predominantly been used in recent investigations, the use of genetically engineered organisms have also been reported [*6, 7*]. Naturally occurring organisms, however, are preferred for bioremediation due to the regulatory difficulties of releasing genetically engineered organisms into the environment. None of the over one hundred EPA clean up sites currently using bioremediation utilize genetically engineered organisms.

The necessary conditions for microbial growth such as a utilizable energy source, proper nutrients, pH and temperature must be present. The nutritional requirement of the microorganisms is a major factor affecting biodegradation. Most of the constituents of petroleum sludges are biodegradable if the appropriate conditions are provided. Refining sludges, however, have proven to be resistant to biodegradation under natural field conditions. The low rate of degradation under field conditions is due primarily to low nutrient levels. Macronutrients nitrogen and phosphorous, micronutrient sulfur and trace nutrients K, Mg, Ca, Fe, Na, Co, Zn, Mo, Cu and Mn are typically required.

Organic substances in the waste generally supply the necessary carbon for microbial growth. In some cases, additional carbon sources are added as cometabolites [*3, 5*]. Cometabolism refers to the degradation of a compound only in the presence of other organic material which does not serve as the primary energy source. This raises certain implications for biological treatment and the applicability of biodegradation studies performed using a single carbon source and pure microbial cultures. Due to the potential for both cometabolism and the synergistic effect of mixed cultures, these types of studies may seriously under-evaluate the potential viability of bioremediation for the compounds being examined.

A range of other environmental factors are also important for biological degradation. Bioremediation may be inhibited if the waste is sufficiently toxic in nature. High concentrations of heavy metals, toxic organic compounds and/or inorganic salts can inhibit microbial growth [*6*]. The optimum treatment usually occurs at a neutral pH and a temperature between 20 and 25 degrees centigrade [*2*]. While most of the studies have been done in aerobic environment, anaerobic and anoxic biodegradation studies also have been reported [*13*].

MATERIALS AND METHODS

Sludge Characterization:

The consistency of the sludge from the site can be described as a viscous semi-solid material. The material found in the lagoon varies from solid at some locations to a liquid at others. The material also varies with depth in the lagoons and typically ranges from a solid material at the bottom to liquid containing sulfuric acid and rain water at the surface. To eliminate sludge characteristics as a variable, a single composite sample was used throughout the experiment. This sample was composited from the surface to a depth of two feet and from various locations in one of the lagoons.

The sludge was initially mixed well by hand and passed through a 2 mm (No. 10) U.S. standard sieve to eliminate larger particles. It was stored in a sealed container until used in the experiments. The sieved petroleum sludge was initially characterized according to its physical and chemical properties using standard laboratory methods for waste water and sludges [*9*]. Characterization tests by standard methods included oil and grease content, total solids content, phosphates, nitrates, sulfates, chlorides, metals, pH, total organic carbon (TOC) and semi volatile organics by gas chromatography/mass spectrophotometry (GC/MS). A standard plate count was also done to establish the presence of microorganisms in the sludge. Table 1 shows the baseline characterization of the sludge. A GC/MS chromatogram is shown in Figure 1, identifying some of the major semi-volatile organic constituents of the sludge. Many of the major peaks are seen to be branched hydrocarbons. These compounds are generally considered to be biodegradable, though the ease of biodegradation decreases for highly branched compounds [*6*]. The chromatogram in Figure 1 also shows an area of unresolved peaks. This "hump" is common to sludge extracts and may represent the greatest amount of organic material actually extracted from the sam-

Table 1 Initial Characterization of Sludge

Analysis	Results	
Oil and Grease	37	% of dry solids
TOC	429,000	ppm (dry weight)
Nitrate	0.08	ppm
phosphate	0.00	ppm
sulfate	20.6	ppm
chloride	2.11	ppm
Ca	4.00	ppm
Pb	0.07	ppm
Ni	0.00	ppm
Zn	0.13	ppm
Fe	6.30	ppm
pH	6.3	
Std. Plate Count	32,500,000	per g of wet sludge
Moisture content	60	percent
Dry Solids	40	percent

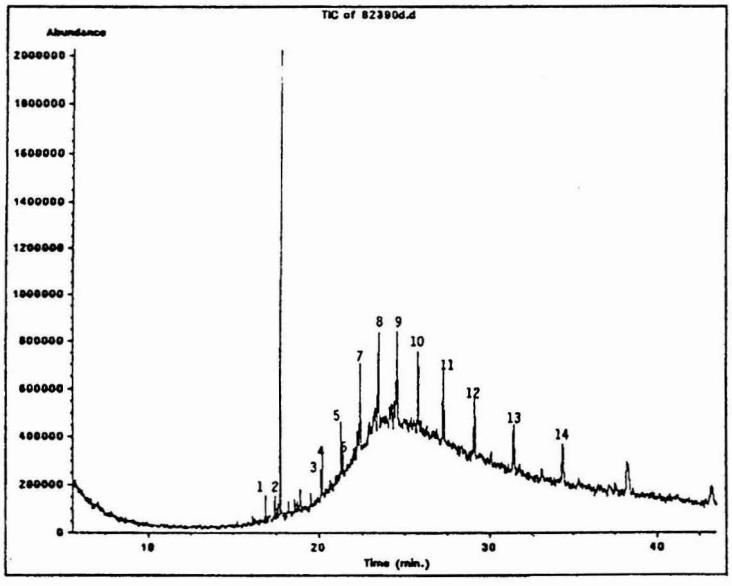

FIGURE 1. Gas chromatograph showing primary peaks obtained. 1: Dibenz(B,F)azepine; 2: 2-Pentanone, r-cyclohexyliden-3,3-diethyl; 3: Heptadecane; 4: Heptane, 2,6-dimethyl; 5: Octadecane; 6: Nonahexaconganoic acid; 7: Nonadecane; 8: Eicosane; 9: Heptadecane; 10: Docosane; 11: Octadecane; 12: Tetracosane; 13: Pentacosane; 14: Hexacosane.

ples. It is likely that the majority of unidentified compounds are alkanes and alkenes comprising anywhere from 15 to 40 carbons. Similar unresolved peaks in other samples from the site have also been found to be aromatics of fifteen carbons and greater [*10*].

Preliminary laboratory investigations were undertaken to determine the methods and solvents to be used in the analyses. Various solvents were tested for oil and grease, GC/MS and nutrient analyses. The oil and grease in the sludge was measured by Soxhlet extraction followed by gravimetric analysis. Chloroform and methylene chloride were both examined as solvents for the extraction. Chloroform was selected over methylene chloride as the preferred solvent for extractable oil and grease because of higher recovery of oil and grease (Table 2). This result was also found by Marks *et al.* [*18*]. A modified gravimetric method similar to 5520E in Standard Methods [*9*] was used.

Analyses for nitrates and phosphates were done using a IONPAC-AS4A column dionex chromatograph. Two sample preparation techniques were examined and compared using the ion exchange column. One sample was obtained from a modified toxicity characteristic leaching procedure (TCLP) of the sludge [*11*]. Another sample was obtained by simple dilution of the sludge sample with water followed by filtering through a 0.45 micrometer filter. The water sample obtained from the second method was found to have better recovery rates (Table 2).

Two sample preparations were also examined for the organic analysis on the GC/MS. One sample technique was the TCLP extraction. The second sample method was extraction with methylene chloride. The sample was obtained by mixing two grams of sludge with sodium sulfate and soaking it in 200 milliliters of methylene chloride overnight. Condensed samples were then injected through the GC/MS for analysis. The extraction with methylene chloride proved to be the more effective of the two techniques.

The total organic content (TOC) was analyzed using a Dorman DC-80 automated laboratory total organic analyzer. The samples to be analyzed were filtered through a 0.22 micrometer filter and diluted by a factor of 1:100 before analysis.

Biodegradation Studies

A series of shake flask experiments were conducted to determine the feasibility of bioremediation as a viable treatment for the petroleum sludge. This study was designed to determine the rate and extent of biodegradation of the oily sludge constituents by the microbial population under well aerated conditions at room temperature. Table 3 is a summary of the conditions of the various shake flask experiments. The microbial sources selected included both indigenous site microorganisms and cultures from a local sewage treatment facility.

Bushnell-Haas media was used to provide the necessary macro and micro nutrients for microbial growth in the shake flasks. The sludge concentration in Bushnell-Haas media in the initial studies was approximately 30 weight percent. Aeration of the sludge-media mix was achieved by rotating the flasks on a shake table. Controls were designed with each study

Table 2 Results from Preliminary Laboratory Investigation

Analysis	Description	Results
Oil and grease	Solvent-chloroform	8.4 mg/100 g sludge
Oil and grease	Solvent-methylene chloride	0.4 mg/100 g sludge
phosphate	TCLP extract	0
phosphate	sludge diluted in dist. water	0
nitrate	TCLP extract	.03 ppm
nitrate	sludge diluted in dist. water	.08 ppm

Table 3 Summary of the Shake Table Experiments

Series Number	Description of Treatment: Sludge (grams)	Media (ml)	Sewage Water (% v/v)	pH	Carbon Source	Duration of test (days)
1	60	200	—	NA	—	28
2	60	200 + N + P[1]	—	NA	—	28
3	60	200 + N + P[1]	10	NA	—	28
4	150	500	10	7.0[2]	acetate[4]	42
5	15	750	—	7.0[3]	—	42
6	15	750	10	7.0[3]	—	42
7	15	750	—	7.0[3]	acetate[4]	42

NA—not adjusted
1—additional nitrogen and phosphorous added in the amounts of 3 g/l each
2—pH adjusted to 7.0 at the beginning of the study
3—pH adjusted to 7.0 once in two weeks
4—acetate: N:P was added in the ratio 2:1:1

to determine volatilization or other abiotic losses of organics. The sterile control flasks contained one volume percent formaldehyde which was successful in inhibiting the growth of microorganisms.

While the above conditions were used in the initial studies, modifications were introduced in specific later series. Conditions were modified in each experiment in accordance with the results obtained in the previous series. The first three series of 500 ml shake flasks contained 60 grams of sludge in 200 ml media. In these studies, sample flasks and control flasks were run for a period of 28 days. The pH was not adjusted in these three studies. Additional nitrogen and phosphorous compounds were added to series 2 due to an apparent depletion of nutrients (phosphate) after two weeks in series 1. Wastewater (10 percent v/v) obtained from a sewage treatment plant was used as an additional microbial source in series 3. Series 4 examined the effect of acetate addition as a possible cometabolite. The time of the experiment was extended to 42 days. Acetate was added in the ratio of acetate:N:P equal to 2:1:1 [5] to the flasks in this series. The pH was adjusted to 7 at the beginning of the experiment with calcium hydroxide.

The effect of the sludge concentration was examined in series 5 through 7. This parameter has been found to have an effect on the rate and degree of bioremediation attainable. High concentrations of sludge containing either oil and grease or toxic organic/inorganic substances may inhibit biodegradation. The level of contamination that is inhibitory varies according to the material being treated. Watts *et al.* (1989) report that high total petroleum hydrocarbon levels were detrimental to the bioremediation of soil contaminated with jet fuel. It has elsewhere been suggested that an oil and grease level of 5–10% may be tolerated for bioremediation [*12*]. Conversely, Marks *et al.* [*18*] state than an oil and grease content of 65% was not found to be inhibitory during the bioremediation of production pit sludges.

Samples taken from the test flasks and the control flasks were frequently analyzed to measure the extent of biodegradation. The analyses included oil and grease content, total organic carbon and semi-volatile organics by GC/MS. Standard plate counts and nutrient levels were also measured in order to determine the microbial growth and nutrient uptake rates. A final measure of bioremediation was toxicity measurements utilizing a Microtox Toxicity System. All sample data reported for the various assays are the average of at least triplicate experiments.

RESULTS

Shake flask experiments inoculated with refinery sludge and/or microorganisms from a municipal sewage treatment plant demonstrated rapid cell growth under the conditions provided. The growth was seen to be affected by a number of factors, primarily the varying amounts of nutrients added. In series 1, cell numbers declined after the depletion of phosphate (Figure 2). This phenomenon was remedied in series 2 and 3 by adding increased levels of phosphate and nitrates to the media. The addition of acetate in series 4, however, led to a rapid utilization of nitrates and a subsequent sharp decline in cell number, after having achieved very high cell densities during the early period of the run (Figure 3). In all cases, the control flasks exhibited no growth, establishing the effectiveness of the 1% formaldehyde addition.

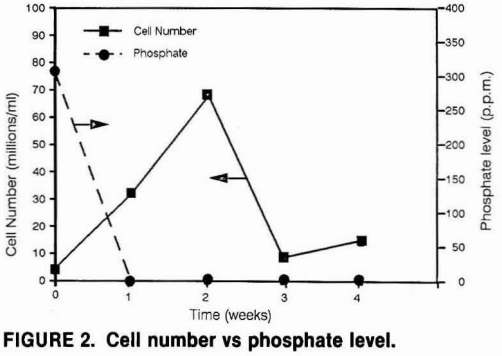

FIGURE 2. Cell number vs phosphate level.

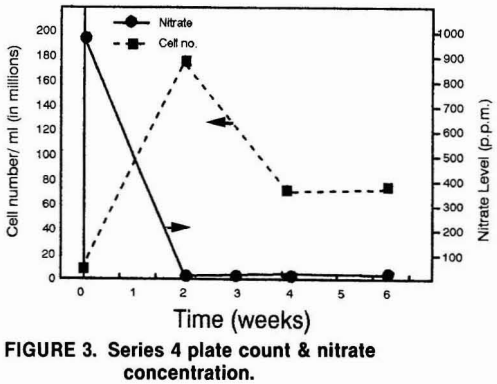

FIGURE 3. Series 4 plate count & nitrate concentration.

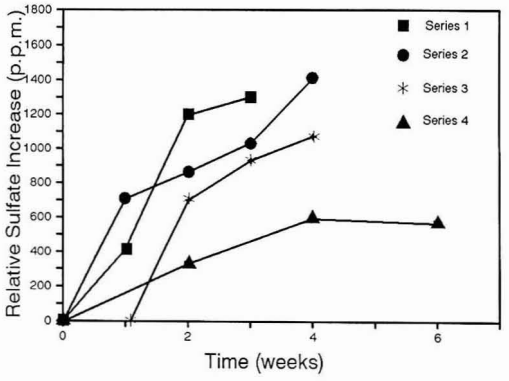

FIGURE 4. Relative sulfate production vs time.

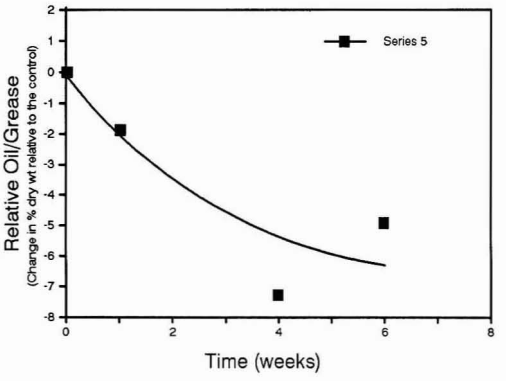

FIGURE 6. Relative oil and grease levels vs time (Series 5).

In the first three series of the studies where pH was not adjusted, pH dropped from 6.5 to approximately 5.4 at the end of seven days and remained at that value throughout the rest of the study. The pH was adjusted to 7.0 in the fourth series but dropped to 5.5 at the end of the 42 day period. The pH in series 5 through 7 was controlled at 7 by the addition of calcium hydroxide.

The concentration of sulfate showed a change in all of the shake flasks of the first four series utilizing the higher sludge concentration (Figure 4). The data presented is the difference between the sample and the control, normalized to remove the effect of any differences in initial concentration. The test flask levels show a gradual increase in sulfate concentration throughout the study relative to the controls. The extent of sulfate production appears to be somewhat depressed by the addition of acetate. This generation of sulfate was not found in series 5 through 7 where decreased levels of sludge were used and the pH was controlled at 7.

A significant change in chloride concentration was observed for series 5. No significant change was observed in the chloride concentration for any series except series 5. Figure 5 shows the increase of chloride concentration in the sample relative to the control, normalized for any difference in initial concentrations. The growth curve for series 5 is also shown. There appears to be a correlation between the cell growth and chloride production.

Both TOC and oil and grease levels were monitored for evidence of biodegradation of organics. No significant decrease is apparent in either the TOC or oil and grease analyses in any series other than series 5. There is some scatter evident in the oil and grease data, especially in the earlier series. The effect of microorganisms on the oil and grease content in series 5 is shown in Figure 6. The data are presented as the difference between the oil and grease levels in the control without microorganisms and the samples inoculated with sludge. While there was again some slight scatter in the data, samples show a decreased level of oil and grease relative to the control (a difference of approximately 7% dry weight or 18% of the initial oil and grease content).

Toxicity data for series 5 are shown in Figure 7. Data are reported in EC 50 units. This number indicates the concentration of material required to reduce the light emissions from the luminescent bacteria employed in the Microtox technique by 50% from their original level. A less toxic compound requires a greater concentration to decrease the light emission by a set amount. Therefore, a higher EC50 indicates a decrease in the toxicity level of the sludge. It is seen that the toxicity of the sample decreased by a factor of approximately 5 (when viewed as the amount of material required to reduce life emission by 50%) over the course of the experiment. No experimental conditions other than those for series 5 resulted in a measured decrease in toxicity.

It is possible to indirectly compare results of the bioremediation investigation with those obtained in the parallel stabilization study. Percent reductions in TOC due to stabilization are available (Evans, personal communication). A reduction on the order of approximately 80% in TOC levels was found for some stabilization conditions. This may be contrasted to the maximum of 18% reduction achieved in this study. Data on the effectiveness of stabilization refer to changes in the TCLP leachate, rather than reflecting any changes in the inherent contaminant levels of the sludge itself. This is an important consideration when comparing the two approaches.

Chromatograms of the TCLP leachate before and after stabilization, are also available [*16*]. The data show a significant

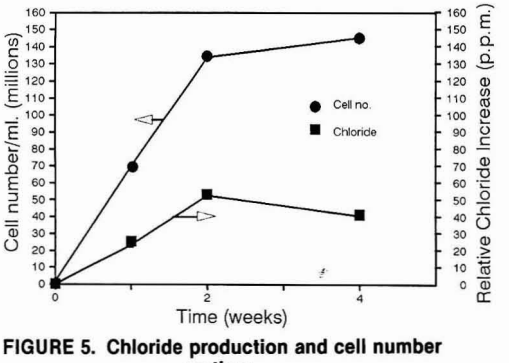

FIGURE 5. Chloride production and cell number vs time.

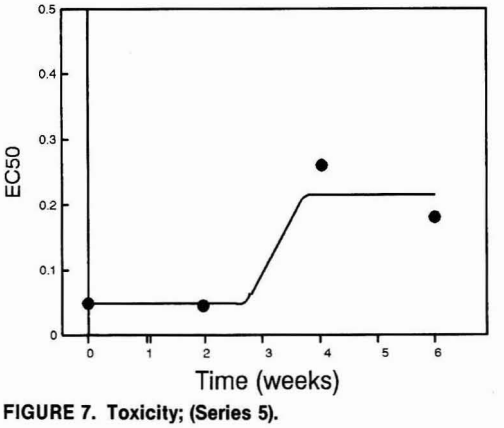

FIGURE 7. Toxicity; (Series 5).

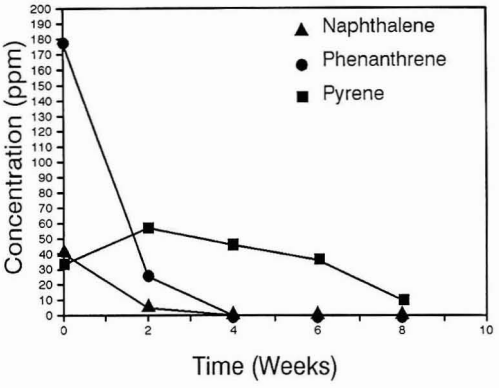

FIGURE 8. Biodegradation of polycyclic aromatic hydrocarbons.

reduction in the levels of several compounds due to treatment. Typical reductions are in the range of 90% for several compounds. Chromatograms of the sludge before and after treatment for series 5 are inconclusive. Due to the lower contaminant level in this series and the amount of scatter in the results, it is not possible to determine if there is a statistically significant reduction in contaminant levels. However, some chromatographic evidence of bioremediation potential is available. Cultures from the site under investigation were used to examine the biological degradation of polycyclic aromatic hydrocarbons (PAHs) as part of an independent study [*2*]. Naphthalene, phenanthrene and pyrene were found in significant quantities in the sludge from several locations at the site. Quantities of these chemicals were added to Basal media and inoculated with raw sludge. Results are shown in Figure 8. Control flasks were used with formaldehyde to inhibit biological activity. No degradation is apparent in the controls, indicating that abiotic losses did not contribute to the decrease in PAH concentration seen in Figure 8.

DISCUSSION

There was initial concern that the toxic nature of the sludge would limit the number of indigenous microorganisms and hence the potential for bioremediation. The levels found at the current site, however, are well within the typical level for contaminated soil, reported to be 10^3 to 10^7 units per gram soil [*12*]. The predominantly branched hydrocarbons evident in Figure 1, while not necessarily the only organics present, are considered to be biodegradable. The sludge itself, however, does not contain sufficient nutrients to support high levels of microbial growth. This is apparent from both the lack of phosphates shown in Table 1 and by the significant growth of microorganisms found in the presence of media. The data also suggest that for the increased levels of sludge used in series 1 through 4, nutrients should be supplemented throughout the course of the run. In these series, nitrates and phosphates are quickly depleted from the standard Bushnell-Haas media. This is especially pronounced with the addition of acetate which leads to very rapid growth and high cell densities. The depletion of nutrients at high sludge loading implies that significant amounts of nutrients would need to be supplied during treatment to maintain high levels of cell growth.

One possibility for the production of sulfates in series 1 through 4 is the presence of *Thiobacilli* as a predominant bacterial species. These are common bacteria known for their ability to oxidize either sulfur or thiosulfate to sulfate, with the coincident production of hydrogen ions [*22*]. The latter would be one explanation for the drop in pH evident in the experiments, though pH reduction is a common result of a wide range of metabolic activities. In addition, these bacteria are chemoautotrophs which utilize CO_2 as their carbon source. This might explain the apparent lack of significant oil and grease or TOC reduction despite the growth of bacteria over the course of the experiment. Acetate was added as an easily degraded carbon source to promote the growth of chemoheterotrophs. There is a reduced level of sulfate generated in series 4, indicating that this addition may have had some of it's desired effect. However, no decrease in TOC or oil and grease levels were found with the addition of acetate. This may be due to the rapid depletion of nitrates and the subsequent decline in cell number.

The source of the sulfur compounds which were precursors to the sulfate produced in series 1 through 4 is unknown. Two likely possibilities exist. One is that these sulfur compounds were present in the original lubricating oil. Sulfur is typically present in lubricating oils both from the base oil and from additives. The sulfur content of the base oil may be as high as 6% [*14*]. The second likely source of sulfur compounds is the sulfuric acid which was added during processing. The sulfate from the acid may have been transformed to reduced sulfur compounds through microbial action [*4*]. For example, sulfates may be reduced to sulfites, sulfides or organic sulfur compounds as part of the sulfur cycle. These compounds in turn may be re-converted to sulfates under certain conditions. For example, sulfates may be converted to sulfites which can be further transformed to thiosulfate. Thiosulfate in turn is one of the possible precursors of sulfate production by thiobacillus. At this point, any number of hypotheses are possible and no conclusive evidence has been found to support any one particular mechanism.

The use of lower concentrations of sludge in series 5 through 7 produced a number of interesting results. Sulfate production, consistently seen in series 1 through 4, is not detectable at higher dilutions. This may also have been the result of pH control, as this is an additional parameter changed from the earlier experiments. It is hypothesized that the absence of sulfate production is due to reduced levels of *Thiobacilli* growth under these conditions and the possible predominance of other microorganisms in the culture.

The increase in chloride concentration in series 5 may be indicative of dehalogenation reactions. This phenomenon is frequently found in the successful bioremediation of halogenated compounds. While there are no halogenated compounds evident among the major peaks of the GC/MS analysis, there are obviously a number of unidentified compounds. In addition, small quantities of methylene chloride, trichloromethane, dichloropropane and other chlorinated compounds were found in the ground water at the site. It is interesting to note that chloride production seen in Figure 5 mirrors cell growth, which further suggests that it is due to metabolic activity.

There is some indication of bioremediation at the lower concentrations of sludge used in series 5. Series 6 and 7, however, do not show this trend, suggesting that the addition of acetate or the use of domestic waste water microorganisms are not effective for remediation of this refinery sludge. Evidence of some degree of bioremediation in series 5 is summarized by Figures 5, 6 and 7. In addition to the production of chloride previously mentioned, which is indicative of dehalogenation reactions, there is an apparent decrease in both the normalized oil and grease levels and the toxicity for these conditions. No such observations are true for the other series. The data therefore suggest that the conditions of series 5 are the most favorable for bioremediation of those examined in this preliminary feasibility study.

The data do show that the microbial population present is capable of degrading polycyclic aromatic hydrocarbons. The percent reduction of naphthalene and phenanthrene are comparable to those found for the stabilization study, though different initial concentrations were used.

The results of this initial feasibility study on the use of biological treatment support a number of preliminary conclu-

sions. Gas chromatography shows the dominant organics present to be primarily branched hydrocarbons which are known to be biodegradable. Examination of the sludge shows the presence of high levels of indigenous microorganisms potentially capable of degrading the contaminants found. The microorganisms were shown to degrade certain PAHs. The site microorganisms were also shown to decrease levels of oil and grease levels in the sludge and performed better than other cultures examined.

Sufficient nutrients for high levels of microbial growth, however, are lacking and need to be supplemented, particularly if high sludge loading is anticipated during treatment. Dilution of oil and grease levels to approximately two weight percent and control of the pH at 7 provided the best results of the conditions examined. The degree of bioremediation achieved in these initial experiments is admittedly low. The data, however, do indicate some potential for successful treatment. Additional experiments are needed to examine further optimization of environmental conditions in order to achieve more significant reductions in contaminant levels.

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In Situ Treatment of Soil for the Extraction of Organic Contaminants

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The initial progress of an ongoing laboratory investigation is described in which phenol and aniline were mixed into a slightly organic, loamy soil and various aqueous solutions used to attempt to extract these organic contaminants. Extraction compounds consisted of deionized water, hydrogen peroxide at varying concentration and sodium hydroxide at varying pH. Two methods were used to affect desorption. The first method, which is simple and quick, has been termed the "successive reverse isotherm" (SRI) method, and the second method, which is very labor intensive and time-consuming, but which represents better the conditions that exist in an in situ *extraction operation, was the permeation method. The SRI method indicated that an aqueous solution of hydrogen peroxide in concentration of 200 to 500 mg/L extracted about 45% of the phenol, while an aqueous solution of sodium hydroxide at a pH of 10 extracted in excess of 70% of the phenol. On the other hand, none of the solutions extracted more than 25% of the aniline. Further tests conducted in permeameters indicated that approximately 80% of phenol was recovered by permeation with either hydrogen peroxide or sodium hydroxide and that both were measurably more effective than deionized water. Neither the phenol nor any of the decontaminants had any major effect on hydraulic conductivity or physical index properties of the soil. From the results of the tests to date, the SRI test appears to provide a viable method of predicting whether permeameter tests will yield productive results.*

INTRODUCTION

A porous medium such as soil is capable of capturing and trapping organic compounds from a fluid in its pore spaces while permitting the fluids to pass through. Depending on the specific physico-chemical properties of the organic compounds and the soil, compounds dissolved in the fluid may be deposited at the soil-fluid interface or incorporated into the soil matrix. The amount and types of organic compounds retained in the soil will influence the likelihood of success of subsequent washing techniques to transport the contaminants to sites where they can be treated, possibly biologically.

The objective of this paper is to describe the effects of laboratory washing of loamy soil having two different organic contaminants with various potential desorbing liquids, including water, and to describe the effects of two physical techniques to accomplish the extraction process. These techniques include (1) simple contact shaking of the contaminated soil with an aqueous solution of the extracting agent, primarily to assess the effectiveness of the extraction solution (termed here the successive reverse isotherm, or "SRI," procedure), and (2) permeation of extraction liquids through reconstituted, contaminated specimens of soil under controlled hydraulic gradients to simulate *in situ* soil, stress state and hydraulic

conditions. The SRI test is viewed as a screening test for the more definitive permeation test. The investigation was limited to nearly-saturated soils. The information reported consists of initial data from an ongoing study that will include the effects of other contaminants and desorption solutions.

BACKGROUND

Sorption of Organic Compounds in the Soil Environment

Organic compounds become sorbed to the various constituents of soil, which include primarily clay minerals, indigenous organic matter, and occasionally amorphous oxides-hydroxides of metals. Clay minerals are two- and three-sheet layered silicates composed mainly of silica tetrahedral and octahedral structures. Basal planes contain primarily hydroxyl and oxygen ions, while central planes normally consist of silicon and aluminum ions, with the net result that faces of the layers possess local negative charge. Two-sheet silicates such as kaolinite typically bond into large domains and tend to sorb relatively little contaminant per unit weight, while three-sheet silicates such as smectite either do no bond into domains or do so very weakly. Further, their negative faces are normally exposed to the pore spaces, which permits sorbing of positive ionic compounds directly onto the faces of the mineral and capturing others in the diffuse double layer [*1*]. If the contaminating material is polar, it can penetrate between layers of weakly bonded clay minerals and become sorbed internally within the domain.

Sorption of organics onto clay minerals influences the thickness of the diffuse double layer of the clay domain [*2*], which can affect the physical properties of the clay, including its hydraulic properties [*3*, *4*, *5*], which could in turn affect the sorption (and desorption) rates.

Sorption onto amorphous compounds within the soil and indigenous organic matter appears to be largely pH dependent [*6*]. Hydrophobic organic compounds such as chlorinated hydrocarbons can sorb onto these materials [*7*].

Sorption is an important mechanism of mass transfer. Sorption and aqueous-vapor equilibrium of the organic compound in the soil environment determine the amount of the compound that is in each phase (solid, aqueous, and vapor). Manos *et al.* [*8*] showed that the sorption of organic compounds onto natural soils significantly affected the mass transfer of the compounds, as compared to that predicted by mechanical diffusion alone. According to Roberts *et al.* [*9*], sorption slows the rate of transport of the organic contaminants by processes such as aqueous-phase advection and dispersion. Mayer *et al.* [*10*], in their study of the rate of biodegradation of herbicides incubated with soil, reported that soils with high clay content, especially soils containing smectite, had an inhibitory effect on biodegradation of the herbicides. This was attributed to sorption by clay particles that rendered the herbicides less vulnerable to microbial attack. Weber and Miller [*11*] showed that the portion of a compound that is sorbed is not available for biodegradation, and chemical transformations proceed at different rates depending on which phase the solute occupies.

The term "sorption" is used here to include both adsorption (organic compounds concentrating at the boundaries between the various phases—solid, liquid and gas) and absorption (transference of organic compounds in the bulk state from one phase to another) [*12*]. Sorption can involve combinations of interactions between polar, nonpolar, or charged compounds with polar, nonpolar, or charged sorbing sites. Sorption processes can be driven by a variety of forces and mechanisms [*6*, *12*, *13*]. These include physical adsorption (primarily through London-van der Waal's forces), hydrogen bonding, ion exchange, coordination bonding (generally nonionic polar compounds that attach to a metallic ion in a clay domain—which is generally stronger than bonding in the ion exchange process), chemical bonding of contaminants to soil solids, and hydrophobic sorption. Hydrophobic sorption results from a partitioning of nonionic compounds of low water solubility into the indigenous organic matter within the soil, where that organic matter functions as a bulk solvent phase [*14*, *15*, *16*, *17*]. It is an important sorption mechanism for nonionic compounds and appears to correlate with indigenous organic content of the soil, the solubility of the compound and the octanol/water partitioning coefficient of the organic contaminant [*7*, *14*, *16*, *18*, *19*, *20*]. Sorption onto clay minerals can occur through any of the above mechanisms except for hydrophobic sorption, while the hydrophobic sorption process appears to be associated with the indigenous organics and amorphous compounds.

While the nature of the material onto which the organic contaminant sorbs is important, the properties of the organic contaminant compound and the solvent medium also influence the sorption process. The most important broad characteristic of the organic contaminant is its ionic nature (ionic—cationic, acidic or basic, or nonionic—such as chlorinated hydrocarbons, organophosphates, benzonitriles, phenylamides and esters) [*6*, *21*]. The solvent medium is water, such that organic molecules that move by diffusion to adsorption sites must compete with the polar water molecules. In this process the pH of the solvent plays an important role. Acid organic compounds are not sorbed by clay minerals at high pH because the faces of the clay domains are negatively charged. Some adsorption can occur at low pH because the edges of the domains will become positively charged [*21*]. Basic organic compounds adsorb best onto clay minerals near the pK_a of the compound. The number of protonated molecules decreases as pH increases, thereby decreasing sorption [*6*, *21*]. When metal cations exist in the water solution, H^+ can be produced by hydrolysis, and hydrogen bonding can develop between the organic compounds and the surfaces of the clay domains.

While separating all of the effects described above may not be possible, it is generally observed that the weight of substance sorbed per unit weight of soil is a power function of the concentration of the contaminating solution at equilibrium [*22*].

Desorption of Organic Compounds from Soil

The process of extraction is presumed to be due to desorption, although other processes such as complexation and oxidation may be involved. Desorption of sorbed organic compounds from soil solids has been described in the literature [*6*, *23*]. Adsorption is sometimes not fully reversible; however, desorption generally follows the Freundlich isotherm equation, but with different coefficient values than with adsorption. Water as a washing agent can often remove much of the organic compound sorbed onto the surface of the clay domains, but washing with water is not completely effective in removing tightly bound sheets of ionic organics between the clay layers.

Nonionic organic molecules become physically adsorbed to surfaces of dry clay minerals and also link to the metal cations in the clay because of electrostatic interactions. When water is introduced into the system, the electrostatic interactions become weaker, as the water molecules form a hydrogen shell around the mineral metal cation and the organic molecule becomes linked to the clay mineral through a "bridging" water molecule [*23*, *24*]. This bonding mechanism is likely to break in the presence of a significant hydraulic gradient.

Isaacson and Frink [*25*] reported that desorption was up to three times slower than sorption and that even when equilibrium was established, 13% to 90% of the sorbate was irreversibly held on the soil, depending on the organic matter content of the soil, and on the particle size (% of fine fraction) of the soil. Generally, the proportion of irreversible to reversible sorbate increased with the total sorption capacity and was higher in the finer fraction than in the coarse fraction. Hydrogen

peroxide treatment of the soil prior to adsorption, to decrease the organic matter content of the soil, decreased the amount of irreversible sorbate.

Removal of organic contaminants from soil can be achieved through, among other means, soil flushing or "washing." One process involves the elutriation of contaminants from the soil matter for recovery and treatment. The soil is flooded with an appropriate flushing solution. The elutriate is collected, treated, and recycled back into the soil. This technique combined with controlled biodegradation of the organic constituents removed from the elutriate can be an effective *in situ* treatment [*26*] or the treatment can be accomplished in a plant with agitation of the flushing solution and excavated soil. *In situ* treatment may be preferable economically when contaminants exist in small volumes of soil at large depths.

Flushing solutions may include water, as well as aqueous solutions that are acidic or basic or contain oxidizing compounds or surfactants. The principle of the removal technique through soil flushing with aqueous solutions relies on altering, *in situ*, either the surface chemistry of the soil particle or the nature of the sorbed organic compounds so that compounds will be desorbed, transported through the liquid phase, and available for treatment. More strongly adsorbed organics like surfactants may be used to displace more weakly sorbed material by competitive adsorption. The effectiveness of soil flushing depends on the strength of the physico-chemical bonds between the soil and contaminant and the ability of the flushing solutions to break the bonds [*27*].

Aqueous Acidic or Basic Solutions

In principle, acidic solutions may be used for the recovery of basic organic compounds, i.e.: amines, ethers, and amilines, whereas basic solutions may be used for the recovery of acidic organic compounds, i.e.: phenols, carboxylic acids, complexing and chelating agents [*6*]. Basic solutions of calcium hydroxide or sodium hydroxide can alter the macroscopic properties of clay-based soils. Depending on the valency of the sorbed cations, cation exchange reactions of the calcium or sodium ion with the clay particle can reduce the thickness of the diffuse double layer surrounding each clay particle, thereby decreasing the amount of pore fluid bonded to the clay mineral [*28*]. High pH solutions cause the dispersion, or breakup, of clay sheets [*28, 29*], which may be effective in exposing tightly bound organics between the clay layers to exchangeable ions that may displace them into the liquid phase.

The effects of the desorption process on soil permeability, or hydraulic conductivity, are important from the perspective of *in situ* treatment involving permeation of a desorbing solution. Both acidic and basic solutions may affect the soil hydraulic conductivity and thereby influence the physical effects of forced movement of the desorbing fluid under a controlled hydraulic gradient. Calcium carbonates on the clay may react with acidic solutions, generating carbon dioxide gas that escapes, resulting in a loss of mass that increases the hydraulic conductivity [*2*]. Basic solutions (NaOH) will affect the soil sodium adsorption ratio and change the thickness of the diffuse double layer of the clay that will, in turn, affect permeability [*6*].

Aqueous Oxidant Solutions

Oxidation of an organic compound to intremediates renders them more polar. In the drinking water treatment process of adsorption onto granular activated carbon (GAC), oxidizing organic compounds makes them less adsorbable on GAC because they become more polar [*30, 31*]. The same principles are expected to hold for sorption onto indigenous organic components of soils, although the opposite effect might be expected for sorption onto the clay minerals. Because oxidation is nonselective, it can result in a decrease of natural organic material within the soil that will in turn result in decreased sorption capacity of the soil for the organic compounds. Oxidation of organic compounds also promotes their biodegradability [*26*]. Certain compounds (e.g., phenols, aldehydes, and aromatic amines) are more oxidizable in soils than others (e.g., halogenated hydrocarbons, benzene, and saturated aliphatic compounds). Generally, compounds that have aromatic or fused ring structure, extensive conjugation, and ring substituent fragments are more likely to undergo oxidation [*26*]. Oxidizing agents such as hydrogen peroxide thus can become effective desorbants under appropriate circumstances and can extract organics through other processes as well.

Aqueous Surfactants

Surfactants are compounds that have one polar (water soluble) end, while the other end is nonpolar (organic soluble). Thus, they promote aqueous dissolution of hydrophobic organic compounds. They also dislocate weakly sorbed materials through competition of adsorption sites and are therefore potentially attractive as flushing agents. Surfactants are categorized as anionic, nonionic, and cationic. Rickabaugh *et al.* [*32*] indicate that a blend of two surfactants is more effective than a single surfactant in enhanced oil recovery. Any aqueous solution of surfactants used in the soil-sorbate system would have to be biodegradable from a regulation perspective.

Past Experimental Studies of Desorption with Aqueous Solutions

Huibregste *et al.* [*33*] developed a mobile soil scrubber to extract contaminants from excavated soil. In pilot-scale experiments two types of soils, organic and inorganic, were spiked with phenol or polychlorobiphenyls (PCB's). Contaminated soils were mixed in the apparatus while being rinsed vigorously with water at low pH, or at high pH, or with water containing surfactants. Starting with very high initial contamination concentrations of phenol, removal for all treatment chemical solutions ranged between 70% and 90%. The soil residual contaminant concentration after treatment was also high, however, ranging between 1–150 mg phenol/g of dry soil. For PCB, a more tightly adsorbed compound, initial contamination concentrations ranged between 3–25 mg PCB/g of dry soil, and removal after treatment with surfactants ranged between 20% and 48%. Generally, contaminants were easier to remove from inorganic soils than from organic soils. This was attributed to the affinity of the organic contaminants to the soil organic matter, and, especially in the case of PCB, to the hydrophobic nature of the compound. Soil scrubbing and rinsing with water solutions has the highest potential for being an effective treatment with organic compounds that have a high water solubility and greater affinity for water than for soil.

Ellis *et al.*, [*34*] performed experiments to remove organic contaminants from soil of a low cation exchange capacity (CEC = 8.6 meq/100 g), and a very low organic matter content (0.12%). The experiments were performed *in situ* by compacting the contaminated soil in glass columns and leaching it with aqueous surfactants. The organic compounds used separately to contaminate the soil were chlorinated phenols and PCB. Initially, the contaminated soil columns were permeated with ten pore volumes of water followed by ten pore volumes of an aqueous surfactant solution. Their results indicated that chlorinated phenols were effectively removed (70% removal) with water washing alone, whereas, only 10% of the PCB was removed with water washing. An additional 50% of the PCB was removed by washing with three pore volumes of aqueous surfactant solution. High removals were attributed to the low adsorption capacity of the soil (very sandy).

Permeation of Soils under Controlled Hydraulic Gradient

In situ flushing with an imposed hydraulic gradient may accelerate the desorption process; however, hydraulic properties of the soil can be changed in the process, primarily through change in the thickness of the diffuse double layers, which according to Guoy-Chapman theory [*28*] is proportional to the square root of the dielectric constant of the flushing fluid, inversely proportional to the square root of the concentration of cations in the solution, and inversely proportional to the cation valence. Contaminating fluids with low dielectric constants (neutral organics such as acetone, methanol, heptane, trichlorethylene) can cause cracking as the double layers compress, producing increases in hydraulic conductivity. However, if they are later permeated with dilute aqueous solutions, which have dielectric constants close to that of water, double layers can expand, producing decreases in hydraulic conductivity during the extraction process. This effect would have to be overcome in practice by increasing the hydraulic gradient.

Several studies have been reported on the effects of forced permeation of organics and nonorganics in aqueous solutions through soils on hydraulic conductivity in laboratory permeameters [*35*, *26*, *37*, *38*]. One of the principal findings of such studies [*39*, *40*, *41*] is that hydraulic conductivity is strongly influenced by degree of saturation because the liquid-filled pores can transmit flow most effectively. Reducing the degree of saturation below 100% has a major effect on conductivity. Daniel [*40*] reported a four-order-of-magnitude drop in hydraulic conductivity as the degree of saturation of the soil dropped from 100% to 20%.

Summary

The literature cited above suggests that the addition of acids, bases, oxidants, or surfactants may promote the desorption of organic contaminants from soil. Flushing the soil with such solutions may mobilize the contaminants so they can be transported and treated. On the other hand, flushing the soil may change its properties and possibly affect adversely its hydraulic conductivity, reducing the rate of removal in an *in situ* treatment process. In order to evaluate the treatment potential of these techniques, a laboratory study is being performed that involves first the contamination, or "spiking," of a loamy soil having a low organic content with phenol and aniline. Attempts at removal of those compounds were made, first by elutriation in the SRI process to evaluate the potential of each of several aqueous extraction compounds, and second by selective permeation under a controlled hydraulic gradient for those combinations of spiked soil and desorbing compounds that appeared promising. The remainder of this paper addresses the preliminary phases of the laboratory study.

LABORATORY STUDY

Several soils and several spiking compounds were studied [*42*]; however, this paper concentrates on one soil and two spiking compounds.

Test Soil

The test soil consisted of a weathered natural silty clay (Lake Charles soil series) of low plasticity recovered from the B horizon (about 0.5 m deep) from a site on the University of Houston campus. The parent soil is a member of the Beaumont clay formation whose primary mineral components are illite, calcium smectite and finely ground quartz. Routine tests conducted on this soil indicated that its organic content was 5.1%, cation exchange capacity (CEC) was 35 meq/100g, liquid limit was 32%, and plastic limit was 16%. The liquid and plastic limits are ratios of liquid weight to solid weight (as a %) at the lower and upper bounds of plastic soil consistency and are termed "Atterberg limits." These serve as practical indices of the ranges of physical properties (strength, compressibility, and swell potential) of the soil. Investigation of the effects of extraction on these indices serves to indicate whether the chemical extraction treatment will have any effect on the mechanical properties of the soil.

Prior to all testing in a permeameter, this soil was mixed in equal proportions by weight with a uniform, fine siliceous sand recovered from the Gulf of Mexico, producing a CEC of 21 meq/100g and organic content of 2.7% in the combined test specimen. The combined soil can be classified as a loam. The natural silty clay was mixed with the fine sand in order to increase the hydraulic conductivity of the test soil so that permeation tests could be conducted within a reasonable period of time (one to two weeks). Samples of the B-horizon soil were first oven dried at 105°C, pulverized mechanically, and passed through a No. 50 (300 μ particle diameter) sieve. Samples for the permeameter test were then blended with the fine siliceous sand. Samples for the SRI tests were conducted on the B-horizon soil, without blending with sand.

Compaction tests [*43*] indicated that the optimum moisture content of the blended clay-sand soil compacted at standard compactive effort with deionized water was approximately 14%. Permeated samples were further prepared by compacting (at standard compactive effort) the fraction of oven-dry clay passing the No. 50 sieve blended with sand with an aqueous solution of the contaminant at a moisture content of 17% (3% above optimum), which produced a sample having a degree of saturation of approximately 90%. Compaction was performed in a Harvard miniature compaction mold, having a diameter of 35 mm and a length of 71 mm, which produced specimens for permeation of the same size.

Contaminants

Several classes of compounds have been suggested for subsurface contaminant research [*44*]. These include amines, phenols, basic and neutral aromatic N-Heterocycles and others. Based on the observations made in the previous section of this paper, two of these classes of compounds were chosen for initial study: Aniline (amine) and phenol. Both compounds are polar. Aniline is weakly basic, while phenol is weakly acidic. Their structure is very similar, with the exception that the OH^- radical in the phenol ring becomes NH_2 in aniline. The test soil was contaminated phenol and aniline, whose properties are outlined further in Table 1.

Table 1 Chemical and Physical Characteristics of Contaminants

	phenol	aniline
Molecular formula	C_6H_5OH	$C_6H_5NH_2$
Molecular weight	94.11	93.12
Boiling point (°C)	181.7	184.4
Melting point	43	−6.2
Specific gravity	1.058	1.022
Water solubility (mg/L @ 15°C)	82,000	34,000
Log K_{ow} (octanol-water partition coeff.)	1.49	1.18
Concentration tested (approx.) (mg/L[a])	50	50
pK_a	9.89	4.58

Data from Refs. 45 and 46
[a]—weight of soil per liter of contaminant

Extraction Compounds

Tests, described subsequently, were conducted with several extraction compounds: (1) deionized water, (2) hydrogen peroxide (oxidant) at concentrations of 120–200 and 500 mg/L, and (3) sodium hydroxide (weak and strong base) at pH's of 8 and 10.

Adsorption Rate Studies and Adsorption Equilibrium Study

Adsorption rate studies were conducted for phenol as follows. Fourteen replicate 40-g samples of the B-horizon soil (uncut with sand) were placed in 65 mL bottles and each mixed head-space-free with 40 mL of phenol in aqueous solution at a concentration of 19.3 mg/L. The mixture was de-aired by kneading the soil with a glass rod. Two blanks (bottles containing no soil) were also prepared to ensure that phenol was not being lost by any mechanism other than adsorption onto the soil. Samples were centrifuged periodically, and 4.2 μL samples of the supernatant liquid were extracted with syringes and analyzed for phenol concentration on a gas chromatograph [*42*]. The concentration of phenol reached equilibrium at about 16.0 mg/L 24 hours after mixing, and no further adsorption occurred. Further studies were conducted at a phenol concentration of 54.0 mg/L, with a similar time to equilibrium and an equilibrium concentration of 42.7 mg/L. A similar study with the second component of the test soil, Gulf sand, indicated no adsorption of phenol.

Adsorption rate studies were also conducted with aniline at an initial concentration of 50.0 mg/L and uncut B-horizon soil. These studies indicated an equilibrium time of slightly less than 24 hours and an equilbrium concentration of aniline in the supernatant of 39.0 mg/L. Loading was 11 mg (contaminant)/g (dry soil) at solution concentrations at equilibrium (C_e) = 42.7 mg/L for phenol and 9.2 mg/g at C_e = 39.0 mg/L for aniline, indicating that similar amounts of the two contaminants had been sorbed per unit mass of the soil.

The adsorption rate studies for phenol were conducted at room temperature, but those for aniline were conducted at 7°C, because preliminary studies indicated that some biodegradation was occurring during aniline adsorption at room temperature.

Once the equilibrium time of 24 hours was established, adsorption equilibrium tests ("isotherm" tests) were conducted in which duplicate bottles containing 30 g of B-horizon soil and 40 mL of aqueous phenol solutions varying in concentrations of from 4.6 to 27 mg/L were agitated by tumbling for 24 hours and centrifuged. Samples were then taken of the supernatant liquid and analyzed in the gas chromatograph for equilibrium phenol concentration (C_e). Knowing the weights of soil and volumes and concentrations of phenol, the factor X/M (mass adsorbed per unit mass of the dry soil) was calculated and plotted against C_e on a log-log scale to determine whether phenol adsorption on the B-horizon soil could be described by the Freundlich equation. It could, with an R^2 value of 0.962, and the constants K and n^{-1} in the Freundlich equation were found to be 0.438 μg/g(L/mg)$^{n^{-1}}$ and 0.621, respectively. Isotherm tests have not yet been conducted with the aniline solutions.

DESORPTION STUDIES BY SRI METHOD

1. Based on the adsorption rate studies, each contaminant was mixed thoroughly with the initially dry, powdered soil for 24 hours on a shaking table at 7°C. Approximate sample sizes were 6 g of soil and 5 mL of contaminant solution at a concentration of 54 mg/L. This mixing process may result in placing contaminant both on the surfaces of the soil domains and in the interstices between the layers within the domains.

2. Sample vials were centrifuged at 2000 rpm, and approximately 2.5 mL of the clear supernatant solution decanted. The concentration of the contaminant in the supernatant solution was then determined by gas chromatography. A Perkin-Elmer Model Sigma 300 gas chromatograph with a Sigma 15 chromatography data station was used for in this process. The gas chromatograph was equipped with a glass acid packed column with an inside diameter of 2 mm. The detector used was a flame ionization detector. Different temperature programs were used to ensure separation of the various test compounds.

3. An aqueous solution of the decontaminant compound equal to the amount of liquid decanted was then added to the sample, and the resulting soil/liquid mixture agitated gently by hand in the vial at room temperature for a period of time necessary to reach equilibrium. Tests performed previously* were conducted to establish that five minutes was sufficient agitation time to reach equilibrium during this desorption step.

4. The sample vials were again centrifuged, and approximately 2.5 mL of the clear supernatant solution was again decanted. Since this supernatant solution contained contributions from both the initial contaminant and contaminant removed from the soil during Step 3, keeping track of the weight of contaminant adsorbed on the soil solids at the end of Step 1 and Step 3 and comparing, as indicated below, was necessary to compute the degree of desorption or "remediation."

5. The process was then repeated several times, decanting the supernatant after agitation and adding back equal volumes of decontaminant solution, until no further removal of contaminant could be observed.

SRI tests were always conducted on replicate samples. Calculations of desorption are as follows:

$$\alpha = \frac{(x-y)z}{1000\text{mL/L}}, \tag{1}$$

in which

α = amount of contaminant contained in the soil in Step 1 in mg,
x = initial concentration of the contaminant in aqueous solution in mg/L,
y = concentration of contaminant remaining in solution after equilibrium, as measured by gas chromatography in the decanted supernatant solution, in mg/L, and
z = volume of contaminant solution, in mL.

Furthermore,

$$\beta_0 = \frac{y(z-\delta)}{1000\text{ mL/L}}, \tag{2}$$

in which

β_0 = amount of contaminant, in mg, still in solution after decanting δ mL of supernatant liquid.

*In order to determine the necessary length of time of agitation with the decontaminating solution, preliminary desorption rate tests were conducted with both contaminants and all desorption solutions. Five replicate soil samples were prepared for each combination of contaminant and extraction solution. Soil samples were contaminated per Step 1. The contaminated samples were mixed with 5 mL of the desorption compound solution and agitated at 7°C by a mechanical mixing device that reproduced hand agitation. Samples were removed from the mixer after prescribed periods of shaking (up to 24 hours), centrifuged, decanted, and the supernatant liquid was subjected to gas chromatograph analysis. The concentration of contaminant in the supernatant solution became constant after less than five minutes of agitation in every case, so that a standard time of agitation of 5 minutes was established for Step 3.

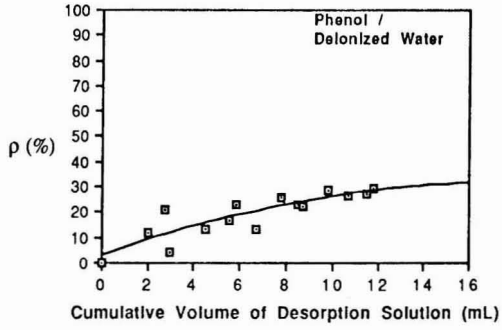

FIGURE 1. Successive reverse isotherm test for phenol deionized water.

Then,

$$\beta_f = \frac{y'(z-\delta)}{1000\ \text{mL/L}}, \tag{3}$$

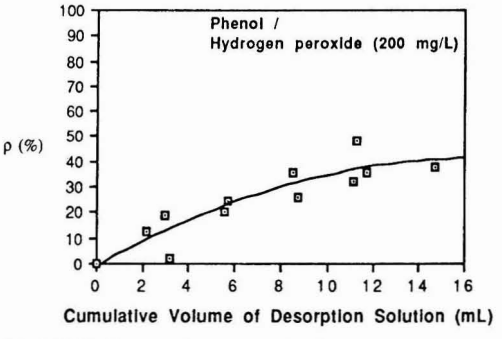

FIGURE 2. Successive reverse isotherm test for phenol with H_2O_2 at 200 mg/L.

in which

β_f = amount of contaminant, in mg, in solution after adding back δ mL of the decontaminating solution, shaking until a new equilibrium condition is reached, and decanting δ mL again, and

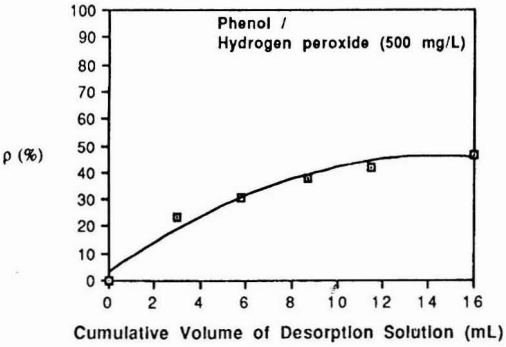

FIGURE 3. Successive reverse isotherm test for phenol with H_2O_2 at 500 mg/L.

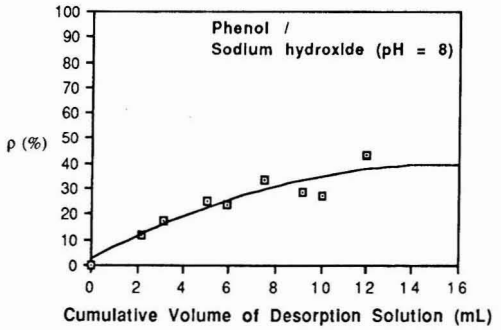

FIGURE 4. Successive reverse isotherm test for phenol with NaOH at pH = 8.

y' = new concentration of contaminant remaining in solution after equilibrium, as measured in the decanted supernatant solution, in mg/L.

Finally, the quantity of contaminant removed in each step, in mg, is $\beta_0 - \beta_f$. Since the process is progressive, the amount

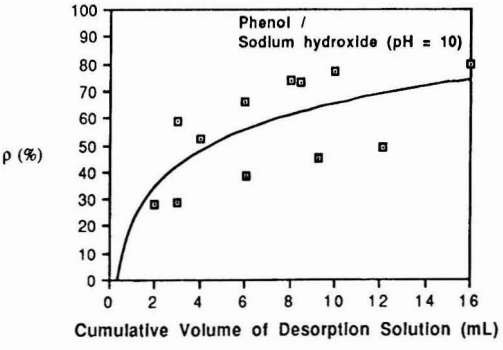

FIGURE 5. Successive reverse isotherm test for phenol with NaOH at pH = 10.

of contaminant removed, ρ, as a percentage by weight of the initial contaminant applied after I washings with the decontaminant solution is given by Eq. 4, where i is the washing cycle number.

$$\rho(\%) = \frac{\sum_{i=1}^{I} (\beta_0 - \beta_f)_i}{\alpha} \times 100. \tag{4}$$

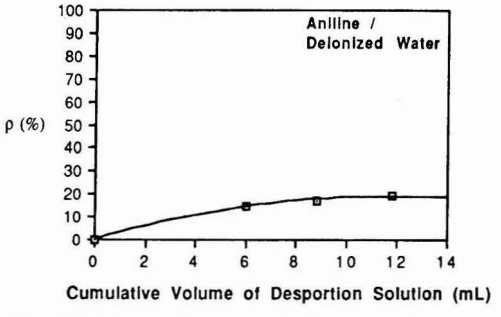

FIGURE 6. Successive reverse isotherm test for aniline with deionized water.

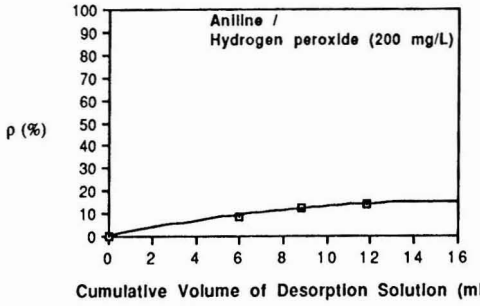

FIGURE 7. Successive reverse isotherm test for aniline with H_2O_2 at 200 mg/L.

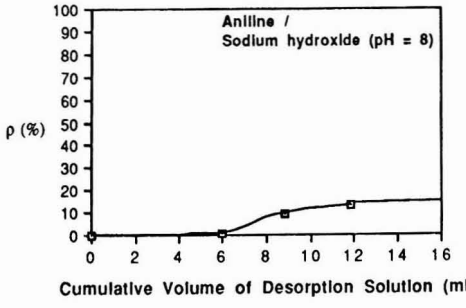

FIGURE 9. Successive reverse isotherm test for aniline with NaOH at pH = 8.

Results

Results of the successive reverse isotherm tests on samples of B-horizon soil contaminated with phenol and aniline are shown in Figs. 1–10 and Tables 2 and 3. Each datum point shown in the figures represents the average value for duplicate gas chromatograph analyses. The results for phenol are shown first, followed by those for aniline. The fitted curves are second or third order least squares polynomials. The concentration of the contaminants in the contaminating solution (Step 1) was 54 mg/L.

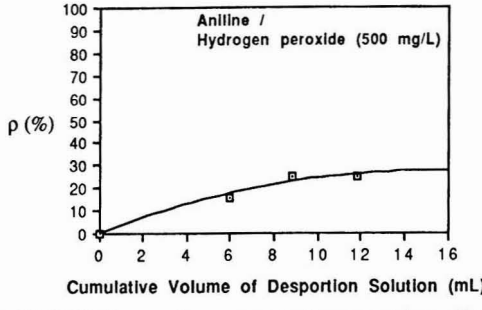

FIGURE 8. Successive reverse isotherm test for aniline with H_2O_2 at 500 mg/L.

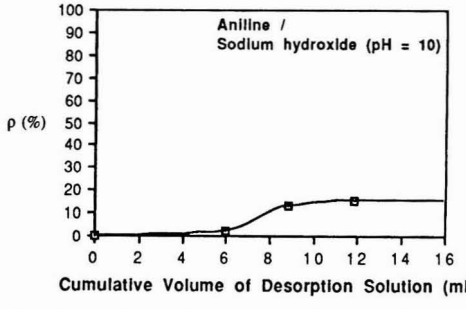

FIGURE 10. Successive reverse isotherm test for aniline with NaOH at pH = 10.

Desorption Studies by Permeation Method

Testing Arrangement

While the SRI tests provide general information on the potential for a compound to remove specific contaminants from soil, they do not replicate the physical behavior of forced permeation of the decontaminant through low-porosity soil. Because forcing decontaminating solutions through soils under a controlled hydraulic gradient is a likely application of the study reported here, extraction tests were also conducted in a permeameter to simulate *in situ* conditions.

Although both fixed- and flexible-wall permeameters were constructed and tested, the flexible-wall permeameter described schematically in Figure 11 was the most successful, and results from tests using that apparatus will be presented. Six such permeameters were built for the project and used in parallel. The flexible wall permeameter allows for the application of mean effective stresses within the soil mass that replicate those that would exist at a known depth *in situ*, provides for the control of the hydraulic gradient within the sample, and is efficient in preventing leakage of fluid around the sample. Control of effective stress in the soil is important because the sorption-desorption reactions can cause swelling, shrinkage and particle reorientation within the soil. Without the proper intergranular confining stresses, volume changes and channeling could occur that would be dissimilar to those

Table 2 ρ (percentage of contaminant extracted, by weight) for Phenol and Aniline at 15 mL of Cumulative Volume of Desorption Solution—SRI Tests

Desorption Solution	Phenol ρ (%)	η (Phenol) = Desorption by Solution/ Desorption by DI Water (Phenol)	Aniline ρ (%)	η (Aniline)
Deionized Water	30	1.0	20	1.0
H_2O_2 at 200 mg/L	42	1.4	17	0.85
H_2O_2 at 500 mg/L	45	1.5	25	1.3
NaOH at pH = 8	40	1.3	15	0.75
NaOH at pH = 10	72	2.4	16	0.80

Table 3 Summary of Recoveries of Phenol from Contaminated Soil by Permeation

Desorbant Solution	No. of Tests	Maximum % Recovery	Minimum % Recovery	Average % Recovery	η = % Rec./ % Rec. for DI Water
Deion. Water	5	63	48	55	1.00
Hydrogen Peroxide (140 mg/L)	2	79	76	78	1.42
Sodium Hydroxide (pH = 10)	4	94	64	80	1.45

that would occur *in situ*, altering the hydraulic conductivity and dispersion of the fluid within the pores. Control of the hydraulic gradient is of concern because it permits an indirect control of contact time and allows for the measurement of hydraulic conductivity on a macroscopic scale. An understanding of the effects of decontaminants on hydraulic conductivity is an issue that affects engineering implementation of the process, because decreasing hydraulic conductivity with increasing desorption could render the process unworkable.

Those parts of the permeameters in contact with the contaminated soil or the permeant were made of non-reactive materials. Influent and effluent lines consisted of small-diameter teflon© tubing, while the end platens were porous stones. The confining membrane consisted of sheet teflon© wrapped around the perimeter of the specimen overlaid by a latex membrane. Latex could not be used directly in contact with the soil because it reacts with the permeants. Further details on the design and operation of the permeameters are given by Lazaridou [*42*].

For a prescribed hydraulic gradient within the specimen, the

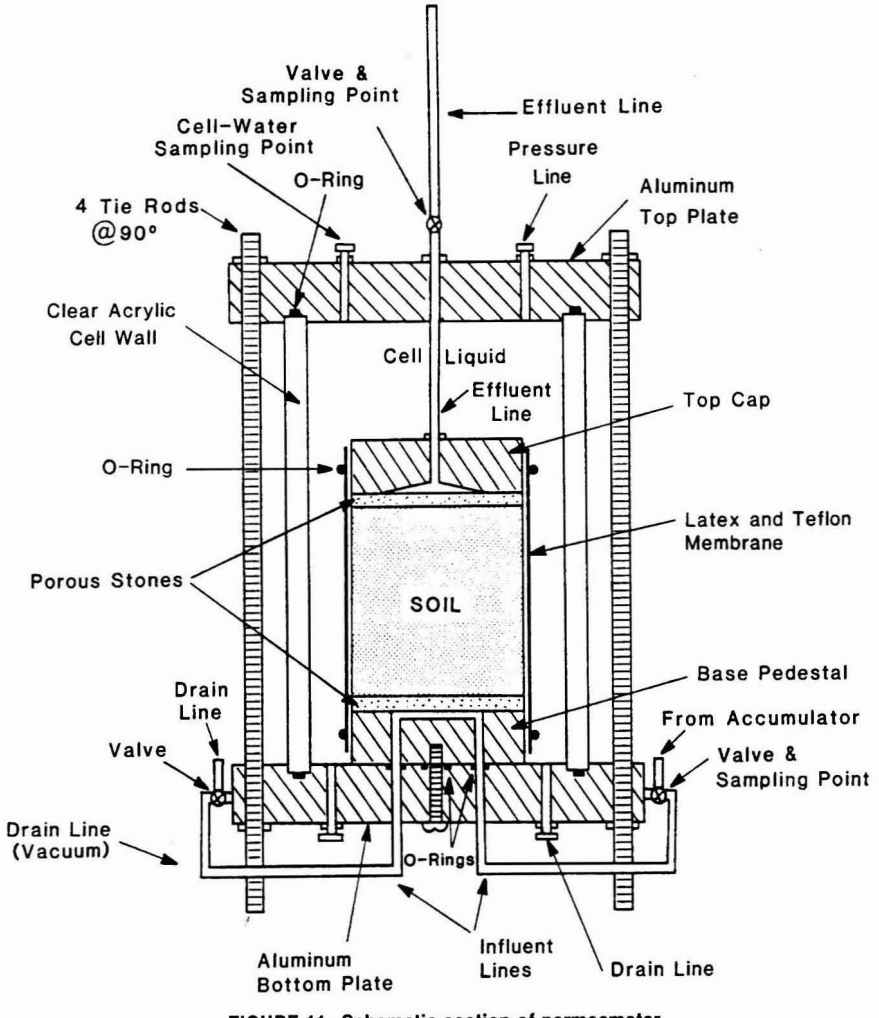

FIGURE 11. Schematic section of permeameter.

effluent side of the specimen was kept under a back pressure of about 10 kPa to minimize gas bubble formation and the pressure on the input side was adjusted to develop the appropriate hydraulic gradient, i, which is defined from Darcy's Law by Eq. 5.

$$i = \frac{\dfrac{(u_{in} - u_{out})}{\gamma_{permeant}}}{\text{Flow Path Length}}, \quad (5)$$

in which u is fluid (permeant) pressure, γ is unit weight of the permeant, and flow path length was 72 mm.

Specimens consisting of the mix of dry B-horizon soil and fine sand, described earlier, were prepared in the Harvard compaction mold, placed in the permeameter, and subjected to forced flow under controlled hydraulic gradient, until approximately two pore volumes of effluent had flowed out of the specimen. The confining pressure, applied to the specimen through de-aired and deionized water within the cell, was kept at 100 kPa above the mean pore fluid pressure in the specimen, as calculated from the mean of the influent and effluent pressures in the permeant.

Extraction testing consisted of forcing a given extraction solution under known pressure at the inlet end through the specimen and periodically monitoring the volume of flow from the outlet or effluent end, while simultaneously sampling the effluent with a syringe from the sampling point shown in Figure 11. Samples 4.2 μL in volume were subjected to gas chromatograph tests to determine the concentration of the contaminant in the effluent. This effluent concentration was plotted against effluent volume. The resulting relationship was integrated numerically to obtain the total weight of contaminant in the effluent after two pore volume exchanges. Because the compacted specimen was prepared with a known volume and a known concentration of the contaminant compound (C_e), the total weight of contaminant in the soil system could easily be determined. The difference between the total weight of contaminant added to the specimen (X) and the total weight recovered in the effluent was assumed to be the weight that

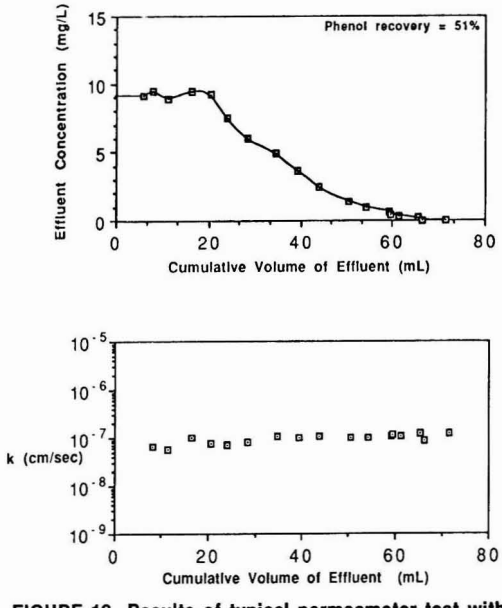

FIGURE 12. Results of typical permeameter test with phenol and deionized water.

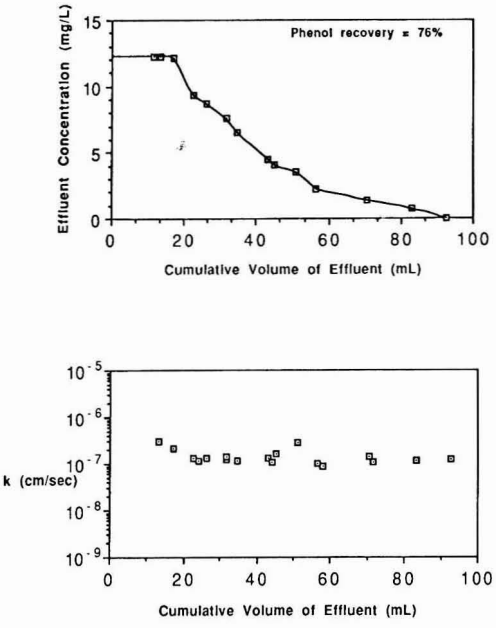

FIGURE 13. Results of typical permeameter test with phenol and H_2O_2 (140 mg/L)

was still in the soil system at the end of the test (X'). The percentage of contaminant recovered was thus $X - X'/X(100)$. Note, however, that this value is the amount recovered from both the liquid and solid phases and not necessarily the amount desorbed from the soil and is therefore not equal to ρ in the successive reverse isotherm tests.

Finally, hydraulic conductivity (k), or coefficient of Darcian permeability, was computed incrementally from the known hydraulic gradient, i, the cross-sectional area of the specimen, A, time increment Δt, and corresponding increment of discharge from the specimen, ΔQ, using Darcy's Law directly:

$$k = \frac{\Delta Q}{iA\Delta t}. \quad (6)$$

All tests were conducted under a hydraulic gradient of 60, except that the hydraulic gradient was increased in steps to 120 with hydrogen peroxide as the permeant. Each test required from 10 to 24 days.

Thus far, only phenol has been tested in the permeameter, but from the results of the successive reverse isotherm tests on phenol and aniline, phenol would be expected to desorb better than aniline in a permeameter test. A series of eleven permeameters tests were conducted using deionized water, H_2O_2 (at a concentration of 140 mg/L) and NaOH at a pH of 10 to compare the results of permeameter testing to those of successive reverse isotherm testing.

Results

Representative effluent volume—concentration relationships, measured as described above, are shown by the data in Figures 12–14. These figures also show the progression of hydraulic conductivity coefficient k as a function of total volume of discharge. It is noted that one pore volume is approximately 30 mL, and that the permeation of two pore volumes is equivalent to a contact of about 0.4 mL of desorbing solution per g of dry soil. This compares to about 2.5 mL/g in the SRI

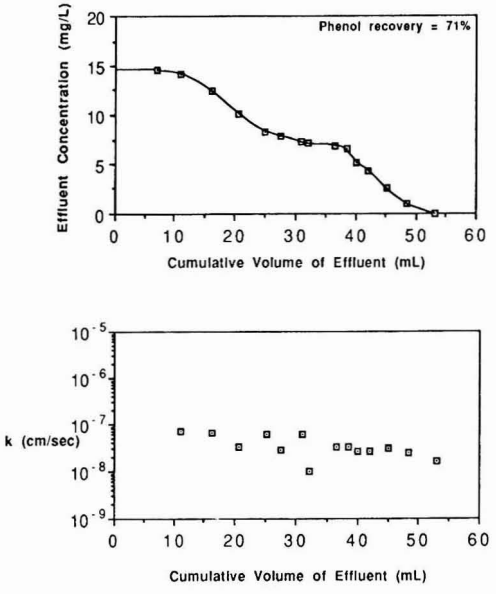

FIGURE 14. Results of typical permeameter test with phenol and NaOH (pH = 10)

tests. The concentration of the contaminants in the spiking solution was approximately 50 mg/L.

Table 3 shows the ranges and average percent recoveries of phenol from the two-phase system by three solutions. An interpretation of the permeameter test data is given in the last column. The absolute weights of phenol desorbed from the soil solids are not known, but the total recovered from the solid-liquid system (which is an important from a practical perspective) is known as a percentage of the weight of phenol applied to the system. The ratios (η) in the last column of Table 3 represent the effects of using either hydrogen peroxide or sodium hydroxide to remove phenol from the soil solids relative to using water. The ratios are of the same magnitude as the corresponding values of η from the SRI tests (Table 2), suggesting that the SRI test is a reasonably valid screening test, at least for phenol.

Atterberg limits tests were performed on the unspiked, spiked and permeated soil blend (B-horizon and fine siliceous sand used in the permeation tests) [*42*]. The initial liquid limit of the blended soil was 18%; the initial plastic limit was 15%. After spiking and permeation, no measurable changes in these values could be detected. Because these indexes did not change, neither the contamination nor the desorption process would likely have significant effects on the physical properties of the soil.

CONCLUSIONS

This paper represents an interim commentary on work in progress; however, certain trends appear to emerge from the laboratory study.

1. The permeameter tests require much longer to conduct and much great technician effort than the SRI tests; however, they represent better the *in situ* flow conditions and stresses than do the SRI tests.
2. Evaluating the strength and degree of contaminant capture by conducting a Freundlich isotherm test is important in understanding the potential difficulty of extraction caused by a given contaminant.
3. Based on the relative recovery ratios (η), Tables 2 and 3, the SRI test apparently represents a valid screening test for phenol extraction.
4. The SRI tests indicated that aniline was much more difficult to desorb with all of the trial solutions than was phenol. Deionized water seemed to be as effective in desorbing aniline as the oxidant and strong and weak bases. This result might be predicted from the background information because aniline is a weak base that would not be expected to desorb as easily as phenol with bases and oxidants.
5. In both the SRI and permeation tests, the strong base (NaOH at pH = 10) appeared to be the most effective solution in desorbing phenol, which is a weak acid. 72% of the spiked phenol was removed by the test, and 80% was removed by the permeation test.
6. Permeation of the phenol-spiked B-horizon clay-fine siliceous sand mixture with the various solutions had little measurable effect on hydraulic conductivity, although a slight reduction in hydraulic conductivity was experienced with NaOH at pH = 10. Neither spiking nor permeation had any measurable effects on the Atterberg limits of the soil used in the permeation study.

The results of this preliminary study provide encouragement that at least some contaminants can be extracted from soils *in situ*, although the extracting compounds must be chosen carefully. The success achieved in this preliminary work has encouraged the authors to continue to study other contaminants and extraction compounds.

FUTURE INVESTIGATIONS

This paper describes the initial portion of an ongoing study. Further SRI studies will be conducted on phenol and aniline using surfactants, and complete SRI studies will be conducted on other contaminants, including nitrobenzene. At least one additional set of permeameter tests will be conducted with a contaminant other than phenol or aniline that has the potential of high desorption by permeation. Once the action of various desorbant solutions on typical organic contaminants is understood through this series of laboratory tests, permeation tests of samples of contaminated soil recovered from the field will be conduced to assess the ability of the method to decontaminate real soils on a laboratory scale. If the success of this method is demonstrated on recovered soil samples, further research will focus on development of pilot studies for field application of the technology.

ACKNOWLEDGMENT

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Effectiveness of Supplemental Aeration and an Enlarged First-Stage in Improving RBC Performance

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A full-scale RBC plant having two parallel trains and treating combined municipal and industrial dairy waste was used to investigate the effectiveness of supplemental aeration and an enlarged first-stage in improving RBC performance. Enlarged first-stage was created by removing the baffles between the first two stages. One RBC train was used as a control and the other train was used to evaluate the combined effectiveness of supplemental aeration and an enlarged first-stage. Composite wastewater samples were collected from influent and effluent of each RBC stage in both trains. Samples were analyzed for soluble COD and BOD_5, ammonia nitrogen, and suspended solids. Wastewater temperature, pH and dissolved oxygen levels were measured in each stage. The study results indicate that it is possible to achieve higher organic loading rates and removal rates when RBC units are provided with supplemental aeration and enlarged first-stage.

INTRODUCTION

The RBC process has been used extensively at hundreds of locations in the U.S. for treating municipal and industrial wastewater [2]. Numerous reports in the literature and in RBC facility surveys [3, 4, 9, 10] have reported difficulties in the initial stages of RBC systems resulting in heavy biofilm growth, the presence of nuisance organisms such as Beggiatoa, and a reduction in organic removal rates. These problems have been attributed to excessive organic loadings that result in low dissolved oxygen conditions which subsequently lead to development of Beggiatoa growth and deteriorating process efficiency. Beggiatoa organisms compete with herterotrophic organisms for oxygen and for space on the RBC media surfaces. Their predominance can result in an increase in the concentration of nuisance organisms on the media while at the same time causing substantial reduction in organic removal per unit area of the RBC disks.

In this study, a four-stage RBC plant serving a population of approximately 6,000, and having two parallel trains was used to treat a combined municipal and industrial dairy waste. This newly built RBC plant had problems meeting effluent limit requirements because of overloaded conditions in the first and second stages and because of the low dissolved oxygen levels in the wastewater entering the plant. This plant was found to be ideal for evaluating the effectiveness of use of supplemental aeration and a modified step-feeding process which lowered first-stage loadings by removal of the baffle between the first and second stage. The plant was operated using one four-stage RBC train as a control by removing the baffles between the first two stages while the second parallel four-stage RBC train was used to evaluate the combined effectiveness of supplemental aeration and an enlarged first-stage. Earlier, the plant had been operated to evaluate the effect of plant operation with and without (control) supplemental aeration [9]. The plant loading was increased in an incremental fashion by adjusting the degree of pretreatment provided for the industrial waste at the dairy plant.

BACKGROUND

Fixed-Film trickling filter processes found early application in wastewater treatment but their use declined with the advent and widescale use of activated sludge processes. However, with the development of plastic media in the early 1960's interest in fixed-film processes has grown once again. This new interest in plastic media led to the development and commercialization of rotating biological contactors (RBCs) which provided many of the advantages of rock-media trickling filters without some of their disadvantages. Because of the new media developments and the smaller energy requirements of RBC treatment units compared with those of activated sludge units, RBC units were designed and used extensively during the mid and late 1970s. Unfortunately, early RBC installations experienced shaft and media failures, and displayed several operational problems. These problems eventually resulted in a decline in the use of RBCs as these problems created a question of their reliability.

A survey of 23 RBC installations [*3*] suggested that whenever the first stage load exceeded 0.03 Kg of total BOD_5/day/m^2 (6.4 lbs of total BOD_5/day/1000 sq. ft.), problems associated with the presence of sulfide oxidizing organisms occurred. This loading corresponds approximately to a soluble BOD_5 ($SBOD_5$) loading in the range of 0.013 to 0.018 Kg/day/m^2 (2.6 to 3.8 lbs/day/1000 sq. ft.). A total of 45 RBC plants were included in an inventory and analysis study conducted by EPA Region VII [*11*]. Approximately half of the treatment plants in the EPA study experienced a failure of some type due to high organic loadings and low dissolved oxygen conditions, predominately relating to shaft or media failures. Beggiatoa growth was observed in several of these plants.

It has been observed [*10*], that Beggiatoa growth is prevalent whenever the soluble BOD_5 loadings in the first stage exceed 0.012 Kg/day/m^2 (2.5 lbs/day/1000 sq. ft.), or when dissolved oxygen concentrations in the incoming wastewater are low. At higher organic loadings, zero-order kinetics have been found to prevail in the initial RBC stages because of the oxygen-limiting conditions [*9*]. Thus, at most of the RBC plants which are overloaded, the available oxygen was the limiting factor and not the organic load in the incoming wastewater. The lack of adequate oxygen resulted in nuisance organism growth. Supplemental aeration, provided under RBC units, can increase the dissolved oxygen levels in the early stages and also control the thickness of the biomass, thereby increasing the diffusion of substrate and oxygen into the biofilm. This can improve RBC performance and simultaneously eliminate the growth of undesirable Beggiatoa and other nuisance organisms [*9*].

It may be desirable to operate RBC plants with an enlarged first stage, particularly when the first stage is organically overloaded. Stepfeeding or step aeration, as it is called when applied to activated sludge processes, is used extensively in activated sludge plants to improve the oxygen demand situation at the head end of treatment systems which otherwise might be organically overloaded. To avoid a high oxygen demand at the beginning end of an activated sludge aeration tank, the incoming wastewater is distributed along the aeration tank at several locations to result in a more even oxygen demand throughout the tank. Similarly, an enlarged first stage can be used effectively to reduce the danger of overloading the first stage of an RBC plant and to attenuate variations in wastewater characteristics, thereby eliminating oxygen-limiting conditions and the development of nuisance organisms in the enlarged first stage. Fortunately, an enlarged first stage can usually be created simply by removal of the baffle between the first and second stages of an RBC treatment train.

A recent nationwide RBC teleconference [*10*] publicized the results of an EPA study. A significant finding of the study was that heavy biological growth due to high organic loading and corresponding low dissolved oxygen concentrations which lead to the development of heavy sulfide-oxidizing organisms were in part responsible for failure of media observed at a number of plants. The EPA study suggested that RBC plants should be designed with adequate flexibility, including wastewater recirculation, positively controlled alternate flow systems, such as step feed or use of an enlarged first stage, supplemental aeration, and other such means of operating flexibilities to optimize performance. Papers by Albert [*1*], Lagnese [*5*], McCaan and Sullivan [*6*] and Srinivasaraghavan *et al.* [*7*] reported on benefits derived from use of supplemental air in RBC treatment. Consistent with the findings reported above, the benefits can be summarized as:

- Increased dissolved oxygen concentrations
- Reduced biomass film thickness
- Higher $SBOD_5$ removal rates
- Higher nitrification rates
- Elimination of Beggiatoa growth
- Enhanced shaft and media life

To date, however, no RBC plant has been constructed with extensive step-feeding facilities and relatively few plants have extensive operating data to quantify the significance of supplemental aeration. This study was designed to provide data to increase our understanding of the effectiveness of supplemental aeration and use of an enlarged first-stage to improve the operational flexibility and performance of the RBCs. Provisions for use of supplemental air and an enlarged first stage can be incorporated in the design of an RBC plant with little additional cost and these flexible operating tools could be used effectively in improving RBC performance. Further, the elimination of Beggiatoa growth due to improved dissolved oxygen levels and a better distribution of biomass growth should enhance both shaft and media life.

MATERIALS AND METHODS

Facility Description

The wastewater treatment plant described in this study served a population of 6000. The RBC plant included a manual bar screen, communitors, a grit chamber, a raw sewage pumping station, two circular primary clarifiers, rotating biological contactors, three rectangular final clarifiers, two chlorine contact chambers, and two anaerobic sludge digestors. The wastewater at this plant flows by gravity through the bar screen, grit chamber and communitors to the raw sewage pump station. The wastewater is then lifted to the primary clarifiers and then flows by gravity to the RBC units, the final clarifiers, and the chlorine contact chambers. The disinfected effluent is discharged to the receiving stream. The treatment plant was designed to meet standard secondary effluent limits of 30 mg/L BOD_5 and 30 mg/L SS. However, the new RBC plant had difficulty consistently meeting these effluent standards when operating at 68 percent of its design load. The plant experienced media failure because of heavy biomass growth in all stages. Table 1 shows the design basis of the 1.1 mgd RBC plant.

The objectives of this study were to investigate the effectiveness of supplemental aeration and an enlarged first stage in improving RBC performance. To accomplish this goal, it was necessary to have a treatment plant that had a minimum of two parallel RBC trains, so that one train could be used as a control (with enlarged first stage only) and the other train could be used to evaluate treatment improvement using supplemental aeration and an enlarged first stage. The RBC treatment plant used in this study had two parallel trains with four stages in each train as shown in Figure 1. All of the north RBC units were provided with supplemental air by installing fine-bubble Reef diffusers. Four diffusers that were 0.61 m × 0.46 m (2 ft × 1.5 ft) were provided in each RBC stage and a total of 16 diffusers were installed in the four stages. The air was supplied from an existing 0.134 m^3/s (320 cfm) blower using PVC and flexible piping. These fine-bubble diffusers had high oxygen transfer capacities with air flow rate capacities of

Table 1 RBC Design Criteria and Dimensions

Parameter	
Design flow, mgd	1.1
Influent BOD_5, mg/L	155.0
Influent BOD_5, lbs/day	1422.0
Hydraulic loading rate for design, gpd/sq ft	2.2
Percent BOD_5 removal assumed	87.1
Overall hydraulic detention time, hrs	1.30
Number of RBC trains	2
Stages in each train	4
Total media surface area, sq ft	500,000
Surface media area of each stage, sq ft	62,500
RBC disc diameter, ft	11.5
Number of shafts	4
Length of each shaft, ft	24.0
Shaft drive motor hp	7.5
Rotational speed, rpm	1.4

0 to 1.52 $\times$ 10^{-1} $m^3/s/m^2$ (0 to 30 cfm/ft^2). Each air diffuser unit was provided with separate shut-off valves so that each unit could be individually removed, inspected, cleaned and returned to service in the basin without disturbing the air flow through the other units. An enlarged first stage was created in both north and south trains by removing the wooden baffles between the first and second stages. An enlarged first stage can be considered as partial stepfeed to equalize the organic load in the first two stages.

Sampling and Analyses

The study at this plant was conducted for approximately six months. Eleven 24-hour composite samplers were used to collect wastewater samples of the influent, effluent and from each RBC stage in both trains. The composite samples were analyzed for soluble COD, ammonia nitrogen, suspended solids, and volatile suspended solids on a daily basis. Samples were also analyzed for soluble BOD_5 (inhibited, to suppress nitrification) once a week. Stage oxygen uptake rates were measured periodically. Wastewater temperature, pH and dissolved oxygen levels were measured in each stage. The biomass thickness in the RBC stages was measured periodically, and the growth conditions were observed and noted on a daily basis. The biomass thickness was measured by scraping biomass from a known area of the media. Knowing the biofilm weight and the area measurements, the biofilm thickness was calculated. All other tests were conducted according to Standard Methods [8].

RBC PERFORMANCE

RBC performance was investigated separately under low and high organic loading conditions to find an optimum organic loading range above which oxygen limiting conditions would prevail. At the start of this study and during the transition from low to high organic loadings, an RBC acclimation period of 10 to 15 days was allowed to attain a steady state operating condition. During the higher loadings, the plant loading was increased in an incremental fashion over a period of time by adjusting the degree of pretreatment provided for an industrial waste originating at a dairy plant.

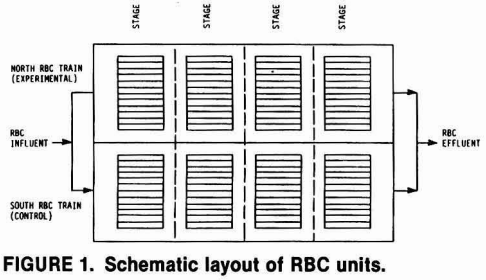

FIGURE 1. Schematic layout of RBC units.

Table 2 RBC Influent Wastewater Characteristics at Lower Loadings

Parameter	Mean	Range	Standard Deviation
Flow, mgd	0.786	0.573–1.20	0.161
Soluble COD, mg/L	239.2	130–300	50.4
Ammonia-N, mg/L	22.1	20.5–26	2.1
SS-mg/L	182.0	100–332	55.2
VSS-mg/L	133.6	85–249	41.2
DO-mg/L	1.00	0.60–1.30	0.22
pH	7.17	7.00–7.35	0.09
Temperature, °F	68.5	66–70	1.50

Start-Up

After installation of aeration equipment in the north RBC train, air was introduced through the sixteen fine-bubble Reef diffusers from the blower. During the first few days of air use, the biomass from the north RBC units sloughed heavily, creating a solids overloading problem in the final clarifiers. Biomass sloughing was significantly less in the second week of operation. Since the biomass was thick and heavy in all stages prior to air use, it was decided to continue the aeration for three weeks prior to initiation of sampling. Intermittent 24-hour composite sampling of each stage was carried out to observe when steady-state conditions prevailed. The sampling results indicated steady-state conditions existed at the beginning of the third week. During the entire period of this study, the existence of steady-state conditions was based primarily on the uniformity in the effluent COD of each stage.

Wastewater Characteristics

The wastewater coming into this plant was a mixture of domestic and industrial waste. However, the industrial waste contribution to the organic load was insignificant when compared to the total domestic waste load that is contributed to the plant. Tables 2 and 3 list the influent wastewater characteristics observed during this study. At lower organic loadings, the RBC mean influent soluble COD was 230 mg/L and varied between 130 to 300 mg/L. During the higher loadings, the mean soluble COD concentration was 362.5 mg/L, and the

Table 3 RBC Influent Wastewater Characteristics at Higher Loadings

Parameter	Mean	Range	Standard Deviation
Flow, mgd	0.706	0.407–0.935	0.138
Soluble COD, mg/L	362.5	270–540	76.4
Ammonia-N, mg/L	20.4	15.5–25.0	3.5
SS-mg/L	207.6	146–348	52.9
VSS-mg/L	159.5	109.5–233.2	33.6
DO-mg/L	1.02	0.90–1.30	0.12
pH	7.06	6.8–7.2	0.10
Temperature, °F	66.9	63–70	2.10

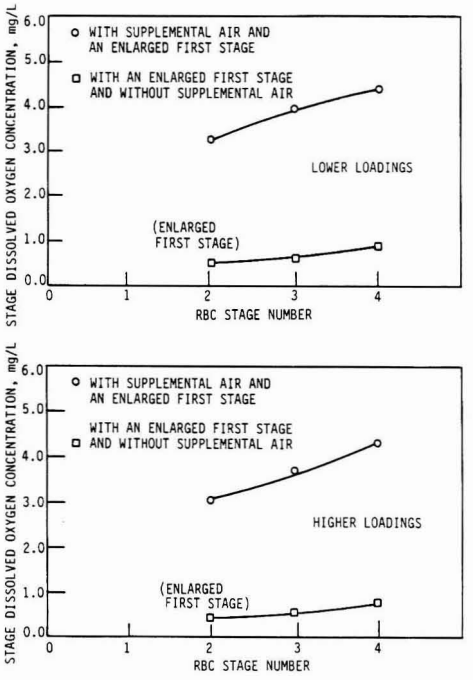

FIGURE 2. Stage mixed-liquor dissolved oxygen concentration profile.

range varied between 270 and 540 mg/L. The influent ammonia nitrogen concentrations were approximately the same during both the low and high organic loadings with a mean in the range of 20 mg/L. The higher suspended solids at higher organic loadings were due to reduced wastewater pretreatment at the dairy plant. Mean influent dissolved oxygen concentrations at both the low and high organic loadings remained at 1 mg/L. At lower loadings, the influent dissolved oxygen concentrations were somewhat lower and varied between 0.60 and 1.30 mg/L. The influent mean pH values were above 7.

Dissolved Oxygen

The mixed-liquor dissolved oxygen concentration generally increased as the wastewater passed through the RBC stages. Figure 2 shows the mixed-liquor dissolved oxygen profile observed during low and high organic loadings. As can be seen from the figure, the dissolved oxygen levels with supplemental air and an enlarged first stage were approximately *the same* at both organic loading levels. However, the dissolved oxygen levels were significantly less without supplemental aeration at both the low and high organic loadings. At lower loadings, the enlarged first stage dissolved oxygen levels varied between 0.30 and 1.15 mg/L, and at higher loadings, the DO levels ranged between 0.30 and 0.70 mg/L. The mean mixed-liquor dissolved oxygen in all stages was always less than 1 mg/L without supplemental air. The results of this study suggest that higher mixed liquor dissolved oxygen levels can be achieved with supplemental air and an enlarged first stage when compared to use of supplemental air alone [9]. These results also suggest that supplemental air in the initial RBC stages, where the organic loadings are high, is essential to overcome potential oxygen limitations at both low and high organic loading rates. The use of an enlarged first stage is helpful to some extent at lower organic loading rates, but, at higher organic loading rates, the use of only an enlarged first stage will not be enough to overcome oxygen limitation problems.

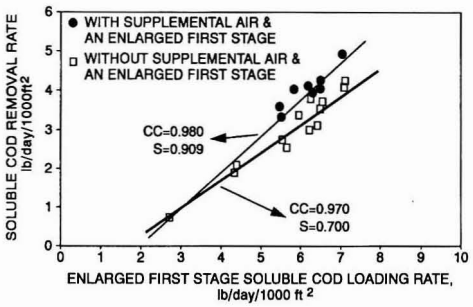

FIGURE 3. Enlarged first-stage soluble COD removal vs loading at lower loadings.

Soluble COD Removal

In this section, soluble COD removal at low and high organic loading rates are discussed separately. Figure 3 shows the relationship between the enlarged first stage applied SCOD load and its removal at lower organic loadings. It can be seen that linear relationships were observed both with and without supplemental air and the correlation coefficients were high. However, the soluble COD removal rates were higher with supplemental air due to the higher available dissolved oxygen levels in the various stages. The slopes (S) of these linear relationships were 0.909 and 0.700 with and without supplemental air, respectively. The steeper slope observed with supplemental air indicates higher removal rates. At a first stage loading rate of 0.0146 Kg/day/m^2 (3 lbs/day/1000 sq. ft.), the removal rates were approximately the same with and without supplemental air. However, the removal rates increased in the presence of air as the organic load increased. At a maximum first stage loading rate of 0.037 Kg/day/m^2 (7.5 lbs/day/1000 sq. ft.), the removal rate with supplemental air was 0.024 Kg/day/m^2 (4.93 lbs/day/1000 sq. ft.), whereas, without the air, the removal rate was only 0.02 Kg/day/m^2 (4.07 lbs/day/1000 sq. ft.). Thus, the supplemental air increased SCOD removal in the first stage by 21% (4.93/4.07 = 1.21).

The overall organic loadings vs removal relationships were also linear with high correlation coefficients (CC), as shown in Figure 4. The slope was 0.989 with supplemental air and 0.900 without supplemental air. The overall soluble COD removal rates suggest that there was not much difference in removal rates with and without the air. This is due to existence of substrate limiting conditions after the first stage, as most of the SCOD removal takes place in the enlarged first stage.

For example, with supplemental air (Figure 3) a SCOD loading rate of 7 lbs/day 1000 sq. ft. (0.034 Kg/day/m^2) and removal is 4.5 lbs/day/1000 sq. ft. (0.022 Kg/day/m^2) or 64%

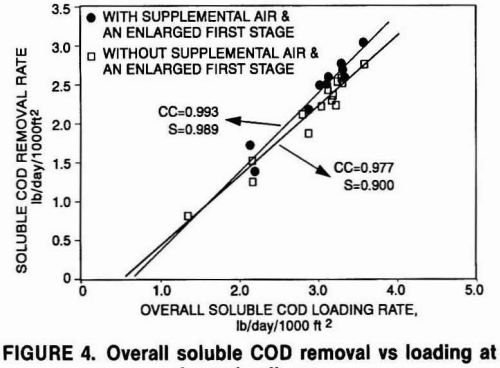

FIGURE 4. Overall soluble COD removal vs loading at lower loadings.

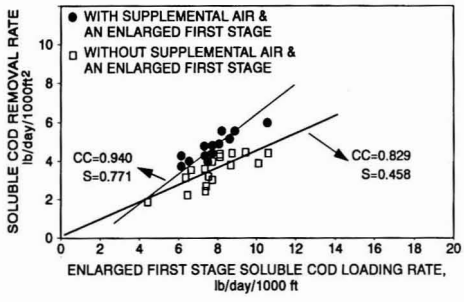

FIGURE 5. Enlarged first-stage soluble COD removal vs loading at higher loadings.

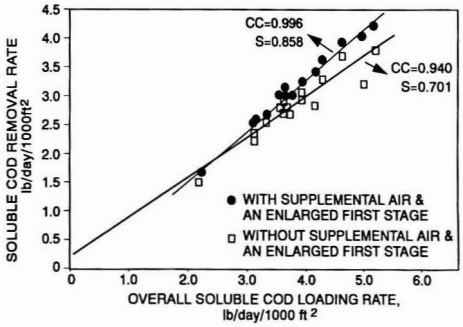

FIGURE 6. Overall soluble COD removal vs loading at higher loadings.

is removed in the first stage. As a result, only 36% is available for removal in the other two stages.

The relationship between soluble BOD_5 (inhibited) and soluble COD was as follows:

$$SBOD_5 = 0.60\ SCOD - 11.06 \text{ (Influent to RBCs)}$$

$$SBOD_5 = 0.21\ SCOD - 1.43 \text{ (Effluent from RBCs)}$$

Figure 5 shows the relationship between the enlarged first stage soluble COD loading and removal at the higher organic loadings. The relationships were linear with and without the air. The results at higher organic loadings suggest that as the organic loading increased, the SCOD removal rate in the absence of air tended to fall off. For example, up to a loading of 7 lbs SCOD/day/1000 sq. ft. (0.034 Kg/day/m^2) (Figure 3) with supplemental air, the slope of the removal curve was 0.909, but at loading 6–10 lbs SCOD/day/1000 sq. ft. (0.029 – 0.049 Kg/day/m^2) (Figure 5), the slope of the removal curve dropped to 0.771.

Table 4 shows the enlarged first stage soluble COD removal rates with and without the supplemental air. Without the supplemental air, the removal rates were lower suggesting oxygen limitation at increased loadings. However, with air, the removal rates increased as the organic loading increased. At a maximum organic loading rate of 0.05 Kg/day/m^2 (10.5 lbs/day/1000 sq. ft.), the removal rate with supplemental air was 0.033 Kg/day/m^2 (6.83 lb SCOD/day/1000 sq. ft.) and in the absence of air, it was only 0.023 Kg/day/m^2 (4.75 lbs/day/1000 sq. ft.).

The higher dissolved oxygen levels resulted in Beggiatoa-free growth and a reduced biomass thickness. This contributed to increased SCOD removal in the units receiving supplemental air. It has been suggested that thinner biofilms will have higher substrate removal rates because of more effective substrate and oxygen diffusion within the biofilms. The Beggiatoa growth in the absence of air was reduced somewhat in the first stage because of baffle removal; however, it was still present in all stages at the higher organic loading rates. Without air, zero-order kinetics were observed at higher organic loadings; whereas, the kinetics were found to be first-order with supplemental air [9]. This suggests that use of supplemental air is essential at high organic loadings even with an enlarged first stage. An enlarged first stage is helpful to reduce the organic load on first stage media but is still not adequate to overcome the oxygen-limitations. It is important to recognize that, without the baffle removal, the organic load in the first stage would have been double that in the enlarged first stage. The baffle removal allows the incoming organic load to be distributed more evenly to the first two stages.

Figure 6 and Table 5 shows the observed overall plant soluble COD removal rates with and without the supplemental air at high organic loadings. The relationships are linear and the correlation coefficients are high. The slopes with and without the air were 0.858 and 0.701, respectively. The overall SCOD removal rates in Table 5 indicate that at an initial loading of

Table 4 Enlarged First Stage Soluble COD Removal Rates at Higher Loadings

	With an Enlarged First Stage and With Supplemental Air	With an Enlarged First Stage and Without Supplemental Air
Soluble COD Loading Rate lb/day/1000 ft^2	Soluble COD Removal Rate lb/day/1000 ft^2	Soluble COD Removal Rate lb/day/1000 ft^2
4.5	2.25	2.00
5.0	2.63	2.20
5.5	3.00	2.45
6.0	3.40	2.65
6.5	3.77	2.90
7.0	4.15	3.15
7.5	4.55	3.35
8.0	4.92	3.60
8.5	5.30	3.80
9.0	5.68	4.05
9.5	6.06	4.25
10.0	6.45	4.50
10.5	6.83	4.75

Table 5 Overall Plant Soluble COD Removal Rates at Higher Loadings

	With an Enlarged First Stage and With Supplemental Air	With an Enlarged First Stage and Without Supplemental Air
Soluble COD Loading Rate lb/day/1000 ft^2	Soluble COD Removal Rate lb/day/1000 ft^2	Soluble COD Removal Rate lb/day/1000 ft^2
2.0	1.60	1.60
2.5	2.00	1.94
3.0	2.43	2.30
3.5	2.85	2.65
4.0	3.28	3.00
4.5	3.72	3.35
5.0	4.15	3.70
5.5	4.58	4.05

Table 6 Summary of Soluble COD Removal Efficiencies (%) by Stage

	With an Enlarged First Stage and With Supplemental Air		With an Enlarged First Stage and Without Supplemental Air	
Stage	At Lower Loadings	At Higher Loadings	At Lower Loadings	At Higher Loadings
Enlarged[a]				
Stage 1	58.3	59.0	47.9	43.8
Stage 3	31.9	38.4	30.4	28.3
Stage 4	25.0	30.5	28.6	33.1
Overall	78.7	82.4	74.1	73.0

[a] Stage 1 and 2 combined.

0.01 Kg/day/m^2 (2 lbs/day/1000 sq. ft.), the removal rates and percent removals were approximately the same with and without the supplemental air. However, as the loading rate increased, the SCOD removal rate decreased without the supplemental aeration. With supplemental air, the SCOD removal rates increased as the loading increased. Further increase in organic loading rates, probably up to an overall loading rate of 0.049 Kg/day/m^2 (10 lbs/day/1000 sq. ft.) would have made it possible to see a clear oxygen-limitation (flat curve) condition in Figure 6, particularly in RBC units where supplemental air was not provided. However, due to production cut-down at the dairy plant, this was not feasible.

Table 6 contains a summary of soluble COD removal efficiencies observed during this study. This table shows that the enlarged first stage SCOD removal efficiencies at higher loadings were 59.0 and 43.8 percent, respectively, with and without the supplemental air. The results also demonstrate that the overall COD removal efficiency was higher with supplemental air than without the air.

As mentioned earlier, this RBC plant was designed only to meet standard secondary effluent limits for BOD; however, this plant showed ammonia nitrification efficiencies of approximately 40 percent with supplemental air both at low and higher organic loadings. Without the air, the ammonia nitrification was insignificant.

The higher soluble COD removal rates with supplemental air could be attributed to higher dissolved oxygen levels, and thinner, Beggiatoa-free, growth which enhanced mass diffusion of oxygen into the inner layers of active biomass. The observed lower SCOD removal rates in the absence of supplemental air could be due to mass diffusional resistances because of the thick, heavy biomass, along with substrate saturation and oxygen limitations. Beggiatoa growth in the absence of air was predominant in all the stages. With supplemental air, the enlarged first stage effluent suspended solids were high, particularly at higher loadings, resulting in a suspended growth system within the tank which contributed to additional SCOD removal in the presence of the high dissolved oxygen levels. The activity of the fixed film system was also enhanced because of the thinner active biomass in the presence of air.

CONCLUSIONS

Based on the experimental results in this study, the following conclusions can be made:

1. Given the same amount of media, it is possible to achieve higher organic loadings and removal rates when RBC units are provided with supplemental aeration and an enlarged first stage. Regardless of the organic loading rates, units receiving supplemental aeration demonstrated remarkable performance and ability to adapt to higher organic loading rates without substrate saturation.
2. Most of the soluble COD is removed in the first stage and the removal efficiencies with supplemental air and an enlarged first stage are considerably higher than those observed in the absence of supplemental aeration, particularly at higher organic loading rates.
3. Dissolved oxygen levels in the earlier stages increased significantly when the RBC units were operated with supplemental air and an enlarged first stage. Without the air, the dissolved oxygen levels increased to a certain extent with an enlarged first stage, but were still less than 1 mg/L.
4. The use of an enlarged first-stage, enlarged by removal of the baffle between the first and second stages, reduced the organic loadings in the initial stages and increased soluble COD removal efficiency. Removal rates obtained from RBC units supplied with supplemental air and an enlarged first stage were comparatively higher than with an enlarged first stage only.

ACKNOWLEDGMENTS

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The views/opinions expressed in this paper are those of the authors and should not be construed as opinions of the United States Environmental Protection Agency.

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The Fate of BDAT Polynuclear Aromatic Compounds during Biotreatment of Refinery API Oil Separator Sludge

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A 16 week laboratory study was conducted to assess the biotreatability of regulated (BDAT list) polynuclear aromatic compounds (PNA) in refinery API oil separator sludge. The three different treatments consisted of a biotic, nutrient amended, inoculated aerated slurry reactor, a second biotic oxygen-sparged reactor, and a sterile, nitrogen-sparged control. Naphthalene, anthracene, phenanthrene, and benzo(a)pyrene were completely biodegraded in the first 4 weeks in both biotic treatments. Chrysene disappeared within 4 weeks in the aerated bioreactor, whereas it required 16 weeks to degrade in the oxygen-sparged reactor. Pyrene degraded only 30% in the aerated bioreactor and did not exhibit any significant concentration changes in the oxygen-sparged reactor. Phenanthrene, chrysene, and pyrene concentration levels did not change significantly during the 16 week treatment period in the nitrogen-sparged control reactor indicating the absence of stripping losses for these PNAs. By contrast, naphthalene, anthracene, and benzo(a)pyrene levels remained constant during the first 2–4 weeks in the control but decreased to below detection limits (5 mg/kg) at the end of the treatment. It is not clear whether the disappearance of these compounds is due to stripping, irreversible sorption or some anaerobic/aerobic biodegradation processes. In conclusion, the aerobic biotreatment of refinery API oil separator sludge was successful in removing most BDAT PNA compounds. The reduced biodegradability of pyrene may be explained in terms of either the inherently low biodegradation rate of this compound or the limited bioavailability in the weathered oily sludge system.

INTRODUCTION

In 1990, the U.S. Environmental Protection Agency (EPA) issued "landban" pretreatment standards for refinery hazardous wastes listed in the Resource Conservation and Recovery Act (RCRA). The regulation requires that listed hazardous wastes are pretreated prior to land disposal using a technology that meets or exceeds treatment standards established by a best demonstrated available technology, or BDAT [*1*]. Accordingly, the sludge must meet certain BDAT concentration standards for organics (BTEX and PNAs) and leachable (TCLP) metals prior to land disposal or land treatment (landfarming). Since polynuclear aromatic hydrocarbons (PNAs) are generally known to be biodegradable [*2–7*] the aerobic biotreatment of API oil separator sludges might provide a way to reduce PNA concentrations below regulated BDAT levels. Only limited information is available regarding the fate of BDAT PNAs from API oil separator sludges after the controlled application on soils for bioremediation purposes [*2, 8–10*]. Even less is known about the effectiveness of slurry biotreatment of API oil separator sludges in meeting BDAT pretreatment standards for the listed PNAs [*11*]. It is therefore the objective of this study to investigate the fate of BDAT PNAs under different biotreatment conditions in controlled laboratory experiments.

MATERIAL AND METHODS

Seed Acclimation

Approximately 2 L of waste activated sludge from the final clarifier at a Shell refinery were added to a 4 L Erlenmeyer flask. Initial nutrient amendments consisted of 440 ppm KH_2PO_4 (= 50 ppm P), 560 ppm K_2HPO_4 (= 50 ppm P), and 1000 ppm NH_4NO_3 (= 175 ppm N). After pH adjustment with NaOH to ca. pH 7, the sludge was mixed at ca. 300 rpm and aerated with air at a flow rate of 500 mL/min. Approximately 150 g of API oil separator sludge was added as substrate to the flask to initiate the seed acclimation. Over the next two week period, a total of 100 mL oil separator sludge were added in small increments (25 mL) to the seed flask to enhance indigenous microorganism acclimation. The total acclimation period prior to reactor inoculation lasted approximately 4 weeks.

PNA Mineralization Assay

Prior to bioreactor inoculation the acclimated seed culture was tested for phenanthrene and pyrene biodegradation potential using a ^{14}C mineralization assay. Approximately 500 g of acclimated seed was sent to ReTec, Inc. in Seattle, WA, for conducting the polynuclear aromatic hydrocarbon mineralization assay. The PNA biodegradation potential was determined using ^{14}C-phenanthrene and ^{14}C-pyrene as indicator substrates. The biodegradative response of indigenous microorganisms was quantified in the seed culture by measuring the cumulative production of radiolabeled carbon dioxide from cellular metabolism of the radiolabeled test substrate. In addition, the effect of seed inoculation with proven PNA degrading microorganisms from ReTec's culture collection on PNA mineralization was also assessed.

Prior to initiating the mineralization assay, approximately 500 g seed culture was transferred to a 1000 mL flask and inorganic nutrients (nitrogen as NH_4NO_3 and phosphorus as an equimolar mixture of KH_2PO_4 and K_2HPO_4) were added at 75 and 40 ppm, respectively. The nutrient amended seed culture was mixed and homogenized.

Reactors for mineralization testing were prepared by adding 20 grams of the homogenized sludge to 160 mL Wheaton bottles fitted with Teflon-lined screw caps. The indigenous substrate mineralization potential was evaluated in six replicate reactors; whereas, triplicate reactors were used to measure the mineralization in both the positive and negative control treatments.

The positive control consisted of seed which was inoculated with a mixed culture of known PAH degraders. Inoculation was accomplished with either phenanthrene—or pyrene degraders (to appropriate test reactors) from ReTec's culture collection. Triplicate abiotic (negative) controls were prepared by amending the reactor contents with two percent mercuric chloride as a biological inhibitor.

Radiolabeled phenanthrene and pyrene (primary working stocks prepared in acetone and benzene, respectively) were added at concentrations of 58.6 and 43.3 nCi to each reactor bottle. The specific activities of the test substrates were 13.1 mCi/mmol for phenanthrene and 55 mCi/mmol for pyrene. Following the addition of the radioactive substrate, 0.3 mL of 1.5 N NaOH was added to the polypropylene trapping cup suspended from the bottle cap. Test reactor bottles were tightly sealed and incubated at 20°C on a shaker table. The amount of $^{14}CO_2$ trapped in the NaOH solution was monitored after 2 and 6 days incubation.

The radiolabeled carbon dioxide in the base trapping solution was sampled and quantified at each time point by liquid scintillation spectrophotometry using ScintiVerse II (Fisher Scientific, Pittsburgh, PA) fluor. The extent of biodegradation was recorded as a function of time for each test condition, with results expressed as the cumulative percentage of added ^{14}C-phenanthrene or ^{14}C-pyrene recovered as $^{14}CO_2$. Experimental counts per minute (CPM) values were corrected by substraction of background counts obtained from the scintillation fluor.

API Oil Separator Sludge Amendments

Prior to treatment in the biotic reactors, the API oil separator sludge (density 1.01 kg/L) was amended with 2860 ppm NH_4NO_3 (= 1000 ppm N) and 645 ppm H_3PO_4 (= 200 ppm P). The sludge which was designated for the control reactor did not receive any nutrient additions and was sterilized with sodium azide (2% wt) and mercuric chloride (2% wt) to inhibit microbial activity.

Reactor Operation

All three reactors (2 biotic, 1 control) consisted of 4 L Erlenmeyer flasks which were agitated continuously with an overhead mechanical mixer at 500 rpm. All reactors received 1500 mL amended API oil separator sludge. Both biotic reactors were inoculated with 150 mL acclimated seed (see above), whereas 150 mL distilled water were added to the control reactor to account for dilution effects in the biotic reactors. The pH of the reactor contents was adjusted to 6.5–7.5 with either NaOH or HCl if necessary. Biotic reactors 1 and 2 were aerated with air and 100% oxygen, respectively, whereas the control reactor was sparged with house nitrogen. All gases were humidified and the volumetric gas flow rate was adjusted to 500 mL/min for each gas. In order to enhance the mass transfer of the gases into the liquid phase a gas diffuser stone was used for sparging the reactor contents.

Sampling

The reactor contents were sampled at specified time intervals and analysed for pH, dissolved oxygen (DO), polynuclear aromatics (PNA), oil and grease (O&G), total solids (TS), and total aerobic heterotrophs (concentration of microbial cells) as described below. At each sampling event, the agitation was stopped and the mechanical mixer was removed. The reactor content was shaken vigorously and 250 mL were poured into a glass beaker. Subsamples of appropriate sizes were taken from the well-mixed beaker contents for PNA, O&G, TS and total heterotroph analyses. For PNA analyses, two independent subsamples were submitted for each reactor at a specified sampling event.

Analytical Methods

PNA analysis: Two grams of a well-shaken sample were transferred into a 10 mL volumetric flask and diluted to 10 mL with methylene chloride according to EPA Method 3580 [*12*]. A one (1) mL aliquot of the clear liquid extract was prepared and analyzed by GC/MS based on EPA Method 8270 [*12*]. This resulted in a 1 to 5 dilution and a detection limit of 5 ppm (mg/kg) for all semivolatile compounds (PNA) of interest. *O&G analysis* Gravimetric O&G (oil and grease) analyses were performed according to Standard Method 5520 E [*13*]. *Total solids* were determined on the sludge according to Method 2540 B [*14*]. *DO and pH* were measured with respective probes in a well-mixed reactor. *Total heterotroph bacterial counts* were determined by a tube dilution method as follows. Ten grams of reactor slurry were transferred to a 250 mL sterile serum vial and slurried with 90 mL sterile Bushnell-Haas medium. Slurries were shaken in a wrist-action shaker for 60 minutes and then serially diluted (1:10) up to 10^{-12} in 9 mL sterile Trypticase Soy Broth (3% w/v) which served both as mineral and energy source for bacterial growth. Cultures were incubated for 7 days at 30°C and the highest dilutions showing turbid growth were selected to compute the approximate number of bacteria/g reactor slurry. For example, if the 10^{-5} dilution tube were the highest dilution showing turbid growth, the number of bacteria present were about 10^5/g slurry.

RESULTS AND DISCUSSION

PNA Mineralization Assay

The laboratory data collected during the mineralization assays are summarized in Table 1 and plotted in Figure 1. Table 1 shows the cumulative percent of ^{14}C recovered in $^{14}CO_2$ during the mineralization of the labeled test substrates ^{14}C-pyrene and

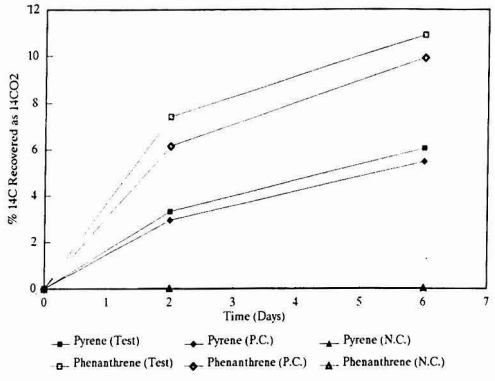

FIGURE 1. Pyrene and phenanthrene mineralization.

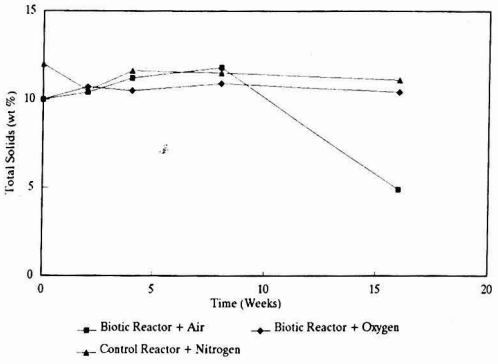

FIGURE 2. Total solids concentration profiles during biotreatment of API oil separator sludge.

^{14}C-phenanthrene (= 100% ^{14}C activity). Cumulative percent mineralization was measured after 2 and 6 days in 6 test replicates, in 3 negative (N.C.) and in 3 positive controls (P.C.).

Results from the killed controls for both test substrates indicate that less than 0.05% of the test compounds were degraded (or volatilized) through abiotic processes following six days of incubation. By contrast, approximately 11 and 6 percent of the initially added ^{14}C was recovered as $^{14}CO_2$ in the acclimated seed culture after 6 days of incubation during the mineralization of phenanthrene and pyrene, respectively. A degradation lag period was not observed. This indicates the presence of indigenous microorganisms which are well acclimated to both pyrene and phenanthrene and therefore did not require time for genetic induction prior to degradation. The presence of known PNA degraders in the positive control cultures did not contribute to a faster initial mineralization rate or a higher cumulative mineralization potential when compared to the indigenous microorganisms in the test cultures.

TS, O&G, DO, and pH

The total solids (TS) content (wt %) of the sludge is presented as a function of treatment time for each reactor as shown in Figure 2. The initial TS content is approximately 10% (wt) in each reactor and stays constant during the entire treatment time (16 weeks) for both the control and the biotic oxygen reactor. This indicates that no water was lost due to evaporation during the gas sparging processes (gases were humidified prior to entry into the reactors) and that the sludge sampling procedures were reproducible from one sampling event to the next. In the biotic air reactor the total solids content stayed at 10% (wt) for the first 8 treatment weeks but dropped to ca. 5% (wt) at the end of the experiment. This change in TS content was caused by a reactor spill at treatment week 11 where most of the spilled liquid but not all solids were recovered in order to continue the experiment. Since part of the O&G and most of the PNAs are likely to be associated with the sludge solids

Table 1 Cumulative Percent ^{14}C Recovered as $^{14}CO_2$ During the Mineralization of ^{14}C-Pyrene and ^{14}C-Chrysene, Respectively, in Test Cultures Containing Acclimated Seed Organisms, Positive and Negative Controls.

Substrate	Treatment	Percent ^{14}C Recovered as $^{14}CO_2$			
		T = 2 Days	Mean	T = 6 Days	Mean
Pyrene	Test Culture (1)	4.34	3.33	8.48	6.06
	Test Culture (2)	2.35		4.98	
	Test Culture (3)	2.16		4.62	
	Test Culture (4)	3.68		4.95	
	Test Culture (5)	3.14		6.58	
	Test Culture (6)	4.29		6.72	
	Neg. Control (1)	0.007	0.008	0.020	0.021
	Neg. Control (2)	0.006		0.014	
	Neg. Control (3)	0.011		0.028	
	Pos. Control (1)	4.39	2.96	7.00	5.47
	Pos. Control (2)	2.15		5.29	
	Pos. Control (3)	2.35		4.13	
Phenanthrene	Test Culture (1)	4.19	7.41	8.03	10.9
	Test Culture (2)	7.09		10.2	
	Test Culture (3)	5.48		9.00	
	Test Culture (4)	11.0		14.8	
	Test Culture (5)	7.84		10.7	
	Test Culture (6)	8.83		12.8	
	Neg. Control (1)	0.05	0.04	0.05	0.05
	Neg. Control (2)	0.07		0.08	
	Neg. Control (3)	0.01		0.02	
	Pos. Control (1)	10.3	6.16	14.9	9.91
	Pos. Control (2)	4.20		7.65	
	Pos. Control (3)	3.98		7.19	

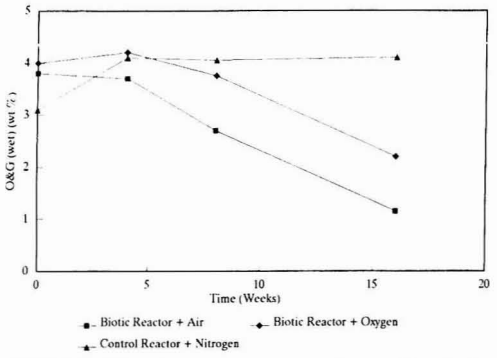

FIGURE 3. Oil and grease concentration profiles during biotreatment of API oil separator sludge.

it is important to know the solids content in the waste. If the TS content stays constant during the treatment, any change in organics (O&G, PNAs) must be the result of some removal mechanism (biodegradation, chemical oxidation, evaporation, etc.) and cannot be attributed to sampling or dilution problems.

Oil and grease (O&G) concentration profiles for the three treatments are presented in Figure 3. The initial O&G concentration is approximately 4% (wet weight basis) in all reactors. No change in O&G was observed in the control reactor indicating a successful suppression of O&G biodegradation processes in the presence of biocides under anaerobic conditions (N_2). By contrast, a 50% decrease in O&G was noted in the biotic oxygen reactor. The rate of O&G degradation was fastest in the biotic air reactor reaching a final O&G concentration of approximately 1.15%. It is not entirely clear whether the large decrease in O&G in the biotic air reactor results from enhanced biodegradation in the presence of air (vs. oxygen) or is caused by the loss in TS (drop from 10% to 5%, see above) since a large fraction of the (weathered) O&G is expected to be associated with the sludge solids.

The dissolved oxygen (DO) concentration ranged from 22 to 45 mg/L in the biotic oxygen reactor and was below 0.5 mg/L in the nitrogen sparged control reactor during the entire treatment period. The DO concentration in the biotic air reactor was measured at 0.5 mg/L during the first treatment week and increased to 7 mg/L at treatment day 9. Subsequently the DO remained approximately 7 mg/L for the remainder of the treatment. The low dissolved oxygen levels at the beginning of the biotic air treatment can be attributed to the high oxygen demand for the biodegradation of easily degradable organics (BTEX) in the sludge. After these organics have been degraded during this initial oxygen-limited treatment phase, more difficult (slower) to degrade organics are left behind demanding less oxygen (rate) for biodegradation processes. Consequently the reactor is no longer oxygen-limited and the DO remains at its saturation concentration of 7 mg/L.

The pH of the sludge was measured periodically (at 0, 1, 2, 4, 8, 16 weeks) and varied from 6.5 to 8.2 in the different treatments.

Aerobic Heterotrophs

The concentration of aerobic heterotrophic bacteria was measured in duplicate after two weeks of treatment in each reactor. The bacterial counts in the sludge were 10^9/g and 10^{10}/g in the biotic air reactor, 10^9/g and 10^9/g in the biotic oxygen reactor, and 10^3/g and 10^4/g in the nitrogen sparged sterile control reactor. The relatively high bacterial counts in the control reactor are indicative of the fact that these microorganisms survive even in the presence of microbial inhibitors under anaerobic conditions. It is possible that a fraction of aerobic microorganisms survives in micro-nitches on (within) the sludge solids which are not easily accessible to the microbial growth inhibitors. Even though the microbial activity is not entirely inhibited, the control reactor is subsequently labeled sterile or inhibited control.

Polynuclear Aromatics (PNA)

Before interpreting the subsequent PNA concentration profiles for each treatment it should be pointed out that each plotted PNA concentration is the average of 4 analyses. Each of the two subsamples (see Material and Methods) were analyzed for the specific PNA in duplicate (2 subsamples * 2 analyses/subsample = 4 total analyses). The method detection limit for each individual PNA was 5 mg/kg. Any PNA concentration below the detection limit was treated as non-detect or 0 mg/kg for the computation of the average of 4 PNA concentrations. The variability in PNA concentrations between the two subsamples as well as between duplicate analyses of the same subsample was relatively small and acceptable indicating proper sampling and analytical techniques. Consequently, the observation of significant changes in PNA concentrations during the 16 week treatment period can only be explained in terms of specific loss mechanisms (biodegradation, volatilization, etc.) and not in terms of sampling and analytical errors and inaccuracies.

The fate of the PNAs of concern (BDAT) are discussed in the paragraphs below. Starting with the 2-ring, most water soluble and volatile PNA naphthalene, the subsequent PNAs are discussed in order of increasing ring size and molecular weight, and decreasing aqueous solubility and volatility as outlined in Table 2.

Naphthalene

Naphthalene concentration profiles for all three treatments are presented in Figure 4. The initial levels of naphthalene were

Table 2 Physical Properties of Representative Polynuclear Aromatic Compounds [5]

Compound Name	Number of Rings	Molecular Weight	Aqueous Solubility	Partition Coefficient	Vapor Pressure
		(g/mole)	(mg/L)	(log K_{ow})[1]	(torr)[2]
Naphthalene	2	128	30	3.37	$4.92*10^{-2}$
Phenanthrene	3	178	1.29	4.46	$6.80*10^{-4}$
Anthracene	3	178	0.07	4.45	$1.96*10^{-4}$
Pyrene	4	202	0.14	5.32	$6.85*10^{-7}$
Chrysene	4	228	0.002	5.61	$6.30*10^{-7}$
Benzo(a)pyrene	5	252	0.0038	5.98	$5.00*10^{-7}$

[1]Logarithm of the octanol:water partition coefficient.
[2]At 20°C.

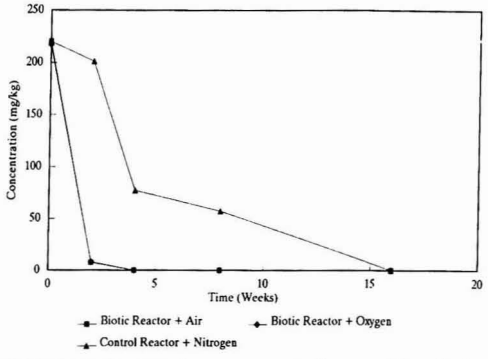

FIGURE 4. Naphthalene concentration profiles during biotreatment of API oil separator sludge.

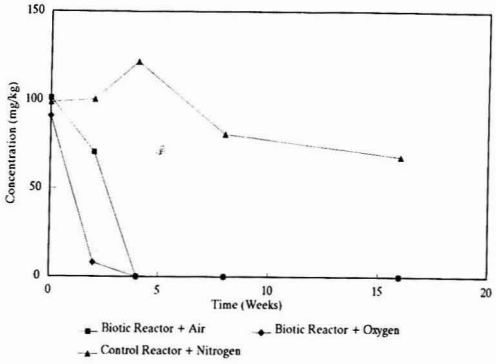

FIGURE 6. Phenanthrene concentration profiles during biotreatment of API oil separator sludge.

ca. 220 mg/kg in each reactor and are therefore well above the BDAT treatment standard of 42 mg/kg. During the initial 2 week treatment period naphthalene concentration decreased from 220 mg/kg to 8 mg/kg in both biotic reactors. By contrast, only a slight change of naphthalene concentration (220 mg/kg to 200 mg/kg) was observed in the sterile control during this time interval. It can therefore be concluded that the drastic drop in naphthalene levels in both biotic reactors is due to biodegradation and not the result of stripping losses. Within 4 weeks, naphthalene was no longer detectable in the biotic treatments. Naphthalene concentration levels dropped significantly from 200 mg/kg to 77 mg/kg between treatment weeks 2 and 4 in the control reactor. After 4 weeks of treatment, the naphthalene concentration continued to decrease slowly (at the same rate as during the first 2 weeks) until it reached non-detectable levels at week 16. It is not entirely clear whether the observed naphthalene loss in the sterile nitrogen sparged control is merely due to stripping or is additionally caused by anaerobic (or aerobic) biodegradation processes (see discussion below).

Phenanthrene

The initial phenanthrene concentration was around 100 mg/kg and is therefore approximately three times higher than the BDAT treatment standard of 34 mg/kg. Phenanthrene was completely biodegraded in both biotic reactors after 4 weeks of treatment (see Figure 5). The phenanthrene biodegradation rate in the biotic oxygen reactor was significantly higher than in the biotic air reactor during the first 2 weeks of treatment. This observation can be explained by the fact that the biotic air reactor was severely oxygen-limited during the first 8 treatment days (see DO above) while the biotic oxygen reactor was characterized by high levels of DO during the entire treatment period. It is therefore likely that easily degradable organics are preferably biodegraded during the initial oxygen-limited phase in the biotic air reactor resulting in a delayed biodegradation of the more slowly degrading (or available) PNAs in the waste. No significant change of phenanthrene concentrations was observed in the sterile control during this four week time period. This is indicative of the fact that the phenanthrene loss in both biotic reactors is due to biodegradation processes and not stripping.

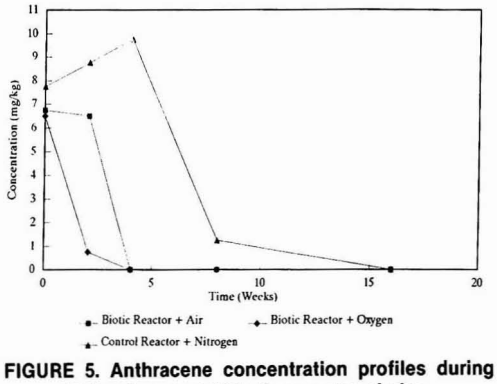

FIGURE 5. Anthracene concentration profiles during biotreatment of API oil separator sludge.

Anthracene

The anthracene concentration profiles presented in Figure 6 resemble in principle the phenanthrene profiles discussed above with the exception that anthracene reached non-detectable (zero mg/kg) levels at the end of the experiment in the sterile control reactor. The initial anthracene concentration in each reactor was around 7 mg/kg which is significantly below BDAT (28 mg/kg) levels. Consequently, anthracene is of no regulatory concern in this particular waste. Anthracene was completely biodegraded in both biotic reactors after 4 weeks of treatment. As in the case of phenanthrene, the initial anthracene biodegradation rate was significantly higher in the biotic oxygen reactor than in the biotic air reactor (see discussion above). In the sterile control, anthracene levels increased slightly (sampling and analysis errors?) during the first 4 treatment weeks and decreased drastically therefore reaching non-detectable concentrations at the end of the experiment.

Pyrene

Pyrene concentration levels (see Figure 7) did not change significantly in the control and biotic oxygen reactor during the first 8 weeks of treatment but exhibited an apparent 50% increase during the last 8 weeks treatment period. It is not clear whether the concentration increase is due to analytical and sampling inaccuracies or reflects an increase of extraction efficiency for pyrene as a result of sludge weathering (biotreatment). A slight decrease of pyrene from an initial 12 mg/kg to 8 mg/kg after 8 weeks was observed in the biotic air reactor reflecting a 30% loss possibly due to biodegradation (large uncertainty). The drop in pyrene concentration (from 8 mg/kg to 4 mg/kg) during the last 8 weeks of treatment is not related to biodegradation but to the change in total solid concentrations (from 10% to 5%) in this reactor (see explanation above). Since most of the PNAs are expected to reside on the sludge solids, a decrease of solid concentrations is related to

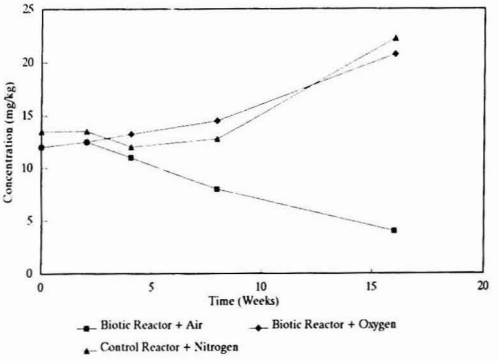

FIGURE 7. Pyrene concentration profiles during biotreatment of API oil separator sludge.

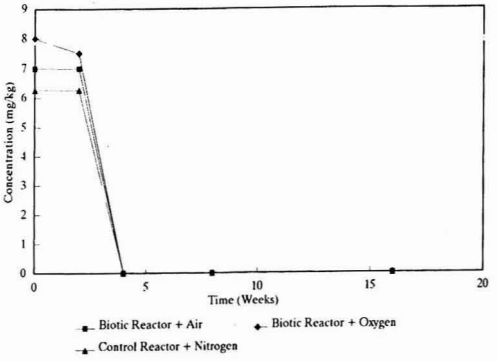

FIGURE 9. Benzo(a)pyrene concentration profiles during biotreatment of API oil separator sludge.

a decrease of PNA levels. In fact, the pyrene concentration based on the mass of sludge solids (mg pyrene/kg solids) is the same at week 8 and 16 in the biotic air reactor indicating the absence of biological loss processes. Finally, the initial pyrene level (12 mg/kg) is below BDAT (36 mg/kg) and therefore pyrene is of no regulatory concern in this particular sludge.

Chrysene

Figure 8 depicts the concentration profiles for chrysene starting at an initial concentration of approximately 15 mg/kg which is equal to the BDAT level for this particular PNA. While no significant changes in chrysene concentrations were detected in the poisoned control, this PNA was completely biodegraded in the biotic air reactor in 4 weeks while it took 16 weeks for chrysene to disappear in the biotic oxygen treatment.

Benzo(a)pyrene

Benzo(a)pyrene is the largest (5 aromatic rings), most water insoluble, least volatile (see Table 2) PNA studied in these three experiments. Nevertheless, benzo(a)pyrene apparently was lost (removed) completely in *all* three reactors between treatment week two and four (see Figure 9). The concentration of this PNA remained constant at the initial 7 mg/kg (BDAT 12 mg/kg) during the first two treatment weeks. Since benzo(a)pyrene is less volatile than pyrene and chrysene both of which did not disappear in the inhibited control, it can be concluded that some biodegradation process must be responsible for the loss of benzo(a)pyrene in the control reactor (see also discussion below).

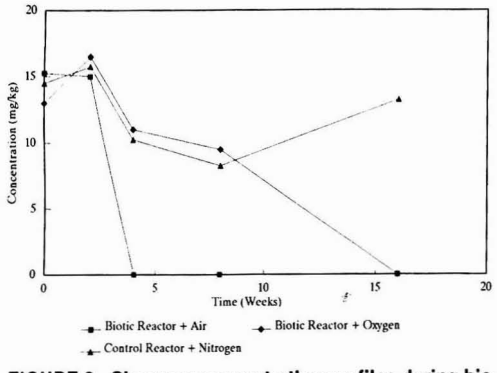

FIGURE 8. Chrysene concentration profiles during biotreatment of API oil separator sludge.

Evidence of PNA Biodegradation Reported in the Literature

Only few literature data are currently available on the fate of PNA compounds during the biotreatment of oily refinery sludges in a slurry phase bioreactor. Vail [*11*] reported the complete disappearance of all BDAT PNA compounds including pyrene during slurry biotreatment of oily separator type sludge in a refinery field pilot. Total PNAs were reduced from 2,710 mg/kg to 0.62 mg/kg during the 16 week treatment period. Pyrene concentrations dropped from an initial 540 mg/kg to 0.02 (?) mg/kg at the end of the treatment. There are, however, some doubts regarding the analytical accuracy and precision since neither methods nor detection limits for the PNA analyses were reported. The majority of the remaining publications deal with the fate of PNAs from refinery sludges after application on soils for landfarming purposes [*2, 8–10*].

Bossert *et al.* [*2*] conducted a 1280 day (3.5 years) laboratory landfarming study for the biotreatment of DAF sludge from a petrochemical plant effluent treatment system. Seven sludge applications during a 920-day active disposal period were followed by a 360-day inactive closure period with no further sludge application. Only 6.9%, 0.2% and 3.1% of the total amount of added anthracene, phenanthrene and chrysene, respectively, remained after the 1280 day treatment period indicating significant biological removal of these PNAs. By contrast, 85.6% and 55.6% of the total amounts of applied pyrene and benzo(a)pyrene remained in the soil at the end of the treatment period indicating an increased resistance towards biodegradation of these two PNAs.

The American Petroleum Institute (API) published a report [*8*] on the landtreatability of listed refinery wastes. A composite of API separator sludges, DAF float, and slop oil emulsion solids were applied at three different loading rates (2%, 4%, and 8% O&G by weight in soil) in two different soils (Kidman Sandy Loam and Nunn Clay Loam) in laboratory batch reactors (beakers). The biodegradation half-lives were computed assuming first order degradation kinetics. The degradation half-lives for anthracene, phenanthrene, pyrene, and chrysene in the different treatments ranged from <9–53 days, <6–43 days, 32–50 days, and 41–77 days, respectively. The half life for benzo(a)pyrene was not reported.

The biodegradation of weathered PNAs was studied in laboratory microcosms using soil samples from the Texaco landfarm (Anacortes, WA) which had received various oily refinery wastes for more than 30 years [*9*]. It was found that only very

slow biodegradation occurs even for more easily degradable PNAs such as phenanthrene. This observation may be explained in terms of the reduced bioavailability (see also below) of these PNAs in a weathered oil/soil matrix.

The Petroleum Association for Conservation of the Canadian Environment (PACE) conducted a study to investigate the fate of polynuclear aromatic hydrocarbons in refinery waste applied to soil [*10*]. Despite intensive analytical efforts (cleanup procedures, etc.) in quantifying the PNAs in the oil/soil matrix, high data variability precluded the accurate estimation of biodegradation rates for most high molecular weight PNAs (>3 rings) during the 200 day monitoring period.

Wang *et al.* [*6*] studied the effect of bioremediation on PNA residues in a simulated diesel oil spill in an outdoor lysimeter unit. The initial soil concentrations of naphthalene, phenanthrene, and pyrene were 8.3 mg/kg, 88.5 mg/kg, and 26.5 mg/kg, respectively. After 12 weeks of bioremediation, naphthalene was no longer detected and only 1.2% and 3% of the initially added amounts of phenanthrene and pyrene remained in the soil.

A number of publications deal with the biodegradation of PNAs which have been added in pure form (or mixtures) to soils in the laboratory. It must be pointed out that the artificial addition of specific PNAs may not accurately simulate the biodegradation characteristics of a weathered oil/soil matrix which contains a number of entrapped PNAs. In fact, Werner [*7*] showed that a number of PNAs artificially added to sand biodegraded successfully (85%) during a 90 day experiment while PNAs present at similar concentration levels in a weathered gas plant waste degraded at most 33% during a 55 day treatment period. Higher ring PNAs such as pyrene, chrysene and benzo(a)pyrene did not biodegrade at all in the gas plant waste, whereas more than 50% degradation was observed for these PNAs when artificially added to sand. This difference in biodegradation of similar PNAs in different soils may also be caused by differences in adsorption of the PNAs to the soil matrix. The gas plant waste consisted of a soil rich in clays which are known for their strong PNA sorption characteristics. By contrast, sandy soils exhibit only weak adsorption for PNAs which in turn are more bioavailable for microbial attack.

Sims *et al.* [*4*] studied the fate of PNAs which were added to two different soils and subjected to bioremediation treatment. Around 30% of the added naphthalene (initial concentration 100 mg/kg soil) was found to evaporate, whereas no significant evaporation losses were detected for higher ringed PNAs. The 95% confidence intervals for the biodegradation half-lives of naphthalene, anthracene, phenanthrene, pyrene, chrysene, and benzo(a)pyrene in Kidman sandy loam (McLaurin sandy loam) were found to be 1.7–2.7 (1.7–3.4) days, 106–182 (42–61) days, 13–18 (27–53) days, 193–408 (131–408) days, 289–533 (257–866) days, and 239–462 (178–315) days, respectively.

The Petroleum Association for Conservation of the Canadian Environment (PACE) published a report regarding the persistence of PNAs in soil [*15*]. Eight PNAs were added to a soil and bioremediated for a 400 day time period. Naphthalene disappeared in less than 12 days from the soil. Assuming first order kinetics (exponential decay), degradation half-lives for anthracene, phenanthrene, and pyrene ranged for different soil loading rates from 17–45 days, 9.7–14 days, and 48–58 days, respectively. Observing zero order decay (linear) for both chrysene and benzo(a)pyrene, the degradation half-lives were 224–328 days and 218–347 days, respectively.

A few investigators studied the mineralization of individual PNAs by using ^{14}C radio-labeled compounds and measuring the production of $^{14}CO_2$ during microbial biodegradation. Evolution of $^{14}CO_2$ was found to be negligible during the 145 day incubation of ^{14}C-benzo(a)pyrene while a significant fraction (15%) of ^{14}C was recovered in $^{14}CO_2$ as a result of the biodegradation of anthracene during a 91 day mineralization experiment [*15*]. By contrast, up to 7% of the added ^{14}C was recovered as $^{14}CO_2$ during the 145 day incubation of ^{14}C-benzo(a)pyrene after an initial acclimation period of approximately 80 days [*10*]. Sims *et al.* [*4*] did not detect any ^{14}C mineralization of 7,12-dimethylbenz(a)anthracene. Since the parent PNA compounds are often labeled at only one specific carbon within the molecule, it is possible that an unlabeled fraction of the molecule is biodegraded while the labeled recalcitrant molecular fraction remains unaffected. Liquid culture experiments using ^{14}C-labeled PNAs and mixed IGT (Institute of Gas Technology) bacterial enrichments indicated that 37%, 27% and 6% of phenanthrene, anthracene, and benzo(a)pyrene were biodegraded as measured by $^{14}CO_2$ evolution [*16*].

It was pointed out earlier [*7*] that limited PNA bioavailability can be the cause for slow or limited PNA biodegradation. The Institute of Gas Technology and the Gas Research Institute [*17*] studied the biodegradation of soil PNAs in a soil slurry and compared the experimental results with the biodegradation of these PNAs in methanol extracts (diluted in water 1% v/v) from the same soil. It was found, that both biodegradation extent and kinetics were significantly higher in the soil methanol extract culture than in the soil slurry bioreactor. This suggests that PNA biodegradation in soils can be reduced due to limitations in PNA bioavailability.

Anaerobic Biodegradation versus Stripping

Three out of the six studied PNAs, namely naphthalene, anthracene and benzo(a)pyrene, completely disappeared in the sterile nitrogen sparged control reactor after 16 weeks while no significant changes were detected in pyrene and chrysene concentrations. Phenanthrene concentrations decreased from an initial 100 mg/kg to 68 mg/kg. The observed losses of the above PNAs could be either due to stripping (evaporation) or anaerobic/aerobic biodegradation in the presence of microbial inhibitors. In order to estimate which loss process is most likely for a particular PNA, the relative stripping potential of each PNA can be estimated as follows.

In general, the rate of stripping for a specific PNA will be related to its volatility (vapor pressure), its maximum aqueous solubility, its concentration on the sludge solids, and its maximum solubility in the oil matrix. High vapor pressures, large aqueous solubilities and high sludge solids concentrations will favor PNA stripping while large maximum PNA solubilities in the oil matrix will reduce the PNA stripping potential. Using these general assumptions and the physical data in Table 2, it is possible to estimate the relative stripping rates of each PNA qualitatively. It is expected that the relative stripping rates would be highest for naphthalene and would decrease in the order given in Table 2 reaching the lowest value for benzo(a)pyrene. Even though the disappearance of naphthalene and possibly phenanthrene and anthracene could be attributed to stripping, it is extremely unlikely that benzo(a)pyrene was stripped from the control reactor. Since the two bacterial inhibitors were ineffective in completely killing all aerobic heterotrophs (see results above) it is possible that some microbial degradation processes are responsible for the observed losses of naphthalene, phenanthrene, anthracene, and benzo(a)pyrene. It has been shown that certain monoaromatics [*18–21*] can be degraded under anaerobic (denitrifying) conditions where nitrate serves as an electron acceptor. Since no nitrate was added in the control reactor, it is unlikely the above four PNAs were biodegraded anaerobically. It is more likely that the nitrogen used for sparging contained trace amounts of molecular oxygen which could stimulate aerobic biodegradation at a slow rate in the control reactor. According to product specifications, the nitrogen gas used in these experiments could contain up to 5 ppmv molecular oxygen as a trace contaminant. Indeed it was found that the dissolved oxygen level in the control reactor was slightly above 0 mg/L at 0.1–0.5 mg/L during the entire treatment period. For future

experiments involving anaerobic stripping controls it is therefore recommended that any trace molecular oxygen be removed from the sparging gas via a gas purifier (e.g. Oxisorb) prior to entry into the reactor.

Bioavailability Considerations

The only compound which did not exhibit a complete loss in either biotic treatment is pyrene. It has been postulated that some lipophilic compounds are not biodegraded since they are not available for microbial attack. The lipophilic compound is locked up in the oil/soil matrix of the sludge and consequently has reduced bio-availability due to mass-transfer (from the oil to the water phase) limitations [*22, 23*]. Even if the compound dissolves in the water phase, the compound concentration may not be high enough to induce microbial enzyme production necessary for subsequent biodegradation. The octanol:water partition coefficient K_{ow} ($K_{ow} = C_0/C_w$, where C_0 and C_w are the equilibrium compound concentrations in the octanol and water phase, respectively [*24*]) is a measure of the lipophilic character of a specific compound. The larger the K_{ow} value, the more lipophilic and less water soluble is the compound under investigation (see Table 2).

If one attempts to explain the absence of pyrene biodegradation in terms of possible bio-availability limitations one has to realize that both chrysene and benzo(a)pyrene are significantly less bioavailable than pyrene as reflected in their larger K_{ow} values and reduced aqueous solubilities (Table 2). But both chrysene and benzo(a)pyrene are biodegraded in either biotic treatment. It could therefore be hypothesized that pyrene is inherently less or slower biodegradable as was reported by a number of investigators [*2, 4, 7*]. On the other hand, Heitkamp *et al.* [*3*] isolated a *Myobacterium* culture which was able to mineralize 5% of the added pyrene after only 6 hours and reached a maximum of 48% mineralization within 72 hours. In addition, 6% of ^{14}C was recovered in $^{14}CO_2$ during the biodegradation of added ^{14}C-pyrene in the mineralization assay performed on acclimated seed used for this study. In summary, it is not clear whether the observed lack of significant pyrene biodegradation is due to inherently slow biodegradation rates or limited bio-availability.

SUMMARY AND CONCLUSIONS

1. Naphthalene, anthracene, phenanthrene, chrysene and benzo(a)pryene are completely biodegraded in either aerated or oxygen sparged biotic treatment.
2. The observed limited (30%) pyrene biodegradation is either the result of an inherently slow pyrene biodegradation rate or is due to limitations in pyrene bio-availability.
3. The losses of naphthalene, phenanthrene, anthracene and benzo(a)pyrene in the nitrogen sparged inhibited control cannot be due to evaporation alone. It is possible that either aerobic or anaerobic biodegradation processes are responsible for the observed losses of these PNAs in the control reactor.

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Bioremediation of Soils Contaminated with Bis-(2-ethylhexyl) Phthalate (BEHP) in a Soil Slurry-Sequencing Batch Reactor

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A bench-scale study was conducted to assess the feasibility of bioremediating phthalate contaminated soil from a polyvinyl chloride manufacturing operation in New Jersey. A bench-scale slurry reactor study which utilized ^{14}C-labeled bis-(2-ethylhexyl) phthalate (BEHP) demonstrated that approximately 50 to 60% of the carbon in BEHP was mineralized directly to CO_2 by indigenous microbial flora, while the remaining 40 to 50% was converted into cell mass. Additional bench-scale studies were conducted in Soil Slurry-Sequencing Batch Reactors (SS-SBR) to evaluate the impact of basic biotreatability parameters (e.g., nutrient requirements and seed acclimation) on the bioremediation of soil contaminated with high levels of BEHP and total petroleum hydrocarbons (TPH). Treatment efficiencies of greater than 96% for both BEHP and TPH were observed in slurry reactors supplemented with nutrients (e.g., 1.4 to 2.0 g N per kg dry soil and 0.16 to 0.4 g P per kg dry soil). BEHP concentrations were reduced from initial levels as high as 24,000 mg/kg to less than 230 mg/kg and TPH concentrations, from 8,000 mg/kg to 160 mg/kg.

INTRODUCTION

Periodic flooding of a separator pit at a northern New Jersey manufacturing site engaged in polyvinyl chloride (PVC) compounding and garden hose and PVC pellet manufacturing caused bis-(2-ethylhexyl) phthalate (BEHP, also known as di-(2-ethylhexyl) phthalate or DEHP) to be spread over the ground surface and contaminate the soils. Analysis of soil samples at the site for base/neutral extractable fractions (base/neutrals) and total petroleum hydrocarbons (TPH) indicated the presence of phthalates (specifically BEHP) in the range of 10 to 25,000 mg/kg and TPH in the range of 10 to 2,000 mg/kg. The estimated volume of contaminated soil to be remediated was approximately 2,300 cubic meters. Groundwater testing for volatile organics, base/neutrals, and petroleum hydrocarbons show only limited contamination with no volatiles and low levels of BEHP and TPH present. There was no evidence of PCB or pesticide contamination at the site.

A preliminary cost analysis suggested that on-site bioremediation in slurry reactors would be 1.5 to 2 times more cost effective than excavation and that the cost for incineration would be prohibitive. The study described herein was conducted because of concerns raised by the regulatory agency that BEHP was nonbiodegradable in soils contaminated with both BEHP and TPH and because data were needed to prepare a preliminary design for the periodically operated Soil Slurry-Sequencing Batch Reactor (SS-SBR) system. Results obtained from a literature review suggested that BEHP may be recalcitrant under anaerobic conditions but that it was biologically degradable in aerobic systems [*1, 2, 3, 4, 5*]. While the results from the aerobic studies strongly suggested that a microbial consortium capable of degrading BEHP would develop in soil slurry reactors, no direct evidence was found in the literature.

BACKGROUND ON PERIODICALLY OPERATED PROCESSES

Reactor based periodic systems consist of one or more identically operated tanks that provide for the time sequencing of two or more processes or operations (e.g., equalization, biological conversions and clarification) during a complete reactor cycle. Each cycle may include up to five periods: fill, react, settle, draw, and idle. Some periodic systems (e.g., those utilizing suspended cultures or slurried soils) employ mixing and/or aeration to keep the microorganisms in suspension during fill and react. Mixing and/or aeration are normally turned off to allow for clarification during the settle period in suspended growth systems. This allows a clear supernatant to be removed from the reactor during draw and an active culture to be maintained within the reactor for the beginning of the next cycle. A settle period is not necessary for a fixed film system and inappropriate for many slurry reactor systems because the resuspension of settled slurries may be difficult.

The Sequencing Batch Reactor (SBR)

Conventional suspended growth SBRs are currently being used extensively for the treatment of domestic [6], industrial, and hazardous wastewaters [7, 8]. The SBR is uniquely suited for the selection and enrichment of desired microbial populations because of the ease with which a diverse array of operating conditions and selective pressures can be implemented [9]. The convenience in its operation stems from the time-oriented nature of the process. Specifically, each tank in the SBR system is filled during a distinct period of time. During this fill period, organism selection can be controlled by manipulating the actual specific growth rates of the microbes and by regulating the oxygen tension in the reactor (e.g., from anaerobic to anoxic to aerobic). After a tank is filled, treatment continues with the SBR operating as a batch reactor. During this react period, further selective pressures are applied by controlling the length of time the organisms are subjected to starvation conditions. These same concepts have been used in the design and operation of soil based reactor systems.

The Soil Slurry-Sequencing Batch Reactor (SS-SBR)

Functionally, the SS-SBR system is simply a set of tanks that are operated on a fill and draw basis. As with the SBR system, each tank is filled during a discrete period of time and then operated as a batch reactor during react. A notable difference between the SBR and the SS-SBR is that the time required for react in the SS-SBR is typically in the order of days as opposed to hours for the SBR. There are, of course, a number of other obvious differences. For example, the treatment of soils in reactors requires significant consideration of materials handling. Screening and pre-mixing tank systems are needed to remove oversized materials and to prepare a slurry prior to addition to the SS-SBR. Final dewatering of the treated soil slurry, either by mechanical means (e.g., filter presses, vacuum drum filters, centrifugation) or by natural evaporation and percolation, must be considered. In addition, laboratory studies for the SS-SBR must be conducted in reactors which allow for the determination of the desired soil to water ratio, nutrient requirements, contaminant destruction rates, volatilization rates, and the need for co-substrates.

Several possible SS-SBR operating strategies can be employed dependent on the nature of the contaminants, the physical properties of the soil and slurry, and on-site factors such as the availability of process water and the need for recycle. For example, when process water is readily available and extensive additional treatment of the effluent slurry water will not be required, a complete reactor cycle includes only three operating periods: fill—time during which slurry is added to the reactor; react—period where most of the contaminants are biologically removed; and draw—time in which the treated slurry is withdrawn from the reactor. After draw, an amount of the treated slurry ranging from less than 5% to over 95% can remain in the reactor as an acclimated seed material for the next cycle. During all periods, agitation and aeration, often provided with a mechanical mixer, are used to keep the reactor contents mixed. An activated carbon air scrubber coupled to a blower system may be used to provide a continuous supply of fresh air in the reactor headspace. If process water is not readily available, system operation must be modified to include the immediate reuse of process water. This water could either be captured during slurry dewatering or obtained as a supernatant by adding a short quiescent settle period to the reactor cycle before draw.

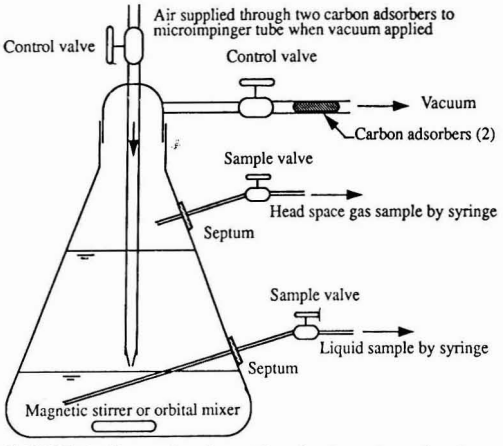

FIGURE 1. General schematic of a bench-scale slurry reactor.

OBJECTIVES

The specific objectives of a two phase slurry reactor study were as follows:

- Evaluation of the impact of basic biotreatability parameters (e.g., requirements for nutrients, supplemental substrates, and seed acclimation) on the biodegradation of BEHP. This evaluation was conducted in the first phase in a series of five soil slurry reactors.
- Development of additional information on nutrient requirements and determine BEHP and TPH removals in reactors containing treated slurry from the previous cycle. These determinations were conducted in the second phase in a series of five additional soil slurry reactors.

MATERIALS AND METHODS

Experimental Apparatus

A general schematic of the bench-scale slurry reactors used in the phase 1 and phase 2 studies is shown in Figure 1. The reactors were mixed by placement on a variable speed orbital shaker table. Air flow (at 2 mL/min) into each reactor was controlled by a vacuum regulator and needle valve. Each day the water lost to evaporation was made up with distilled water.

Soil Preparation

The contaminated soil, composed primarily of a silty sand

Table 1 Initial Phase 1 Slurry Reactor Conditions

Reactor	A	B	C	D	E
10% Slurry (mL)	300	300	300	300	300
Nitrogen (N), added as NH_4Cl (mg N/L)	0	10	10	10	0
Phosphorus (P), added as K_2HPO_4 and KH_2PO_4 (mg P/L)	0	11	11	11	0
Acclimated Seed (mL)	0	0	25	25	0
Succinate (g/L)	0	0	0	1	0
Initial pH	7.87	7.87	7.87	7.87	1.93

Table 2 Initial Phase 2 Slurry Reactor Conditions

Reactor	A2	B2	C2	D2	E2
Contaminated Soil (g)	37	18.5	18.5	18.5	37
Nitrogen (N), added as NH_4Cl (mg N/L)	250	125	125	125	0
Phosphorus (P), added as K_2HPO_4 and KH_2PO_4 (mg P/L)	50	15	15	15	0
Acclimated Seed (mL)	0	150	150	150	0
Initial pH	7.06	6.70	6.06	6.80	2.00

material with a dark grayish green color, was thoroughly mixed in the laboratory in a single large pan. A 1 kg portion of the mixed soil was placed in a 4 L beaker, mixed with tap water to form a slurry, screened through a #10 sieve, and collected into another 4 L beaker. This screened slurry was stored at 3°C and served as the source of contaminated soils for the phase 1 reactors. A second portion (approximately 0.5 kg) of mixed soil was screened directly (i.e., without slurrying) through a #10 sieve. The screened soil was placed in a sample jar and stored at 3°C and served as the source of contaminated soils for the phase 2 reactors.

PAM Medium

Phosphate Ammonia Media (PAM) was mixed with screened soil to test for nutrient requirements. The PAM medium, which was used for ^{14}C label studies, contained 16.95 g K_2HPO_4, 7.26 g KH_2PO_4, 3.96 g $(NH_4)_2SO_4$, and 0.098 g $MgSO_4$ in each liter of solution.

Phase 1 Reactors

Five slurry reactors having an average initial solids concentration of approximately 10% (i.e., 100 grams of dry soil per liter of slurry) and an initial slurry volume of 300 mL were established as described in Table 1. The no action alternative, Reactor A, contained only contaminated soil and tap water. Reactors B, C, and D were designed to test nutrient, seed, and supplemental substrate requirements respectively. Each of these reactors had the same initial concentrations of nitrogen (N) and phosphorus (P). 10 mg/L of nitrogen was added as NH_4Cl and 11 mg/L of phosphorus was added from a solution containing 30.9 mg/L K_2HPO_4 and 24.1 mg/L KH_2PO_4. 25 mL of a TPH acclimated slurry (obtained as a 10% slurry from a slurry reactor treating a diesel fuel contaminated soil) were added to Reactors C and D and 1 g/L of succinic acid was added to Reactor D. The control, Reactor E, was acidified so that volatilization and non-biological processes could be assessed.

Phase 2 Reactors

Five slurry reactors were set up according to the conditions summarized in Table 2. Reactor A2 and E2 (the control) contained 37 g of sieved (#10 mesh) contaminated soil while Reactor B2, C2, and D2 received a blend of 18.5 g of sieved contaminated soil and 150 mL of slurry from Reactors B, C, and D respectively. Nitrogen was added as NH_4Cl and the phosphorus was added from a solution containing K_2HPO_4 and KH_2PO_4. The average initial solids concentration ranged from between 8 and 12% in an initial slurry volume of 300 mL.

Sampling of Phase 1 and Phase 2 Reactors

Because of the limited volume of slurry in each reactor, replicate samples were not taken. When samples were withdrawn, the new liquid level of each reactor was marked to indicate the new operating volume. Samples were withdrawn from each reactor for routine analysis of solids content, pH, BEHP, and TPH. Before sampling the reactors were removed from the orbital shaker and a large magnetic stir bar was placed in each reactor flask. The flasks were placed on a magnetic stirrer and the contents mixed at high speed while sampling with a 10 mL wide mouth pipette. A pH probe was inserted into each reactor for pH measurement. Samples for BEHP and TPH analyses were placed in a 22 mL screw cap vial with Teflon lined septa and immediately extracted with solvent. After sampling, the flasks were removed from the stir plate and placed back onto the orbital shaker table. Oxygen Uptake Rate (OUR) measurements were obtained on 2.2 mL grab samples collected one or two times per week.

After approximately 30 days of phase 1 operation, the granular activated carbon (GAC) adsorption tubes shown in Figure 1 were removed from the reactors and replaced with new GAC tubes. The second set of GAC tubes were removed at the end of the study. Because the results indicated that the BEHP and TPH in these slurries were not volatile, the GAC traps from the phase 2 reactors were not sampled.

^{14}C Studies

^{14}C-label studies were conducted using 250 mL Bellco biometer flasks with side arms containing 5 mL of 0.1 N KOH to trap evolved CO_2. Two flasks contained approximately 2.5 grams of soil and 50 mL of tap water. A second pair of flasks contained 2.5 grams of soil, 25 mL tap water, and 25 mL of PAM. At the beginning of the test each flask was spiked with 1.5 μCi (189.9 nmol) of uniformly ^{14}C-labeled BEHP (Sigma Chemical Co., St. Louis, Mo). After spiking, the flasks were stoppered, placed on an orbital shaker table operated at 90 rpm, and incubated at room temperature for 13 days. At one to two day intervals the KOH was drawn off, mixed with scintillation cocktail and analyzed for ^{14}C activity in a scintillation counter. After each sampling, the side arm of each reactor was refilled with 5 mL of fresh 0.1 N KOH. The study was used to evaluate nutrient limitations.

ANALYTICAL METHODS

The percent moisture content on the soil samples and the solids concentrations of the slurries were measured following the procedure in Method 2540-B of Standard Methods [*10*]. OUR was measured using a Gilson Model K-1C Oxygraph with a 2.2 mL sample cell. The pH of the soils and slurries was measured electrochemically in accordance with EPA Method 9045 [*11*]. ^{14}C-CO_2 was measured by trapping CO_2 in potassium hydroxide and then counting ^{14}C-CO_2 in a liquid scintillation counter.

BEHP and TPH levels in screened soil samples, initial slurries and in slurry samples from each reactor were determined by carbon disulfide (CS_2) extraction followed by gas chromatography (GC). The CS_2 extraction/GC procedure was sim-

ilar to that described in the California Leaking Underground Storage Tank (LUFT) Manual [12], Appendix D, Section A, for Diesel Fuel. The CS_2 extraction/GC method used for BEHP and TPH for soil or slurry samples was as follows: 3 to 8 grams of soil or 10 mL of slurry were placed in a tared 15 mL vial. For soil samples, 10 mL of double distilled water was added to the vial and the vial capped and vortexed for approximately 30 seconds to form a slurry. The vial was then vortexed for approximately 10 seconds after adding 200 μL of a matrix spike recovery standard (50 g/L Di-n-butyl phthalate (DNBP) in methanol). After vortexing, 5 mL of HPLC grade, glass distilled CS_2 was added to the vial. The vial was capped, vortexed for 10 seconds, vigorously shaken for 60 minutes using a mechanical wrist action shaker, and then centrifuged at 1000 rpm for 5 minutes to separate the water from the CS_2 layer. 1.9 mL of the CS_2 extract was withdrawn from the bottom of the vial and transferred to a 2 mL autosampler vial which was sealed with a Teflon lined septa and stored in a freezer until analysis.

GAC adsorption tubes were extracted with CS_2 as follows: 150 mg of GAC (mass of activated carbon per trap) were placed in a 2 mL vial to which 1.25 mL of CS_2 was added. Each vial was then sealed with a Teflon lined screw cap and placed on a shaker table for 24 hours. 1 mL of extract was then transferred to a 2 mL GC autosampler vial for injection into the GC.

A 2 μL sample of the CS_2 extracts was injected into a Varian 3400 Gas Chromatograph equipped with an autosampler and a PE Nelson model 1020 personal integrator. A Petrocol B (Supelco, Bellefonte, PA), 0.51 m long $\times$ 3.175 mm i.d., stainless steel column was used for the analysis. The column oven temperature was increased linearly at 5°C/min from 140°C to 260°C where it was held for 6 min. Both the packed column injector and the Flame Ionization Detector (FID) were operated at 260°C.

Quantification of BEHP, TPH, and DNBP (the matrix spike used for recovery determinations) were made by external calibration. Stock standards of BEHP and DNBP were prepared by dissolving 5 g of pure compound (99+%, Supelco, Bellefonte, PA) in methanol. Calibration standards of 100, 500, 1,000 and 5,000 mg/L were prepared from these stocks and used to construct four point calibration curves. For TPH, a stock standard containing a mix of four paraffins (C22, C24, C28, and C32 each at 12.5 g/L) dissolved in CS_2 was used to prepare calibration standards. Three concentration levels (125, 625, and 1,250 mg/L each) were used to construct a three point calibration curve for TPH quantification. Distilled water blanks were carried through both the extraction and GC procedures to determine background contamination levels.

Total oil and grease in screened soil and slurry samples were determined by Soxhlet extraction and gravimetric analysis [11]. After weighing, these extracts were suspended in 20 mL of CS_2 and analyzed for BEHP and TPH by GC as described above. Analyses for base/neutral extractable fractions using EPA Method 8270-GC/MS [11] for a soil sample, an initial slurry sample, and treated slurry samples from each reactor were also conducted.

PRESENTATION OF RESULTS

The phase 1 soil slurry batch reactors were operated for 90 days and the phase 2 reactors, for 24 days. The feasibility of TPH and BEHP degradation in slurry reactors was shown in phase 1. The results from phase 2 demonstrated both that appropriate levels of nitrogen and phosphorus markedly reduce the lag time and increase the removal rate of both BEHP and TPH in unacclimated slurries and that appreciable BEHP and TPH degradation rates can be maintained in slurry reactors that carry-over acclimated seed from one operating period to the next.

Phase 1 Reactors

The average BEHP and TPH (exclusive of BEHP) concentrations on a dry soil weight basis in six screened soil samples as measured using the LUFT manual procedures [12] (CS_2 extraction/GC) were 16,500 mg/kg ($\pm$1530) and 6,550 mg/kg ($\pm$720), respectively. Percent recoveries of the matrix spike for these samples ranged from 78 to 93%. The average BEHP and TPH concentrations in these samples as measured by GC after Soxhlet extraction were 18,710 ($\pm$290) mg/kg and 7,000 ($\pm$200) mg/kg, respectively. The corresponding concentration obtained using EPA Method 8270 [11] for BEHP was 10,800 mg/kg.

After slurrying, the average BEHP and TPH concentrations, on a dry soil weight basis (via CS_2 extraction/GC), in six replicate initial slurry samples were 29,590 mg/kg ($\pm$5140) and 10,390 mg/kg ($\pm$930), respectively. Percent recoveries of the matrix spike for these samples ranged from 85 to 91%. The average BEHP and TPH concentrations in initial slurry samples as measured by GC after Soxhlet extraction were 19,990 ($\pm$1900) mg/kg and 7,030 ($\pm$670) mg/kg. The corresponding concentration obtained using EPA Method 8270 [11] for BEHP was 19,200 mg/kg. The measured increase in contaminant concentrations after slurrying were believed to be due to the settling out and loss of uncontaminated course sand during the slurrying process. These results indicated that most of the contamination was confined to the finer fractions (fine sand, silt and clay) of the soil. It was this finer fraction that was distributed to the phase 1 reactors for biodegradation testing.

During the first month of operation, there was essentially no removal of BEHP and very little removal of TPH in any of the reactors. Studies were then undertaken to determine if additional nutrients should be applied to the reactors. One set of duplicate biometer flasks contained soil and tap water spiked with ^{14}C-labeled BEHP. A second set of duplicate biometer flasks contained soil mixed with PAM and also spiked with ^{14}C-labeled BEHP. As can be seen from Figure 2, the average production of ^{14}C-CO_2 from the reactors which contained the PAM enriched medium was appreciably greater than those which contained tap water. In fact, between 50 and 60% of the ^{14}C labeled carbon in BEHP was mineralized directly to ^{14}C-CO_2 by indigenous microbial flora in less than 14 days. Additional radiolabeled experiments conducted on BEHP degrading cultures isolated from the soil (data not shown) indicated that as much as 40 to 50% of the carbon in BEHP was incorporated into cell mass. As a result of this study, additional nutrients were supplied to Reactors B, C and D (110

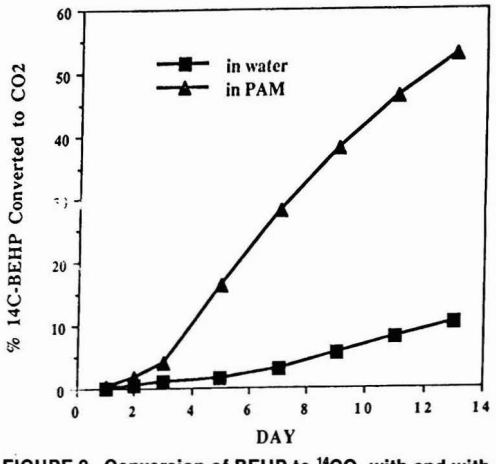

FIGURE 2. Conversion of BEHP to $^{14}CO_2$ with and without nutrient addition.

mg N/L as NH_4Cl and 18 mg P/L as 50.6 mg/L K_2HPO_4 and 39.4 mg/L KH_2PO_4) after approximately 45 days of operation. Nitrogen (110 mg N/L as NH_4Cl) was also accidentally added to Reactor A on the same day. After 60 days of operation, an additional 50 mg N/L of NH_4Cl and 20 mg P/L (56.2 mg/L K_2HPO_4 and 43.8 mg/L KH_2PO_4) were supplied to Reactor C, and 25 mg/L of nitrogen and 31 mg/L of phosphorus, to Reactor D.

After the reactors were supplemented with additional nitrogen and phosphorus, the BEHP and TPH concentrations in Reactors B, C and D decreased significantly and the OURs increased. By the end of the second month, the BEHP concentration in these nutrient supplemented reactors decreased from approximately 20,000-24,000 mg/kg to 700-1,800 mg/kg and the TPH, from approximately 6,000-8,000 mg/kg to 500-1,000 mg/kg. The final BEHP concentrations in these reactors ranged from 150 mg/kg (Reactor D) to 410 mg/kg (Reactor B), and TPH, from 150 mg/kg (Reactor D) to 220 mg/kg (Reactor B).

In contrast, very little degradative activity was observed in Reactor A despite the accidental addition of 110 mg/L of NH_4Cl midway through the operating period. When compared to the results observed for the reactors supplemented with both nitrogen and phosphorus, it is clear that phosphorus was the limiting nutrient even though the ammonia addition did stimulate activity after about 20 days.

Very little removal of BEHP and TPH occurred in Reactor E (acidified test control). This indicated that the target compounds were only slightly (if at all) volatile and that the removals observed in the nutrient supplemented reactors were attributable to biodegradation. In fact, no BEHP nor target hydrocarbons could be detected in any of GAC traps. The method detection limit for this analysis was 630 nanograms (ng) per 150 mg of GAC extracted. This represents less than about one ten thousandths of one percent of the initial contaminant present in the reactor.

Phase 2 Reactors

Reactor A2 was established to determine if the long lag period observed during the phase 1 studies would be eliminated by the addition of a sufficient supply of nitrogen and phosphorus at the outset of the test. Reactors B2, C2, and D2 were set up to mimic conventional SBR operation where settled biomass remains in the reactor for use during the next treatment cycle. In this case, 50% of the initial slurry volume was the slurry that had been treated during the previous cycle and the other 50%, untreated contaminated soil, tap water, and nutrients.

The change in BEHP and TPH concentrations as a function

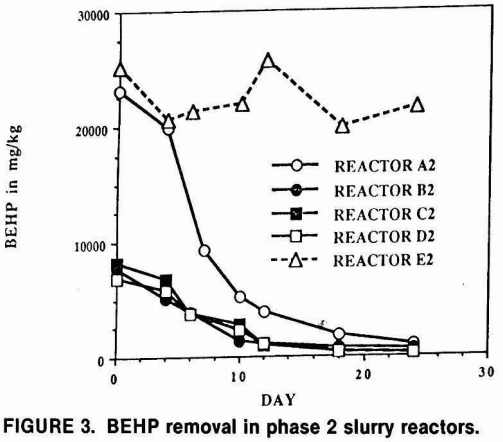

FIGURE 3. BEHP removal in phase 2 slurry reactors.

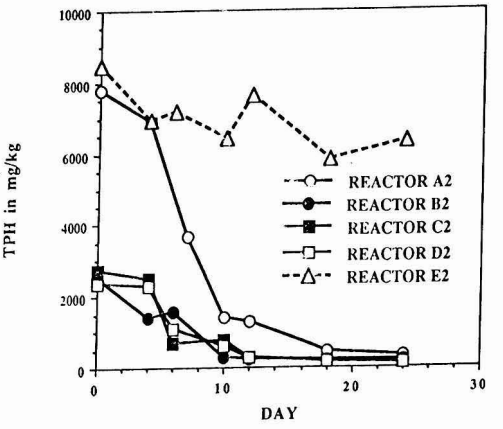

FIGURE 4. TPH removal in phase 2 slurry reactors.

of time are illustrated in Figures 3 and 4 for all reactors. Overall performance for these systems was quite good. The relatively high removal rates and absence of a significant lag period for the reactor that did not use acclimated biomass from phase 1 (Reactor A2) indicated that biodegradative activity of the microbial consortium present in this soil can be easily stimulated by providing sufficient nutrients at the beginning of a batch treatment period. The maximum BEHP and TPH removal rates in Reactor A2 were 3,500 mg/kg/day and 1,080 mg/kg/day, respectively. The contaminant concentrations in the reactors containing acclimated biomass and excess nutrients (Reactors B2, C2, and D2) after 24 days of operation ranged from 230 to 660 mg/kg for BEHP, and from 110 to 180 mg/kg for TPH. Nutrient balances showed that roughly 70 mg of nitrogen and 13 mg of phosphorus supported enough growth to degrade approximately one gram of contaminants (i.e., BEHP plus TPH).

No significant removals of either BEHP or TPH were observed in the acidified control Reactor E2. This observation, along with the ^{14}C-labeled BEHP results shown in Figure 2 and the OUR data presented in Figure 5, clearly indicates that biodegradation was the primary mechanism for both BEHP and TPH removal in these reactors.

DISCUSSION

As can be seen from Figures 3 and 4, both BEHP and TPH

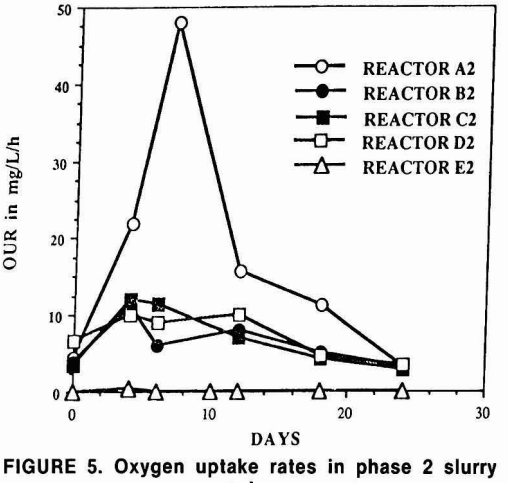

FIGURE 5. Oxygen uptake rates in phase 2 slurry reactors.

removal rates in Reactor A2 seemed strongly dependent upon their respective concentrations until their levels reached roughly 8,000 mg/kg for BEHP and 1,500 mg/kg for TPH, the approximate initial concentrations for each in Reactors B2, C2, and D2. More linear rates, apparently independent of BEHP and TPH, seemed to occur for concentrations less than these levels. The concentration dependence suggests that some combination of a relatively high soluble phase concentration (because of the insoluble nature of these components, relatively high would mean about 4 mg/L in this case) of BEHP and/or TPH, or a large number of BEHP and/or TPH "droplets" (and corresponding total surface area of the droplets) were present when the overall concentrations of BEHP and TPH in the soil were elevated. It is interesting to note that the OUR for Reactor A2 shown in Figure 5 peaks, as it should, at a time that corresponds to the maximum rate of removal of both BEHP and TPH. Such observations are commonplace in systems that deal with the removal of soluble substrates (e.g., activated sludge) and supports a hypothesis that the rate of contaminant disappearance was limited by the rate of consumption because the concentration of soluble carbon sources were in kinetic excess until the lower soil concentrations (and the lower rates of solubilization) were reached. After that time, the rate of consumption evidently exceeded the rate of solubilization and the rate of contaminant disappearance became roughly linear. One possible conclusion from this kind of thinking is that the rate of consumption could be increased by using a higher weight percent of solids in the slurry. Because of a resulting elevated rate of solubilization, the remediation times would be shortened and the treatment costs reduced. The limit on slurry weight percents then, would be fixed by requirements such as mixing and oxygen transfer. Unfortunately, studies were not conducted to test issues such as solubilization rates, droplet size and distribution, microbial colonization of droplets, microbial surfactant production, and contaminant adsorption/absorption to the soil matrix. As a result, the hypothesis remains unsubstantiated at this time.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of the laboratory studies, the following conclusions can be drawn:

1. Biodegradation was the primary mechanism for both BEHP and TPH removal.
2. BEHP and TPH present in the contaminated soil were readily biodegraded without a significant lag period when sufficient levels of nitrogen and phosphorus were supplied to the natural indigenous microbial population.
3. Studies that utilized ^{14}C-labeled BEHP in soil slurries demonstrated that between 50 and 60% of the carbon in BEHP was mineralized directly to CO_2 by indigenous microbial flora in less than 14 days.
4. In slurry reactors supplemented with nutrients (e.g., 1.4 to 2.0 g N per kg dry soil and 0.16 to 0.4 g P per kg dry soil), treatment efficiencies of greater than 96% for both BEHP and TPH were observed. In nutrient supplemented reactors, BEHP concentrations were reduced from initial levels as high as 24,000 mg/kg to less than 150 mg/kg and TPH concentrations, from initial levels as high as 8,000 mg/kg to 160 mg/kg.
5. Roughly 70 mg of nitrogen and 13 mg of phosphorus supported enough growth to degrade approximately one gram of contaminants (i.e., BEHP plus TPH).
6. OURs were found to increase directly with increases in BEHP and TPH removal rates, thus confirming biodegradative activity.

Based on the results of the laboratory studies, the following recommendations made for future treatability studies and for design and operating considerations for a full scale Soil Slurry-Sequencing Batch Reactor system:

1. The level of BEHP and TPH as a function of sieve fraction is needed to design an effective soil pretreatment strategy for the removal of debris and oversized material (e.g., rocks, gravel, coarse sand) that could limit the effectiveness of the slurry bioreactor.
2. Studies should be conducted to determine if the rate of solubilization is dependent on the concentration of the insoluble components in the soil and if the rate of consumption is less than the rate of solubilization until the lower soil concentrations are reached.
3. Additional laboratory studies should be conducted using reactors that have a daily cycle and hydraulic and solids retention times of 10 to 20 days. This corresponds to daily replacements of 5% to 10% of the total reactor volume.
4. Laboratory studies designed to test performance at temperatures less than 13°C and greater than 30°C should be conducted.

ACKNOWLEDGMENTS

Dr. Charles F. Kulpa, Jr., Professor, Department of Biological Sciences, University of Notre Dame conducted the ^{14}C-labeled BEHP nutrient study that demonstrated the need for additional nutrients in the slurry reactors.

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Fundamentals of Bioventing Applied to Fuel Contaminated Sites

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Bioventing entails the use of soil vapor extraction (SVE) systems for the transport of oxygen to the subsurface, where indigenous organisms are stimulated to aerobically metabolize fuel components. Bioventing systems are designed and configured to optimize oxygen transfer and oxygen utilization efficiency, and are operated at much lower flow rates and with configurations much different than those of conventional SVE systems. Bioventing system applications and design are contrasted to those of conventional SVE systems, and the two key elements of bioventing system design evaluation, i.e., in situ microbial activity and air permeability determinations, are highlighted in this paper. The application of bioventing to vadose zone bioremediation was reviewed with particular emphasis on its advantages over aqueous based bioremediation systems in terms of its superior oxygen transfer efficiency. Finally, the application of bioventing and bioventing design concepts are illustrated through a case study of JP-4 jet fuel contaminated soil remediation at Hill AFB, Utah.

INTRODUCTION

Conventional soil vacuum extraction (SVE) systems are designed to optimize system performance to yield a maximum recovery rate of volatiles from contaminated soil. Performance may deteriorate over time, however, due to occluded residual saturation and enrichment of residual contamination in the less volatile waste components.

Bioventing has been successfully applied and documented for the remediation of residual hydrocarbons remaining in soil following high rate SVE. Bioventing entails the use of SVE systems for the transport of oxygen to the subsurface, where indigenous organisms are stimulated to aerobically metabolize fuel components. Bioventing systems are designed and configured to optimize oxygen transfer and oxygen utilization efficiency, and are operated at much lower flow rates and with configurations much different than those of conventional SVE systems.

The bioventing processes is described in this paper, along with details of a recommended design approach for full-scale systems using field *in situ* respiration and air permeability measurements. A case study of the performance of a bioventing system at a JP-4 jet fuel site is briefly summarized, and the implications of results from this study having a bearing on future system design are highlighted.

BIOLOGICAL REMEDIATION OF CONTAMINATED SOILS

The biodegradation of organic compounds in soil environments has been extensively described in the technical literature, and details of metabolic pathways and microbial populations responsible for compound biotransformation have been summarized in a large number of textbooks and reviews on soil microbial ecology [*1, 2, 3*]. For direct biodegradation of hazardous organics to be successful, four conditions must be satisfied. First, the contaminants of interest must be able to serve as a carbon and energy source for the indigenous microbial population, i.e., it must be able to serve as an electron donor. Secondly, an appropriate electron acceptor must be available so that energy can be extracted from these electron donors at environmentally significant rates. Thirdly, macro- and micronutrients essential for the production of cellular material must be available in the appropriate ratio for microbial growth to proceed unhindered. (A C:N:P mass ratio typical recommended for soil bioremediation applications is 100:10:1). Finally, environmental conditions within the contaminated soil/water environment must not be inhibitory to the indigenous microflora. Soil environmental conditions of concern to ensure effective bioremediation include: soil water at 50 to 80 % of soil field capacity $\approx$ 1/3 bar; soil pH from 5.5 to 8.5; soil

Table 1 Carrier Fluid Oxygen Supply Requirements	
Carrier Solution	g(lb) Carrier/g (lb) O_2
Water	
Air Saturated	110,000
Pure Oxygen Saturated	22,000
500 mg/L H_2O_2 (100% Utilization)	2,000
Air (20.9% O_2)	4.5

temperature in the mesophilic range from 15 to 45°C; and an absence of organic or inorganic toxicants that can inhibit microbial activity.

The most critical limitation to successful bioremediation is generally the lack of appropriate electron acceptors. A variety of electron acceptors can be used by soil microorganisms to carry out the oxidation of organic contaminants. These include oxygen, nitrate, sulfate, carbon dioxide and organic carbon. Of these, oxygen provides the organism with the highest energy yield, providing nearly twice that of nitrate, and an order of magnitude higher energy release than sulfate, carbon dioxide and organic carbon. Oxygen metabolism is therefore energetically selected for, and subsequently, oxygen utilizing microorganisms are ubiquitous in soil environments. Oxygen is also the preferred electron acceptor from an engineering standpoint, as accelerated degradation rates generally occur under aerobic (oxygen rich) conditions as compared to anoxic or anaerobic (oxygen deficient) conditions.

These principles of biodegradation have historically been applied to the *in situ* aerobic bioremediation of contaminated soils and ground water using water to carry oxygen to the site of this subsurface contamination. Efforts have been made to increase the level of oxygen in this water by saturating the water with pure oxygen or hydrogen peroxide. These efforts have generally met with limited success, however, because of the inability to transfer adequate oxygen to areas of subsurface contamination due to physical limitations of the transfer of the bulk carrier medium through contaminated soils [*4*, *5*, *6*, *7*, *8*].

The inherent disadvantage of utilizing water as the carrier medium for the transfer of oxygen to the subsurface is graphically illustrated in Table 1. These values represent the mass of fluid required to transfer a unit mass of oxygen under the stated conditions. Due to the low solubility of oxygen in water, prohibitively large amounts of oxygen-saturated water are required even when using pure oxygen or hydrogen peroxide saturated solutions. This oxygen supply limitation is exacerbated by the high oxygen demand of hydrocarbon contaminants as indicated by the simple stoichiometric reactions for hexane oxidation shown below assuming no substrate incorporation into cell material:

$$\underset{3.5\ g\ O_2/g\ C_6H_{14}}{C_6H_{14}+9.5\ O_2 \rightarrow 6\ CO_2+7\ H_2O} \quad (1)$$

Assuming an oxygen requirement of only 3 g O_2/g hydrocarbon for hydrocarbon mineralization, a 3,785 L (1,000 gal) fuel spill weighing approximation 3,175 kg (7,000 lb) would require 9,525 kg (21,000 lb) of oxygen. This equates to an air saturated water volume of approximately 8,744,000,000 L (2,310,000,000 gal), a pure oxygen saturated volume of 1,749,000,000 L (462,000,000 gal), or a saturated peroxide solution volume of 159,000,000 L (42,000,000 gal) to provide the required oxygen for fuel bioremediation. It becomes apparent from these calculations that hydraulic limitations would be severe for the remediation of a spill even as small as 3,785 L (1,000 gal) due to massive water volumes required when using saturated phase bioremediation approaches.

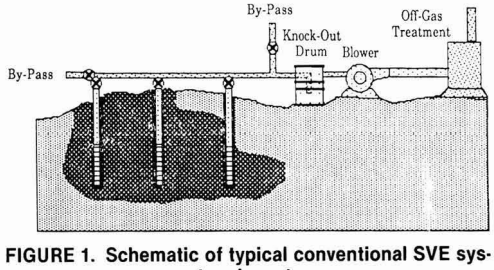

FIGURE 1. Schematic of typical conventional SVE system layout.

BIOVENTING SYSTEMS

Bioventing describes the process in which the air medium is utilized to deliver oxygen to the subsurface to stimulate the *in situ* biodegradation of organic contaminants. As indicated in Table 1, air is an extremely efficient oxygen transfer medium due to its high oxygen content (20.9 vol%, i.e., 20,900 ppmv) and low viscosity as compared to that of saturated water. Bioventing represents a hybrid physical/biological process utilizing soil venting systems for oxygen transfer, while focusing not on contaminant stripping, but rather on *in situ* aerobic contaminant biodegradation.

Consideration of soil vacuum extraction for oxygen transfer to the subsurface was proposed in 1988 by Wilson and Ward [*9*], who noted that systems designed for the removal of volatiles from soil could also be used to transport oxygen. A number of other authors have postulated the potential improvement of *in situ*, aerobic, subsurface bioremediation using SVE for oxygen transfer [*10*, *11*, *12*, *13*, *14*] but it has only been recently that investigators have collected field data showing the effectiveness of bioventing systems for fuel site remediation [*15*, *16*, *17*].

Bioventing systems are composed of hardware identical to that of conventional soil vacuum extraction (SVE) systems, with vertical wells and/or lateral trenches, piping networks, and a blower or vacuum pump for gas extraction. They differ significantly from conventional systems, however, in their configuration and philosophy of design and operation. As indicated above, the primary purpose of a bioventing system is to use moving soil gas to transfer oxygen to the subsurface where indigenous organisms can utilize it as an electron acceptor to carry out aerobic metabolism of soil contaminants. As such, bioventing system extraction wells are not placed in the center of the contamination as in conventional SVE systems (Figure 1), but on the periphery of the site (Figure 2), where low flow rates [4.6 to 23 actual L/s (10 to 50 acfm) versus 46 to 700+ actual L/s (100 to 1,500+ acfm) for conventional SVE systems] maximize the residence time of vent gas in the soil to enhance *in situ* biodegradation and minimize contaminant volatilization.

Because it is a biological treatment approach, however, bioventing does require the management of environmental conditions to ensure maintenance of bioactivity at the site. Management of soil moisture and soil nutrient levels to avoid inhibition of microbial respiration within the vadose zone can

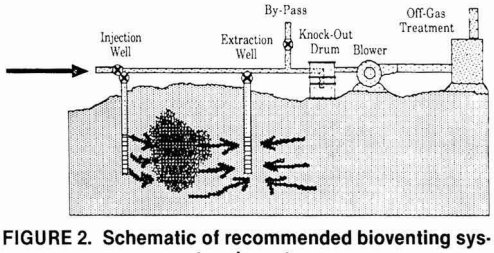

FIGURE 2. Schematic of recommended bioventing system layout.

Table 2 General Design and Application Considerations Appropriate for Conventional Versus Bioventing SVE Systems

Parameter	Conventional SVE	Bioventing
Compound Type	Volatile @ Room Temperature	Biodegradable
Vapor Pressure	>100 mm Hg	—
Hc (dimensionless)	>0.01	—
Aqueous Solubility	<100 mg/L	—
Soil Concentration	>1 mg/kg	<1%
Depth to Ground Water	>20 ft	—
Air Phase Permeability	$>1\times10^{-4}$ cm/s	
Subsurface Conditions	Little or No Stratification	
NAPL Phase	Little or None	Biodegradable
Vent Well Placement	Within Contamination	Outside Contamination
Operating Mode	Maximum Soil Gas Exchange Rate	Maximum Retention Time & Aerobic Conditions
Operating Flow Rates	46 to 700+ actual L/s (100 to 1,500+ acfm)	4.6 to 23 actual L/s (10 to 50 acfm)
Pore Volumes/d	1 to 15	0.1 to 0.5
Optimal Soil Moisture	≈25% Field Capacity	≈75% Field Capacity
Nutrient Requirement	—	C:N:P≈100:10:1
Soil Gas O_2 Levels	—	>2 vol%
Toxicants	—	Little or None

be accomplished fairly easily, and have been used to optimize contaminant biodegradation at field sites when other variables, i.e., toxicity, do not limit microbial activity [*16*, *17*].

Oxygen transfer to the subsurface via SVE systems is generally more rapid than oxygen uptake rates observed under field conditions [*16*, *17*]. This results in the oxygenation of soil gas to near ambient levels if vent system blowers are operated on a continuous basis. To minimize system operating costs, and more importantly to reduce or even perhaps eliminate off-gas treatment requirements entirely, cyclic, or "surge" pumping of vent systems in bioventing operations is recommended. Surge pumping in a bioventing mode entails operating the blower system until soil gas oxygen levels reach near ambient conditions throughout the site being remediated. The system would then be shut off for some period of time during which soil gas oxygen concentrations would be routinely monitored until they reach a level which inhibits aerobic microbial activity. Once this limiting soil gas concentration is reached, the vent system would be restarted, and the on-off cycle would continue once again. Based on a Henry's Law constant for oxygen, this oxygen limitation would be expected to occur at a soil gas concentration of approximately 2.0 vol%, corresponding to soil water oxygen concentrations of approximately 1 mg/L. An inhibition of soil respiration has been reported at the 2.0 vol% soil oxygen level in venting systems treating JP-4 contaminated soils, [*16*] and in vented soil piles contaminated with PCP waste [*19*] suggesting that this value represents a good operating number for field scale applications.

Based on observed field respiration data from various JP-4 jet fuel contaminated sites [*20*] and bioventing of PCP contaminated soil piles [*19*] field oxygen uptake rates of 0.1 to 0.6 vol%/h (2.7 to 16 g O_2/m^3 soil-d @ air filled porosity = 40 vol%) can be expected. These rates can be nearly an order of magnitude lower as remediation progresses to near de minimus soil hydrocarbon levels (Dupont *et al.*, 1991), allowing typical bioventing systems to be operated on schedules of 8 h on, 16 h off at the initation of remediation, to 8 h on, 7 d off near the end of the field effort, while still maintaining aerobic conditions within the contaminated soil during nonventing periods.

Table 2 presents a summary of general design, operational and application considerations appropriate for conventional SVE systems versus those utilized in a bioventing operating mode.

Bioventing System Design

The two major design considerations for bioventing systems are first, whether the contaminants of concern are biodegradable under prevailing site conditions, i.e., whether inhibition or toxicity is evident at the site, and secondly, whether the required terminal electron acceptor, i.e., oxygen, can be effectively transported within the soil to encourage aerobic contaminant biodegradation. The first question can be answered using soil gas composition and *in situ* respiration measurements, while the second question is answered from *in situ* air permeability measurements.

Soil Bioactivity Determinations

To determine the potential for *in situ* biodegradation of vadose zone contaminants via bioventing, existing soil microbial activity should be quantified during site assessment investigations. This can be readily accomplished through the analysis of soil gas O_2 and CO_2 composition prior to venting activity at the site. O_2 and CO_2 concentrations can be measured along with volatile organics during standard soil gas surveys using a variety of measurement techniques. The author has successfully used both wet chemical (Fyrite® oxygen/carbon dioxide analyzer; Bacharach Instrument, Pittsburgh, PA) and electronic (Gastechtor Model 32520X; Gastech Inc., Newark, CA) methods for field soil gas O_2 and CO_2 determinations. While both gases can be easily measured, O_2 concentrations are considered a better indicator of respiration in soil systems because there are no abiotic sinks for oxygen in these environments. Carbon dioxide is produced through anaerobic as well as aerobic microbial activity [*2*] and can also be affected by assimilation or dissolution of carbonate rock.

The key to the evaluation of soil bioactivity using these methods is the determination of the extent of oxygen depletion and carbon dioxide enrichment in soil gas at a site with respect to background, uncontaminated soil levels. It cannot be overemphasized that these determinations must be based on a comparison to uncontaminated soil conditions, as only levels of O_2 depletion and CO_2 enrichment in excess of background are indicative of increased microbial activity compared to normal basal respiration levels seen in uncontaminated soils at the site.

If soil gas organic vapor and soil core data show contamination, but microbial respiration has not yielded O_2 uptake and CO_2 production rates above background soil levels, conditions within the contaminated soil have resulted in soil microbial toxicity or severe inhibition, or significant nutrient or moisture limitations exist at the site. Unless soil moisture is the cause of this limitation, bioremediation has limited application at the site, and alternative remediation schemes should be considered.

If soil contamination exists and microbial activity above background levels is evident from soil gas measurements, quantification of maximum respiration rates under field conditions can be carried out utilizing *in situ* respiration measurement techniques described by Hinchee *et al.* [*20, 21*]. This method entails the oxygenation of contaminated and uncontaminated background subsurface soil around a soil gas probe via air injection for a 16 to 24 hr period, followed by the measurement of O_2 uptake and CO_2 production at the soil gas probe over time. The collected soil gas data are analyzed using either a zero or first order reaction rate model to generate either zero or first order respiration rate values (vol%/hr or 1/h, respectively) from the slope of these linear regression relationships. The background soil values are used to correct contaminated soil values for basal soil respiration taking place at the site. An inert gas tracer can be injected during soil aeration so that respiration rate measurements can also be corrected for diffusion of O_2 away from, or CO_2 diffusion to the sampling probe during respiration rate determinations.

Using these respiration data, *in situ* contaminant biodegradation rates can be estimated assuming the 3:1 O_2:hydrocarbon stoichiometry presented in Equation 1. In addition, required oxygen transfer rates can be estimated, and the feasibility of *in situ* bioventing, and the estimated time for remediation under prevailing site conditions can be assessed.

In Situ *Air Permeability Determinations*

Once bioactivity at the site has been verified, the rate of transfer of the electron acceptor to the contaminated soil remains to be determined. This can be readily accomplished by obtaining *in situ* air permeability measurements at several locations throughout the site. The approach that has become the recommended standard for *in situ* soil air permeability measurements was described in 1990 by Johnson *et al.* [*22*] and is based on Darcy's Law and equations for steady-state radial flow at a vent well. The method entails the use of a single vent well with soil vapor probes placed radially and vertically away from it to monitor soil gas pressure or vacuum throughout the field site when air is extracted or injected at a constant rate at the well head. A schematic of the instrumentation necessary for a typical *in situ* permeability field study is shown in Figure 3 [*22*].

The governing equation for such a system assuming one-dimensional radial flow from the extraction well is shown in equation 2 [*22*]:

$$P' = \frac{Q}{4\pi m\left(\frac{k}{\mu}\right)_{\bar{\epsilon}}}\left[-0.5772 - \ln\left(\frac{r^2\epsilon\mu}{4kP_{atm}}\right) + \ln(t)\right] \quad (2)$$

where P' = "gauge" pressure (g/cm-s^2) measured at the vapor probes some radial distance r (cm) from the vent well at time t(s), m = vent well screen interval (cm), k = soil gas permeability (cm^2), μ = air viscosity (1.8×10^{-4} g/cm-s @ 18°C), ϵ = soil air filled porosity (decimal %), Q = volumetric air flow rate at the vent well (cm^3/s), and P_{atm} = atmospheric pressure (1 atm = 1.013×10^6 g/cm-s^2).

Soil gas pressure or vacuum data collected over time at various vapor probe locations following initiation of vent well pumping allow the determination of *in situ* soil gas permeability and its variability throughout the site. Vapor probe readings are plotted as a function of the natural log of time, generating a straight line with a slope equal to equation 3 [*22*]:

$$\text{Slope} = \frac{Q}{4\pi m\left(\frac{k}{\mu}\right)} \quad (3)$$

Rearrangement of this equation allows the determination of k directly as:

$$k = \frac{Q\mu}{4\text{Slope}\pi m} \quad (4)$$

This approach to data reduction will not be possible if the assumption of radial flow is not maintained at the field site. Radial flow will not occur if a significant vertical air velocity component exists due to shallow contamination and subsequently a small well screen interval (< 10 ft), and if the soil is coarse grained. Under these conditions, pressure/vacuum measured in the vapor sampling points will reach constant values very quickly, requiring that the data be reduced using equations 5 and 6 [*22*]:

$$\text{for vacuum wells} \quad k = \frac{Q\mu\ln\left(\frac{R_w}{R_l}\right)}{H\pi P_w\left[1 - \left(\frac{P_{atm}}{P_w}\right)^2\right]} \quad (5)$$

$$\text{for extraction wells} \quad k = \frac{Q\mu\ln\left(\frac{R_w}{R_l}\right)}{H\pi P_{atm}\left[1 - \left(\frac{P_w}{P_{atm}}\right)^2\right]} \quad (6)$$

where R_w = the radius of the vent well (cm), H = the depth to the top of the well screen (cm), R_l = the minimum radius of vent well influence under steady-state flow conditions, and P_w = the absolute pressure at the well head (g/cm-s^2). R_l can be estimated from inspection of field data, or by extrapolating the relationship of vapor probe vacuum/pressure versus log(r) to a 0 vacuum/pressure value.

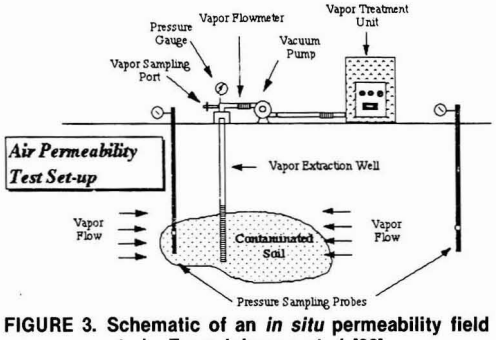

FIGURE 3. Schematic of an *in situ* permeability field study. From Johnson *et al.* [22]

Integration of Field Data

Bioventing system design can now be carried out by estimating the equivalent daily oxygen demand and vent air flow rate as determined from *in situ* respiration measurements, and

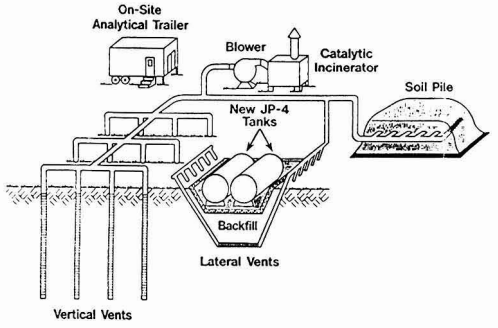

FIGURE 4. Conceptual diagram of the Hill AFB, Utah, field venting site. From Dupont *et al.* [16]

by estimating pump operating conditions at these required air flow rates based on field determined *in situ* air permeability measurements. The feasibility of pulse pumping and vacuum pump/blower scheduling can be assessed based on required versus maximum oxygen transfer rates possible under a given set of field and pump/blower operational constraints. An example of such calculations are presented below in the case study for the bioventing system operated at Hill AFB, Utah.

Case Study—JP-4 Contaminated Site, Hill AFB, Utah

Site Description

The site at Hill AFB, Utah, was the location of a JP-4 jet fuel spill that occurred in January 1985, after the failure of an automatic shut-off valve. Failure of the valve resulted in the release of approximately 102,000 L (27,000 gal) of JP-4, some 7,600 L (2,000 gal) of which were recovered as free product. The balance of the released fuel migrated away from the tank and contaminated an area around it of approximately 0.4 hectares (1 ac) to a depth of approximately 15 m (50 ft). The soil at the site consists of mixed coarse sand and gravel deposits with interspersed, discontinuous clay stringers to a confined ground water table at approximately 180 m (600 feet) below ground surface (bgs). JP-4 contamination resulted in soil total pertroleum hydrocarbon (TPH) concentrations at the site as high as 15,000 mg/kg, with average TPH levels of >1,000 mg/kg. Prior to initiation of the full scale venting system, the fuel tanks were excavated, refurbished, and installed in a concrete cradle above ground.

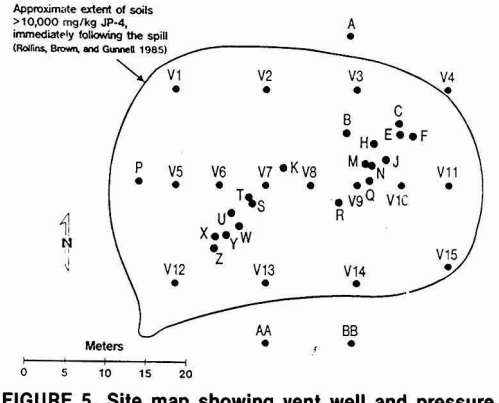

FIGURE 5. Site map showing vent well and pressure monitoring point locations at the Hill AFB, Utah, site. From Hinchee *et al.* [18]

System Configuration and High Rate Venting Operations

A one-well pilot scale vent test was conducted by Oak Ridge National Laboratory (ORNL) to evaluate *in situ* air permeability at the site. This study resulted in the design by ORNL of a venting system consisting of 15 vertical wells and 10 lateral wells in the excavated soil pile and under the tanks (Figure 4). The vertical wells were placed at 12 m (40 ft) intervals to a depth of 15 m (50 ft) bgs and were slotted over an interval from 3 to 15 m (10 to 50 ft) bgs. Twenty-one pressure monitoring points (PMP) were installed at various depths throughout the site to provide point measurements of subsurface pressure and soil gas conditions (Figure 5), and a background well was placed approximately 210 m (700 ft) north of the site in the same geological unit and at the same depth as the vent wells to provide a control for basal soil respiration levels during the study.

Prior to initiation of bioventing studies at the Hill site, the SVE system was operated under a conventional mode to maximize the recovery of volatile components of the JP-4 through volatilization. Venting was initiated at a rate of 36 m^3/h (26 acfm, approximately 0.04 pore volumes/d), and gradually increased to approximately 2,100 m^3h/ (1,500 acfm, approximately 2.5 pore volumes/d) as the hydrocarbon levels in the vent gas decreased over time. Vent gas was collected through Wells V5 to V11 (Figure 5), where the bulk of the soil contamination was located. The venting rate during the start-up period was limited by the operating conditions of the catalytic incinerator used to treat the collected vent gas. This high-rate operating mode continued from December 18, 1988, through September 15, 1989, during which time approximately 7,000,000 m^3 (300,000,000 acf, approximately 340 pore volumes) of soil gas and 62,600 kg (138,000 lb) TPH were extracted from the site due to volatilization and *in situ* biodegradation of the JP-4.

Three *in situ* respiration tests were conducted during the high-rate operating period [*18*] to assess microbial activity at the site during conventional soil venting. These tests were conducted at cumulative extracted air volumes of 970 m^3 (42,000 acf), 13,000 m^3 (540,000 acf), and 1,000,000 m^3 (45,000,000 acf), and showed first order oxygen uptake rates ranging from 0.85/d to nondetectable in the pressure monitoring points throughout the site. Comparison of results from specific monitoring points over time also indicated the incremental removal of residual hydrocarbons as respiration rates declined throughout the treatment period. It was concluded that significant respiration was occurring during conventional SVE without nutrient or moisture addition, and that enhancement of biodegradation could be possible under modified site management conditions. This became of increasing interest as the residual soil TPH levels had not reached the regulatory action level of 30 mg/kg dry wt. soil, and the conventional SVE system hydrocarbon recovery rate decreased significantly over time due to non-volatile residual contaminants accumulating in the soil over time.

Modified Bioventing System Operating Conditions

Based on results of vapor probe and vent gas measurements taken during the high-rate venting period, it was found that at high extraction rates, i.e., 2,100 m^3/h (1,500 acfm), the entire contaminated zone was aerated to near atmospheric O_2 levels. In addition, due to the extraction of vapors from the areas of maximum contamination at the interior of the site, hydrocarbon levels above the allowable discharge limit of 50 ppmv were found in the vent gas. To maximize biodegradation and minimize volatilization, operating flow rates were reduced to the lowest rates possible utilizing the existing venting system, i.e., 490 to 970 m^3/h (350 to 700 acfm), and vent gas was drawn

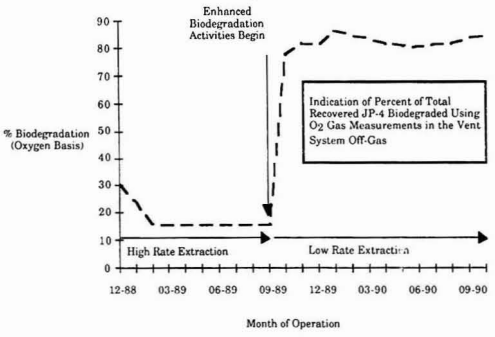

FIGURE 6. Percent recovered JP-4 attributed to biodegradation reactions at the Hill AFB, Utah, field soil venting site based on oxygen depletion measured in the SVE system vent gas.

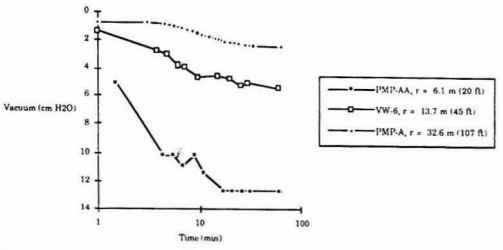

FIGURE 7. Results of *in situ* air permeability study conducted at the Hill AFB, Utah, bioventing field site. Air extracted from Vent Well 13 at 212 actual L/s (450 acfm), m = 1219 cm (40 ft).

from wells on the periphery of the site (Wells V12 to V15 in Figure 5) to maximize the flow path and retention time of vapors in the contaminated zone. Figure 6 presents the results of this operating mode change in terms of the percent of total JP-4 recovery that could be attributed to biodegradation, expressed on an oxygen consumption basis, during both the conventional high-rate and modified bioventing phases of the study. Biodegradation accounted for 15 to 20% of the recovered JP-4 even during high-rate venting. This rate was drastically altered in September 1989, when JP-4 volatilization was reduced from 90 to 180 kg/d (200 to 400 lb/d) to less than 9 kg/d (20 lb/d) by making the stated changes to the system flow rate and extraction configuration. These changes allowed direct discharge of vent gas without expensive off-gas catalytic incineration treatment, and had no detrimental effect on biodegradation reactions. The hydrocarbon biodegradation rates of 32 kg/d (70 lb/d) observed during high rate extraction were maintained at an average rate of greater than 45 kg/d (100 lb/d) following system operating modifications.

In Situ *Permeability Determinations*

In situ permeability measurements were once again made during the bioventing phase of this project using the vent well and vapor probe configuration utilized during bioventing operations. Results presented in Figure 7 were collected from the indicated vent well and pressure monitoring points while extracting vapor from Vent Well 13 at an operating flow rate of 212 actual L/s (450 acfm).

Using the approach by Johnson *et al.*, [*22*] a linear regression through these data yielded Slope values as input to equation 3 as shown in Table 3. These data yielded a mean k value of 223 ± 73 darcys, indicative of the clean sands and gravels present at the site.

Field In Situ *Respiration Test*

A number of field-scale *in situ* respiration tests were conducted during the bioventing study to assess the changes in *in situ* respiration as engineering management options were applied at the site. Three tests were conducted from September 1989 to November 1990 representing different levels of management at the site, i.e., following flow rate and operating configuration modifications at the site, following moisture addition, and following moisture and nutrient addition. All tests were conducted by shutting down the venting system and monitoring changes in soil gas CO_2 and O_2 composition in all pressure monitoring points and vent wells over a 10- to 14-d period. Soil gas samples were analyzed by first evacuating three volumes of the monitoring points and vent wells using a portable sampling pump prior to connecting the Gastechtor instrument.

The moisture addition phase of the field treatability study consisted of the addition of culinary water to the field site to yield soil moisture levels throughout the site of approximately 8 to 12% (30 to 50% field capacity). This moisture was added via surface spray irrigation at rates of approximately 110 L/min (30 gpm), 8 h/d, 7 d/wk, until approximately 3,800,000 L (1,000,000 gal) were applied. Soil moisture measurements made using a neutron density soil moisture probe indicated that soil moisture was successfully increased from pre-irrigation conditions and maintained between 8 and 12% over the entire contaminated depth [*16*].

Nutrients were added to the site in the form of ammonium nitrate and sodium triphosphate at a C:N:P ratio of 100:10:10, based on soil hydrocarbon analyses in September 1989, which indicated residual hydrocarbon levels throughout the site of approximately 100 mg/kg. These nutrients were added in three equal increments, three weeks apart, by surface-applying the dry mix, tilling it into the upper 15 cm (6 inch) soil horizon, and continuing surface spray irrigation at 100 L/min (30 gpm), 8 h/d, 2 d/wk, during this phase of the study.

All field data were analyzed assuming a first order reaction law through linear regression of the natural log transform of

Table 3 *In Situ* Permeability Data Collected from the Hill AFB, Utah, Bioventing Field Site, and Results from Equation 4

Monitoring Point	Depth [m (ft)]	r[m (ft)]	Vacuum† ($g/cm\text{-}s^2$)	Regression Slope ($g/cm\text{-}s^2$)	k(darcys)
A	9.1 (30)	32.6 (107)	2,415	931	270
AA	9.1 (30)	6.1 (20)	12,451	1705	147
VW-6	3–15 (10–50)	13.7 (45)	5,229	1031	244
C	1.8 (6)	25 (82)	2,191	817	307
S	1.8 (6)	10.4 (34)	3,038	1730	145

†Vacuum = steady-state gauge reading at end of *in situ* permeability test.

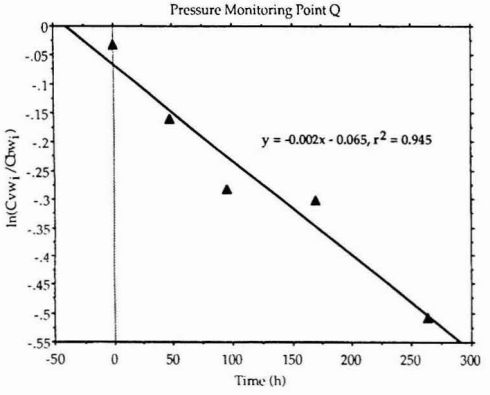

FIGURE 8. A sample first order regression analysis of oxygen uptake rate data obtained during *in situ* respiration measurements.

CO_2 and O_2 concentrations normalized to the background well at each sampling interval, i.e., $\ln(C_{vent\ well}/C_{background\ well})_{time\ i}$ versus time. Each regression line was tested for the significance of its slope, i.e., the probability of the slope not equalling zero being ≥ 0.05. In addition, an evaluation of overlapping 95 percent confidence intervals of each regression slope was used to test for significant differences among treatments.

Figure 8 shows results of a typical oxygen uptake rate determination obtained during these *in situ* respiration studies. O_2 uptake was found to be more consistent and more sensitive than CO_2 production rates in detecting effects of treatments on microbial activity at the site. This was particularly true for the moisture addition cases, where the interaction of CO_2 with the added water greatly affected observed CO_2 production rates.

Mean and maximum O_2 uptake data are presented in Table 4 as a function of engineering management treatment along with equivalent oxygen demand values expressed in kg/d. As indicated in Table 4, the addition of moisture to the field site yielded a significant increase in oxygen uptake rate not observed with nutrient addition. Statistical results presented elsewhere [*16*] based on an analysis of overlapping 95 percent confidence intervals of the slopes of significant regression relationships for the three treatment cases during the bioventing study indicated that in no case did nutrients significantly increase respiration rates above statistically significant levels following moisture addition alone. CO_2 production rates were not found to be significant at any monitoring point or vent well following moisture addition indicating the sensitivity of the CO_2 production measurement to changes in environmental conditions that affect CO_2 distribution in the subsurface.

The O_2 demand data presented in Table 4 were calculated assuming the following: total contaminated soil volume = 61,670 m^3 (2,178,000 ft^3), air filled pore space = 0.4, atmospheric O_2 content = 21%, O_2 density = 1.43 g/L. An analysis of the potential O_2 transfer rate into the Hill site at various flow rates is summarized in Table 5 using the assumptions listed above for soil conditions; the mean *in situ* air permeability value of 223 darcys determined for the site; and equation 5 with $R_I = 4{,}298$ cm (141 ft) at 212 L/s (450 acfm) as determined from the extrapolation of vacuum versus radial distance data from Table 3 to a 0 vacuum value (it was assumed that R_I varies linearly with flow rate in this coarse grained material), $R_w = 7.6$ cm (3 in), $H = 305$ cm (10 ft), and $P_{atm} = 1.013 \times 10^6$ g/cm-s^2 (1 atm).

Table 4 *In Situ* O_2 Uptake Rate Data and Equivalent O_2 Demand Requirements Collected from the Hill AFB, Utah, Bioventing Field Site

Management Treatment	Mean O_2 Uptake Rate (1/d)	Mean O_2 Demand (kg/d)	Max. O_2 Uptake Rate (1/d)	Max. O_2 Demand (kg/d)
Low Rate Venting	0.016	24.4	0.026	40.1
Moisture Addition	0.030	45.3	0.168	261
Nutrient & Moisture Addition	0.016	24.4	0.060	87.1

Table 5 Potential O_2 Transfer Rate Data and Predicted Well Operating Vacuum at the Hill AFB, Utah, Bioventing Field Site

Q[L/s (acfm)]	Potential O_2 Transfer Rate (kg/d)	Vent Well Operating Vacuum [g/cm-s^2 (in H_2O)]
4.7 (10)	120	503 (0.20)
11.8 (25)	300	1,710 (0.69)
23.6 (50)	600	4,110 (1.6)
47.2 (100)	1,200	9,560 (3.8)
70.8 (150)	1,800	15,500 (6.2)
94.4 (200)	2,400	21,700 (8.7)
118 (250)	3,000	28,200 (11.3)
142 (300)	3,600	34,800 (14.0)
165 (350)	4,200	41,500 (16.6)
189 (400)	4,800	48,200 (19.4)
212 (450)	5,400	55,100 (22.1)
236 (500)	6,000	62,000 (24.9)
354 (750)	9,000	97,000 (38.9)
472 (1,000)	12,000	132,000 (53.0)

Upon comparison of Table 4 O_2 uptake estimates with Table 5 potential O_2 transfer rates, it becomes apparent that only very low flows, on the order of 12 L/s (25 acfm), are needed to transfer the maximum uptake rate expected under optimized engineering management conditions. At these low flow rates, however, the radius of influence of the extraction wells is very small, $\approx$244 cm (8 ft) at 12 L/s (25 acfm), limiting the effectiveness of single wells to remediate large contaminated areas. At the Hill AFB site, the extent of contamination was roughly 6,400 cm (209 ft) square, precluding the use of this low flow rate. What could have been implemented, however, was the use of the multiple wells operated at higher flow rates in a sequential fashion for short periods of time to supply the oxygen need for microbial metabolism, while limiting the volume of contaminated air extracted from the soil. This was done to some extent by reducing the vacuum flow rate to 212 actual L/s (450 acfm). However, rather than operating on a continuous basis, all of the daily oxygen demand could have been supplied to the site in little over an hour at this flow rate (261 kg maximum demand from Table 4/5,500 kg/d supplied from Table 5 = 0.048 d = 1.2 h to supply the demand). Because of a radius of influence of $\approx$4,300 cm (140 ft) at 212 actual L/s (450 acfm), the Hill system could have been operated with two wells centered on opposite boundaries of the contaminated area, running sequentially for approximately 0.75 h/d, for a total operating time of 1.5 h/d. This scenario would have supplied the entire contaminated zone with oxygen, and would have produced the minimum volume of extracted soil gas for treatment and/or disposal.

TPH Removal Performance

As indicated above, 65% contaminant recovery was accomplished by conventional high rate SVE during the first nine

months of the study as 62,600 kg (138,000 lb) of TPH were extracted from the site due to volatilization and *in situ* biodegradation. An additional 33,200 kg (73,100 lb) of JP-4 were removed during bioventing between September 16, 1989, and November 14, 1990, resulting in a total mass removal from the site of 95,800 kg (211,100 lb) of JP-4 over the 23 month operating period. Of this total, 53,650 kg (118,200 lb) of JP-4 was attributed to volatilization as indicated by vent gas hydrocarbon concentrations, while the recovery of 42,150 kg (92,900 lb) of JP-4 was attributed to biodegradation as measured from vent gas oxygen deficit determinations. This corresponds to a 56 to 44% volatilization to degradation ratio during the entire operating period.

Final soil TPH concentrations were measured in more then 200 soil cores collected from within the area of contamination to confirm the hydrocarbon recovery data determined from vent gas measurements. These vent gas results were substantiated as the average residual TPH soil concentration was less than 5 mg/kg dry wt. soil at the end of the bioventing period. This soil hydrocarbon level represents greater than 99.5% overall contaminant removal and a residual TPH concentration below those required for closure of the site.

SUMMARY AND CONCLUSIONS

The application of bioventing to vadose zone bioremediation has been reviewed, and its advantages over aqueous based bioremediation systems in terms of its superior oxygen transfer ability has been highlighted. Bioventing system applications and design were contrasted to those of conventional SVE systems, and the two key elements of bioventing system design evaluation, i.e., *in situ* microbial activity and air permeability determinations, were highlighted. Finally, the application of bioventing and bioventing design concepts were illustrated through a case study of JP-4 jet fuel contaminated soil remediation at Hill AFB, Utah. Based on this review of bioventing fundamentals, and of the performance of a field-scale bioventing system, the following conclusions can be made:

1. SVE systems can be utilized as highly efficient oxygen transfer systems for vadose zone oxygenation. Vent system oxygen transfer rates have been shown to be much higher than *in situ* oxygen uptake rates at a number of field JP-4 contaminated bioventing sites, providing an opportunity for optimizing treatment through SVE system operational modifications and venting rate controls.
2. Conventional SVE systems do differ significantly from bioventing systems in their design orientation. Air extraction rates are maximized for contaminant recovery in SVE systems, while bioventing systems attempt to maximize vapor retention within the soil to encourage microbial degradation of contaminant vapors.
3. Methods to reduce vapor extraction rates to maximize vapor retention times in the soil are compatible with enhancing biodegradation reactions. These procedures result in minimizing volatilization, potentially eliminate the need for vent gas treatment, maximize the utilization of oxygen *in situ*, and provide a framework for the development of truly optimized *in situ* biological treatment systems. At the Hill AFB site, reduced flow rates and maximized flow path distances allowed the direct discharge of vent gas without off-gas treatment, while still being below the regulatory limit of 50 ppmv TPH.
4. For bioventing systems to be successful, contaminants of interest must be biodegradable under field conditions at rates that can be effectively exploited. Methods described by Hinchee *et al.* [*20, 21*] for *in situ* respiration rate determinations should be utilized to quantify the presence and rate of bioactivity prior to field scale system design.
5. Methods presented by Johnson *et al.* [*22*] allow the determination of *in situ* air permeability from the collection of simple field data. These methods allow the quantitation of air permeability and its variability under actual field conditions, and are recommended for SVE and bioventing field system design.
6. Conclusive evidence was provided to indicate significant biological activity at the Hill AFB, Utah, field site. Without enhancement, a total of 15 to 20 percent of the recovered JP-4 could be attributed to biodegradation. With enhancement this proportion increased to greater than 80 percent, resulting in 33,200 kg (73,100 lb) of TPH being biodegraded during the 14 month bioventing portion of the study.
7. Nutrient addition at field JP-4 bioventing sites has consistently been shown to be ineffective in stimulating microbial respiration rates, suggesting that nutrient availability is not rate limiting under field conditions at these sites. However, moisture addition to the 30 to 50% field capacity level appears to be essential in order to optimize microbial activity within a bioventing treatment system.
8. Operation of bioventing systems for the remediation of JP-4 jet fuel contaminated sites appears to be optimal for biodegradation, i.e., maximum biodegradation/minimum volatilization, at 0.25 to 0.5 pore volume/d. At this operating flow rate, soil gas retention time is sufficient to yield 80 to 85% hydrocarbon recovery as respiration product gas (CO_2), while minimizing TPH recovery in the form of VOC emissions.
9. *In situ* field respiration studies indicated that O_2 uptake rate measurements were better indicators of biological activity at the site than were CO_2 production rate determinations. CO_2 measurement sensitivity was susceptible to varying soil environmental conditions, notably soil water content. Soil gas CO_2 measurements did not consistently detect respiration changes during the study.
10. Quantification of *in situ* respiration rates and oxygen transfer potential indicated that daily oxygen demand was being satisfied in slightly over 1 hr at the lowest rate at which the Hill AFB bioventing system could be operated, i.e., 212 actual L/s (450 acfm). Oxygen demand could have been satisfied at flow rates much lower than this value, but concerns over limited radii of influence at low extraction rates suggest operating at higher flow rates for short time periods during remediation. Optimal bioventing system design for the Hill AFB site was suggested to be two vent wells operating at 212 actual L/s (450 acfm) for 0.75 hr/d each. This results in sufficient oxygen transfer and ensures coverage of the entire area of contamination, while significantly reducing the volume of extracted air that must be handled prior to discharge.

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The Applicability of UV/Oxidation Technologies to Treat Contaminated Groundwater

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This paper presents information useful in evaluating the applicability of UV/oxidation treatment technologies for groundwater contaminated with organics. The information presented includes a description of the technologies, factors affecting the technologies, and results from two pilot-scale studies of UV/oxidation treatment system applications. The first pilot-scale study describes the performance of a UV/oxidation system, developed by Ultrox International of Santa Ana, California, in treating groundwater contaminated with volatile organic compounds (VOCs). At the optimum operating conditions, the Ultrox system achieved total VOC removals of greater than 90 percent. Most VOCs were removed through chemical oxidation. However, a few VOCs were removed through oxidation and stripping. The treated groundwater met the applicable limits for discharge into a local waterway. No harmful emissions were released to the atmosphere from the Ultrox system, which is equipped with an off-gas treatment unit. The second pilot-scale study describes the performance of another UV/oxidation system, developed by Peroxidation Systems, Inc. of Tucson, Arizona, in treating groundwater contaminated with VOCs and chemical-warfare agent degradation products. At the optimum operating conditions, the system achieved contaminant removal efficiencies of about 96 percent, and the treated water met the federal maximum contaminant levels for drinking water.

INTRODUCTION

Most conventional treatment processes, such as air stripping, steam stripping, carbon adsorption, and biological treatment, although quite effective in treating water contaminated with organics, have certain limitations. For example, stripping and adsorption merely transfer the contaminants from one medium (water) to another (air or carbon), whereas biological treatment processes generate sludge that requires further treatment and disposal. In addition, biological treatment processes have low contaminant removal rates.

Chemical oxidation by ozone, hydrogen peroxide, or some other conventional oxidant could overcome most of the limitations posed by the other conventional processes (for example, merely transferring contaminants from one medium to another). However, because of kinetic limitations chemical oxidation by conventional oxidants has yet to become a competitive treatment option. Several studies have shown that the kinetic limitations could be overcome by using hydroxyl radicals to carry out the oxidation reactions [*1–3*]. The hydroxyl radicals are known to be less selective in carrying out oxidation reactions and have much higher rate constants compared to ozone, hydrogen peroxide, or ultraviolet (UV) radiation.

In commercial applications, hydroxyl radicals are generated by the combined use of (1) UV radiation and hydrogen peroxide, (2) UV radiation and ozone, or (3) ozone and hydrogen peroxide. These processes are commonly referred to as "advanced oxidation processes" or, when UV radiation is used to generate hydroxyl radicals, "UV/oxidation technologies."

This paper briefly describes (1) the chemistry of UV/oxidation technologies and factors affecting these technologies and (2) the results from pilot-scale operations of two UV/oxidation systems.

UV/OXIDATION TECHNOLOGIES: PROCESS CHEMISTRY

The key principle of UV/oxidation technologies is the generation of hydroxyl radicals through UV photolysis of hydrogen peroxide or ozone. When UV radiation is used to photolyze hydrogen peroxide or ozone, the UV radiation may also photolyze some organic contaminants, such as tetrachloroethene (PCE), aromatic halides, and pesticides, increasing their removal. A brief summary of the chemistry of UV/oxidation technologies is given below. More information on this can be found elsewhere [4].

UV Photolysis of Hydrogen Peroxide

Generation of hydroxyl radicals by UV photolysis of hydrogen peroxide may be described by the following equation:

$$H_2O_2 + h\nu \rightarrow 2OH\cdot$$

In commercial applications, low-pressure mercury vapor UV lamps are typically used to produce UV radiation, but these lamps may not be the best choice. The maximum absorbance of UV radiation by hydrogen peroxide occurs at about 220 nanometers (nm). However, the dominant emission wavelength of low-pressure mercury vapor UV lamps is at about 254 nm. Also, the molar extinction coefficient of hydrogen peroxide at 254 nm is low, 19.6 liters per mole-centimeter ($M^{-1}cm^{-1}$). Because of the low molar extinction coefficient, a high concentration of hydrogen peroxide is needed in the medium to generate sufficient hydroxyl radicals. To overcome this limitation, some technology developers (for example, Purus, Inc. of San Jose, California) use xenon UV lamps and adjust the spectral output to match the absorption characteristics of hydrogen peroxide or any other photolytic target.

UV Photolysis of Ozone

UV photolysis of ozone in water yields hydrogen peroxide, which in turn reacts with UV radiation or ozone to form hydroxyl radicals as shown below.

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \rightarrow 2OH\cdot$$

or

$$2O_3 + H_2O_2 \rightarrow 2OH\cdot + 3O_2$$

Because the molar extinction coefficient of ozone is 3,300 $M^{-1}cm^{-1}$ at 254 nm, the UV photolysis of ozone is not expected to have the same limitation as that of hydrogen peroxide when low-pressure mercury vapor UV lamps are used.

FACTORS INFLUENCING PERFORMANCE

Factors influencing the performance of a UV/oxidation technology can be grouped into three categories: (1) waste characteristics, (2) operating parameters, and (3) maintenance requirements. Each of these is discussed below.

Waste Characteristics

The contaminant removal efficiencies depend on the type of contaminants to be treated. For example, organics with double bonds, such as trichloroethene (TCE), PCE, and vinyl chloride, and aromatic compounds, such as phenol, toluene, benzene, and xylene, are easily removed because they are readily oxidized. In systems that use ozone, organics without double bonds and with high Henry's law constants, such as 1,1-dichloroethane (1,1-DCA) and 1,1,1-trichloroethane (1,1,1-TCA), are also removed. However, because they are difficult to oxidize their removal is likely to be primarily due to stripping. Organics without double bonds and with low Henry's law constants, such as diethylamine and 1,4-dioxane, would be difficult to remove because they are not easily oxidized or stripped.

Since UV/oxidation technologies are intended for the destruction of organic contaminants, any other species that consume oxidants are considered an additional load for the system. These species are called scavengers and include anions such as bicarbonate, carbonate, sulfide, nitrite, bromide, and cyanide. Metals present in their reduced states, such as trivalent chromium, ferrous iron, manganous ion, and several others, are likely to be oxidized. These metals, in addition to acting as scavengers, cause additional concerns. For example, trivalent chromium is oxidized to more toxic hexavalent chromium, and ferrous iron and manganous ions are oxidized to less soluble forms, which precipitate in the reactor and can cause UV lamp scaling and suspended solids formation. Nontarget organics (for example, humic compounds) could also act as scavengers. Other parameters such as suspended solids and oil and grease would reduce UV transmission, thereby decreasing the treatment efficiency. For these reasons, pretreatment may be required for proper functioning of UV/oxidation units depending on the waste characteristics.

Operating Parameters

Operating parameters are those parameters that are varied during the treatment process to achieve the desired treatment efficiencies. Such parameters include hydraulic retention time, ozone dose, hydrogen peroxide dose, UV lamp intensity, influent pH level, and gas-to-liquid flow rate ratio.

In general, increasing the hydraulic retention time will increase treatment efficiency up to a certain point. At this point, the system tends to proceed toward equilibrium, and increasing the hydraulic retention time no longer increases treatment efficiency.

The higher the dose of oxidants, the better the treatment rate. However, the molar ratio of the oxidant doses must be considered. For example, when treating water containing TCE and PCE, maximum removals were observed when the molar ratio of ozone dose to hydrogen peroxide dose was equal to two, and the removals were significantly less when the ratio was not equal to two. In this case, the expected stoichiometry for pure water agreed with the molar ratio at which optimum removal was observed; however, several factors may influence the molar ratio [1]. These factors are summarized as follows:

- Hydrogen peroxide can act as a free radical scavenger itself, thereby decreasing the hydroxyl radical concentration if it is present in excess.
- Ozone can react directly with hydroxyl radicals, consuming both ozone and hydroxyl radicals.
- Ozone and hydroxyl radicals may be consumed by scavengers present in the water being treated.

Therefore, the optimum proportion of the oxidants for maximum removals cannot be predetermined. Instead, the proportion needs to be determined for the waste under consideration using pilot- or bench-scale treatability tests.

In addition to photolyzing hydrogen peroxide and ozone to generate hydroxyl radicals, the UV radiation may also photolyze some organic contaminants, such as PCE, aromatic halides, and pesticides, increasing the contaminant removal.

If water has bicarbonate and carbonate alkalinity at a level greater than 400 milligrams per liter (mg/L) as calcium carbonate, lowering the pH to a range of 4 to 6 should improve

Table 1 Maintenance Requirements for UV/Oxidation Systems

Component	Maintenance	Comments
1. UV Lamp Assembly	Clean the UV lamps periodically (once every month to once every 3 months) using dilute acid (for example, acetic acid) wash, mechanical wipers, or ultrasonic equipment.	Frequency of cleaning varies depending on the type of suspended solids present in the influent or formed during treatment (for example, precipitation of iron and manganese). This can be minimized by providing proper pretreatment.
	Replace the UV lamps as necessary (due to lamp failure or significant reduction in UV radiation output with time).	Low pressure mercury vapor UV lamps are rated to last 7,500 hours and xenon UV lamps are rated to last about 500 hours, based on a use cycle of 8 hours.
		Some manufacturers recycle most of the lamp construction materials to minimize waste disposal.
2. Ozonation System (a) Air Preparation System	Replace the air filter at least once every 3 months.	Replacement frequency may vary based on air purity and flow rate.
	Check the air compressor, as recommended by the manufacturer, once every month to minimize feed air contamination by the compressor parts.	None.
	Inspect cooling water lines annually for scaling and deterioration. If a water chiller is used, inspect refrigerant dryer at least once every 3 months.	Tap water (potable water, suitable process water, or treated water) may be used as a cooling water source.
	Inspect desiccant dryer weekly to ensure proper operation. Disassemble the unit and inspect the desiccant annually, as recommended by the manufacturer, to prevent fire accidents. Replace the media once every 10 years.	Heatless absorption dryers may be used to prevent fire accidents. The media may have to be replaced sooner if the dryer has been overloaded or poorly maintained.
(b) Ozone Generator	Clean the dielectric tubes 1 year after startup and determine the future cleaning frequency at the end of first year depending on the condition of the tubes.	Trained personnel should perform the cleaning to minimize breakage or damage to the tubes. Proper maintenance of the tubes helps lower electrical energy costs.
(c) Ozone Contacting Equipment	Check pipings, valves, fittings, supports, brackets, and ozone gas spargers at least once every 3 months for deterioration resulting from a highly oxidizing environment.	Check spargers for plugging due to solids accumulation if a change in gas bubble diffusion pattern is noted. Clean the spargers to minimize cracking of joints and excessive electrical power costs.
3. Ozone Decomposer	Check the unit's temperature once a day for proper operation. Maintain the ozone decomposer as recommended by the manufacturer.	Ozone decomposer normally contains heating elements and a catalyst. The decomposer must be operated at the proper temperature to destroy ozone present in the reactor off-gas.
4. Miscellaneous	Check miscellaneous components of the treatment system, such as valves, flow meters, pipelines, and wastewater and chemical feed tanks (for example hydrogen peroxide and acid) once a week for leaks. Also check pumps and any other components once a week for proper operation.	None.

the treatment efficiency. Low pH decreases the concentration of these scavengers by shifting the equilibrium toward carbonic acid. If the carbonate and bicarbonate alkalinity is low, then a high pH should improve the treatment efficiency. High pH favors hydroxyl radical formation because of the reaction between ozone and hydroxyl ion.

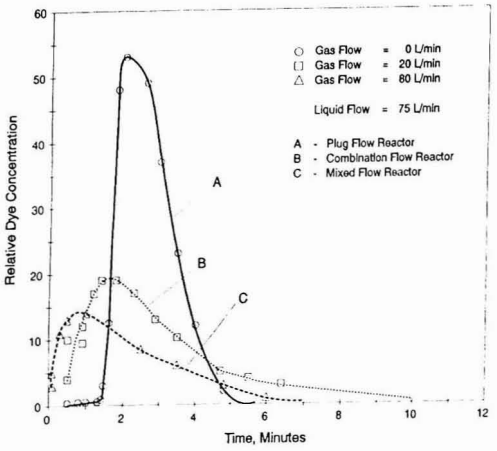

FIGURE 1. Dye tests showing effects of gas flow rates on the mixing characteristics of a bubble diffuser ozone contact basin.

The ozone gas flow rate can also influence treatment rate. In practice, once the ozone dose is selected, several combinations of ozone gas phase concentration and ozone gas flow rate can be applied. According to Venosa and Opatken [5], the ratio of gas flow rate to liquid flow rate will dictate the hydraulic characteristics of the reactor, as shown in Figure 1. This figure shows that, at low gas-to-liquid flow rate ratios, the mixing regime in a reactor is close to that of a plug flow reactor (shown as Curve A); whereas at high ratios, the reactor mixing regime is close to that of a mixed reactor (shown as Curve C). For reactions with a positive reaction order, plug flow mixing characteristics offer higher treatment rate than mixed reactor mixing characteristics [6]. Since most reactions have a positive reaction order, low gas-to-liquid flow rate ratios should be considered. In addition to increasing the treatment rate, low gas-to-liquid flow rate ratios reduce stripping of volatile organics.

Maintenance Requirements

Regular maintenance by trained personnel is essential for a successful treatment operation. The following components require maintenance: (1) ozonation system, (2) UV lamp assembly, (3) ozone decomposer unit, and (4) miscellaneous components. A brief summary of the maintenance requirements for these components is presented in Table 1.

PILOT-SCALE STUDY 1

This pilot-scale study was performed at the Lorentz Barrel and Drum (LB&D) site in San Jose, California. The LB&D site was used for drum recycling operations from about 1947 to 1987. The drums contained residual aqueous wastes, organic solvents, acids, metal oxides, and oils. Groundwater samples collected before the pilot-scale study indicated that several volatile organic compounds (VOCs) were present in the shallow aquifer. VOCs detected at high levels included TCE (280 to 920 micrograms per liter [μg/L]), vinyl chloride (51 to 146 μg/L), and 1,2-trans-dichloroethene (42 to 68 μg/L). The pH of the groundwater was about 7.2; and the alkalinity was about 600 mg/L as calcium carbonate. These measurements indicated that bicarbonate ion (HCO_3^-), an oxidant scavenger, was present at high levels. Other oxidant scavengers such as bromide, cyanide, and sulfide were not detected. Iron and manganese were present at low levels (less than 1 mg/L).

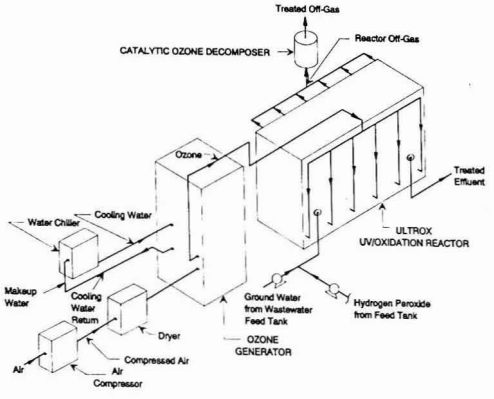

FIGURE 2. Isometric view of Ultrox system.

The pilot-scale study used a UV/oxidation system developed by Ultrox International of Santa Ana, California, and evaluated its effectiveness in treating the groundwater at the LB&D site [7]. A brief description of the Ultrox system, the testing approach, and a summary of results is presented below.

Ultrox System

The Ultrox UV/oxidation treatment system uses UV radiation, ozone, and hydrogen peroxide to oxidize organics in water. The major components of the Ultrox system are the UV/oxidation reactor module, air compressor/ozone generator module, hydrogen peroxide feed system, and catalytic ozone decomposition (Decompzon) unit (see Figure 2).

The UV/oxidation reactor used has a volume of 150 gallons (0.57 m^3) and is 3 feet (0.91 m) long by 1.5 feet (0.46 m) wide by 5 feet (1.52 m) high. The reactor is divided by five vertical baffles into six chambers and contains 24 65-watt UV lamps in quartz sheaths. The UV lamps are installed vertically and are evenly distributed throughout the reactor (four lamps per chamber). Each chamber also has one stainless steel sparger that extends along the width of the reactor. These spargers uniformly diffuse ozone gas from the base of the reactor into the water. Hydrogen peroxide is added to the influent line to the reactor. An in-line static mixer is used to disperse the hydrogen peroxide into the contaminated water in the influent feed line.

The Decompzon unit uses a nickel-based proprietary catalyst to decompose reactor off-gas ozone to oxygen. The Decompzon unit can accommodate flows of up to 10 standard cubic feet per minute (0.28 m^3/min) and can destroy ozone concentrations in ranges of 1 to 20,000 parts per million (ppm) to less than 0.1 ppm by weight.

Testing Approach

The study was designed to evaluate the Ultrox system by adjusting the levels of five operating parameters: (1) influent pH, (2) hydraulic retention time, (3) ozone dose, (4) hydrogen peroxide dose, and (5) UV radiation intensity. Eleven test runs were performed to evaluate the Ultrox system under various operating conditions. After these runs, two additional runs were performed to verify that the system's performance was reproducible. The verification runs (Runs 12 and 13) were performed at the optimum operating conditions (Run 9—influent pH of 7.2; hydraulic retention time of 40 minutes; ozone

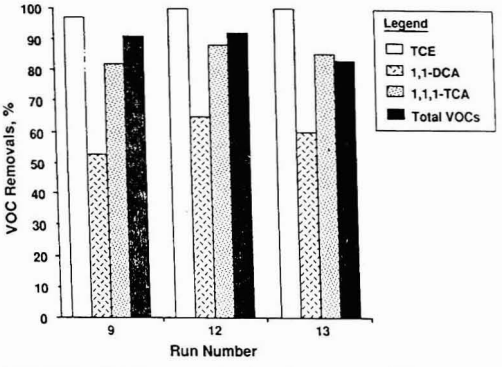

FIGURE 3. VOC removals at optimum conditions.

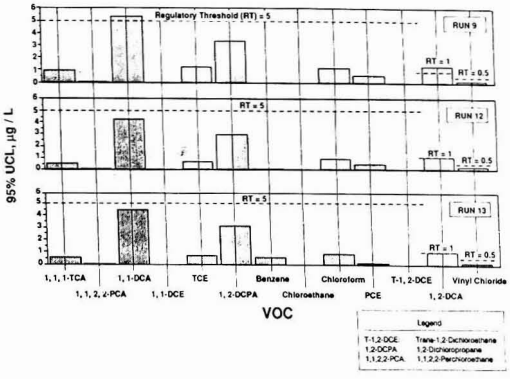

FIGURE 4. Comparison of effluent VOC concentrations.

dose of 110 mg/L; hydrogen peroxide dose of 13 mg/L; and all UV lamps operating).

During the study, a preliminary estimate of the Ultrox system's performance in each run was obtained from the effluent concentrations of three indicator VOCs. The VOCs selected for this purpose were TCE, 1,1-DCA, and 1,1,1-TCA. TCE was selected because it is a major volatile contaminant at the site, and 1,1-DCA and 1,1,1-TCA were selected because they are relatively difficult to oxidize. At the end of the study, data from all samples was used to evaluate the system's effectiveness.

Results and Discussion

This section summarizes the performance of the Ultrox system in verification runs and presents an evaluation of the UV/oxidation technology's effectiveness in removing VOCs from the groundwater at the LB&D site. A detailed summary of the demonstration results, case studies, an economic analysis, and the applicability of the Ultrox UV/oxidation technology is presented elsewhere [8].

Summary of Results for VOCs

Percent removals for the indicator VOCs and total VOCs at optimum operating conditions (Runs 9, 12, and 13) are presented in Figure 3. The figure shows that the total VOC removals were about 90 percent, while removal efficiencies for TCE were about 98 percent and those for 1,1-DCA and 1,1,1-TCA were about 60 and 85 percent, respectively. Higher removal efficiencies for TCE than for 1,1-DCA and 1,1,1-TCA supports the rationale used in selecting the indicator VOCs.

Figure 4 compares the 95 percent upper confidence limits (UCLs) for the effluent VOCs with the National Pollutant Discharge Elimination System (NPDES) limits. The UCLs were calculated using the one-tailed Student's t-test. The effluent met the discharge limits for all regulated VOCs at the 95 percent confidence level in Runs 12 and 13; in Run 9, the mean concentrations for 1,1-DCA and 1,2-DCA exceeded the discharge limits.

The gas chromatography (GC) and GC/mass spectrometry analyses performed for VOCs, semivolatile organics, polychlorinated biphenyls, and pesticides did not indicate the formation of new compounds in the treated water. Because VOCs made up less than 2 percent of the total organic carbon, the general claim that UV/oxidation technologies convert VOCs to carbon dioxide and water could not be verified.

Because the Ultrox system treated the groundwater by bubbling ozone gas through it, some VOC removal could be attributed to stripping in addition to oxidation. To determine the extent of stripping within the treatment system, VOC samples were collected from the reactor off-gas, and emission rates for four VOCs were compared to the VOC removal rates from groundwater. The results are summarized in Table 2. Because the extent of stripping for any particular VOC is expected to be proportional to the ratio of air flow rate to water flow rate,

Table 2 Extent of VOC Stripping in Ultrox System

Run No.	Air Flow Rate ÷ Water Flow Rate	Percent Stripping Contributions 1,1-DCA 0.00043*	TCE 0.0091*	1,1,1-TCA 0.014*	Vinyl Chloride 0.082*
1	2.1	7.4	2.0	43	0.01
2	2.3	9.1	3.4	34	0.95
3	2.1	9.9	2.7	31	0.01
4	2.0	7.4	3.0	29	0.01
5	2.1	17.0	3.5	29	1.7
6	4.5	16.0	1.2	65	0.07
7	1.0	4.9	1.2	12	3.1
8	4.5	23.0	7.5	85	1.2
9	4.5	16.0	6.6	58	0.04
10	4.3	27.0	9.4	73	1.1
11	4.6	44.0	24.0	>99	13.0
12	4.4	34.0	7.0	76	8.9
13	4.3	37.0	26.0	75	1.8

*Henry's law constant of the VOC, atm-m^3/mol.

this ratio is also presented in the table. The ratio for Runs 1 to 5 is approximately 2; for Run 6 and Runs 8 to 13, it is about 4.5; and for Run 7, it is 1. If stripping contributed to the total removal of the four VOCs, the extent of stripping would be expected to be least in Run 7, and most in Runs 6 and 8 to 13. The data presented in the table follow this trend for three of the four VOCs (except for the vinyl chloride in Runs 6, 7, and 9). A quantitative correlation of the extent of stripping cannot be made, because the operating conditions were different in each run. For example, at a given air to water flow ratio, when oxidant doses are varied, the extent of oxidation also varies. Therefore, the extent of stripping will be indirectly affected.

Table 2 presents Henry's law constants for the four VOCs [9]. By comparing these constants for the VOCs, their volatility is expected to increase from left to right as shown below:

$$1,1\text{-DCA} \rightarrow \text{TCE} \rightarrow 1,1,1\text{-TCA} \rightarrow \text{vinyl chloride}$$

However, significant removal fractions for 1,1,1-TCA and 1,1-DCA were observed to be due to stripping. Conversely, the extent of stripping was low for vinyl chloride and TCE. This is because it is easier to oxidize vinyl chloride and TCE than 1,1-DCA and 1,1,1-TCA because of the double bonds between the carbon atoms in TCE and vinyl chloride. In other words, in the UV/oxidation process using ozone, stripping is a significant removal pathway for compounds that are difficult to oxidize.

Performance of the Decompzon Unit

The ozone concentrations in the influent to and the effluent from the Decompzon unit were analyzed in each run. Ozone destruction efficiencies greater than 99.99 percent were achieved in Runs 1 to 10. The effluent ozone concentrations were low (less than 0.1 ppm) for Runs 1 to 8, approximately 1 ppm in Runs 9 and 10, and greater than 10 ppm in Runs 11, 12, and 13. The high ozone levels (greater than 1 ppm) in the effluent are attributed to the malfunctioning heater in the Decompzon unit. The temperature in the Decompzon unit should have been 140°F (333 K) for the unit to properly function, whereas the temperature for Runs 11 to 13 was only about 80°F (300 K).

Although the primary function of the Decompzon unit is to remove ozone, significant VOC removal also occurred when the unit functioned as designed (Runs 1 to 8). For example, the Decompzon unit removed TCE, 1,1-DCA, 1,1,1-TCA and vinyl chloride (present in the reactor off gas at levels of approximately 0.1 to 0.5 ppm) to below detection levels.

The Ultrox system's average electrical energy consumption was about 11 kilowatt-hours per hour (39.6 MJ/h) of operation at a flow rate of 3.75 gallons per minute (0.14 m^3/min).

PILOT-SCALE STUDY 2

This pilot-scale study was performed at the Old O-Field site located in the Edgewood Area of the Aberdeen Proving Ground, Maryland. The site was used for disposal of chemical-warfare agents, munitions, contaminated equipment, and various other hazardous materials during the 1940s and early 1950s. The disposal of these hazardous materials contaminated several media at the Old O-Field site, including groundwater, surface water, and sediments.

Groundwater samples collected during the pilot-scale study indicated that several organics, including VOCs, organosulfur compounds, and explosives, were present at the site in the range of 10 μg/L to 500 μg/L. Iron and manganese were present at levels of 120 mg/L and 2.5 mg/L, respectively [10]. Trace levels of arsenic contamination was also observed in some locations sampled before the pilot-scale studies.

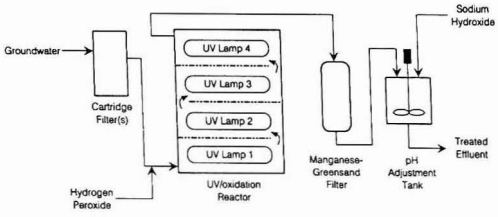

FIGURE 5. Schematic of PSI UV/oxidation system.

As part of the remediation efforts, pilot-scale treatability studies were performed in April and May 1991. A total of 37,000 gallons (140 m^3) of groundwater from three wells was used to perform the treatability studies. Contaminated groundwater was pumped to two holding tanks and then treated by a metals precipitation system. The metals precipitation was performed at pH 11, primarily to remove arsenic observed in samples collected before the pilot-scale studies began; however, the pilot-scale study samples showed no arsenic contamination. Iron and manganese were removed to levels of 0.2 mg/L and 0.02 mg/L, respectively. The pH of the metals precipitation system effluent was adjusted to 7 and then treated using two parallel systems: (1) an air stripping system followed by carbon adsorption for both liquid- and vapor-phase effluents from the air stripper and (2) a UV/oxidation system. The air stripping/carbon adsorption system was developed by Carbonair and the UV/oxidation system was developed by Peroxidation Systems, Inc. (PSI). A brief description of PSI UV/oxidation system, testing approach, and summary of results is presented below.

PSI UV/Oxidation System

Figure 5 shows a schematic of the PSI UV/oxidation system used during the pilot-scale study at the Old O-Field site. The system used during the study consisted of two parallel cartridge filters rated at 10 micrometers (μm) followed by the UV/oxidation reactor. The UV/oxidation reactor had a volume of 80 gallons (0.3 m^3) and was divided by three horizontal baffles into four chambers. Each chamber contained one high intensity, broad band, mercury-arc-type 15-kw UV lamp. A splitter was used so that hydrogen peroxide could be added at multiple points, such as the influent line and at several locations inside the reactor, making hydrogen peroxide available for hydroxyl radical formation throughout the reactor. The effluent from the reactor was passed through an optional manganese-greensand filter to remove any residual hydrogen peroxide, followed by a pH adjustment tank to raise the treated water pH to an acceptable level.

Testing Approach

Four tests were conducted at a flow rate of 15 gallons per minute (0.06 m^3/min) resulting in a hydraulic retention time of about 5 minutes. In Tests 1, 2, and 3, hydrogen peroxide doses were 45 mg/L, 90 mg/L, and 180 mg/L, respectively, with the splitter in operation; and in Test 4, hydrogen peroxide dose was 45 mg/L with the splitter not in operation. When the splitter was used, the total hydrogen peroxide dose was split into three equal parts, which were added at (1) the influent line to the reactor, (2) the effluent line from the first chamber, and (3) the effluent line from the second chamber. In Test 4, when the splitter was not used, all hydrogen peroxide was added at the influent line to the reactor. Treated and untreated water samples were collected for (1) chemical analyses to estimate removal efficiencies and compare them with federal maximum

Table 3 Performance Data for the PSI System at the Optimum Operating Conditions (Test 3)

Compound	Influent μg/L	Effluent μg/L	Percent Removal
Chloroform	41	1.2	97
1,2-DCA	22	<1.6	>92
1,2-DCE	195	<1.6	>99
Methylene Chloride	8	<1.1	>86
TCE	21	<1.4	>93
Benzene	52	<2.0	>96
Thiodiglycol	477	<10.0	>97
1,4-Dithiane	200	<2.2	>98
1,4-Oxathiane	82	<2.14	>97
Benzathiazole	20	<3.47	>82
1,3,5-Trinitrobenzene	15	0.53	96

contaminant levels (MCLs) for drinking water, and (2) bioassay to evaluate whether the water was acutely toxic to fathead minnows, daphnia magna, sheepshead minnows, and mysid shrimp.

Results and Discussion

Table 3 summarizes the influent and effluent contaminant levels and the removal efficiencies of several contaminants at the optimum operating conditions. These results show that for most compounds the effluent levels were below detection levels, and the removal efficiencies for these compounds were greater than 82 to 99 percent. The effluent levels of chloroform and 1,3,5-trinitrobenzene were 1.2 μg/L and 0.53 μg/L, respectively. The removal efficiencies for these compounds were in the range of 96 to 97 percent.

Treated effluent met federal MCLs for all compounds. The influent to and effluent from the PSI system passed the bioassay tests. The pH decreased by about one unit, indicating that some of the oxidation byproducts were acidic. Although the manganese-greensand filter was effective in removing residual hydrogen peroxide, it increased the manganese levels in treated water from about 0.02 mg/L to 1.4 mg/L, which is above National Secondary Drinking Water standard (50 μg/L). Therefore, the use of manganese-greensand filter is not recommended. Instead, other methods should be considered to neutralize any residual hydrogen peroxide in the treated water samples (for example, addition of ascorbic acid, thiosulfate, or catalase-D). If the residual oxidant level is greater than 1 mg/L and is not neutralized, it would continue to react with the contaminants in the sample bottles until analysis could be performed. This continued reaction may introduce a bias in the treatment system evaluation.

The PSI system's average electricity consumption was about 65 kilowatt-hours per hour (234 MJ/h) of operation at a flow rate of 15 gallons per minute (0.06 m^3/min). More details on the PSI system performance is available elsewhere [*10*].

CONCLUSIONS

UV/oxidation technologies appear to be efficient and competitive treatment alternatives for removing organics present in water at low levels (less than about 100 mg/L). For high strength wastes, these technologies may prove cost-effective when used in combination with biological or adsorption processes. In some cases, the UV/oxidation technologies are preferred over adsorption or biological processes, mainly because in the UV/oxidation technologies (1) contaminants are destroyed rather than being transferred to some other medium and (2) no residuals requiring further handling, such as sludge or spent carbon, are generated.

Since the UV/oxidation technologies have been used for only about 5 years long-term operation and maintenance data are currently being developed for several applications. Based on the available data, in some cases, proper pretreatment is essential to minimize frequent shut downs.

More research is needed to identify the byproducts of UV/oxidation of organics. Several technology developers claim that the byproducts of UV/oxidation of organics are carbon dioxide, water, and halides, but little published data are available to support these claims when UV/oxidation is used to treat a multitude of contaminants present in groundwater. Despite this situation, UV/oxidation technologies can continue to be used as long as appropriate physicochemical analyses and toxicity tests are carried out on the effluent, and these analyses and tests indicate that the effluent meets the discharge criteria. In some cases, the economics may favor the effluent's use as process water or sanitary water in industries depending on access and suitability.

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Limitations and Practical Use of a Mass Transfer Model for Predicting Air Stripper Performance

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The Onda Mass Transfer Model is widely used for predicting air stripper performance, yet reports of its reliability vary significantly. Researchers, who generally pay close attention to all aspects of a stripping column's design, construction, and operation, report results closely aligning with model predictions (±30 percent). In practice, however, where design and construction details vary, much wider variations between field performance and model predictions are reported.

This paper discusses design and construction issues that can contribute to performance problems in practice and lead to field deviations from model predictions. The design and construction issues of greatest importance include: liquid distribution, packing material, and adherence to the limitations and restrictions of the air stripping model used, in this case the Onda Model. Some less common problematic areas are also discussed, including: Henry's Law data, fouling, chemical reactions, and end effects.

INTRODUCTION

Countercurrent packed tower air stripping is used extensively for removing volatile organic compounds (VOCs) from water and wastewater. Several models exist for estimating the performance of a packed tower stripper, but the Onda mass transfer model has been widely accepted as the best, at least by researchers. Several researchers have reported the model can predict column performance over a wide range of packing and loading conditions. However, practitioners occasionally report widely different results between the model and actual operation. This paper explores some of the reasons for this apparent discrepancy and provides practical design, construction, and troubleshooting guidelines.

AIR STRIPPING THEORY

The operation theory of a countercurrent packed tower has been well documented in chemical engineering textbooks [*1*, *2*]. The basic principle behind air stripping is the overall mass transfer coefficient, K_L, derived from the two-phase resistance theory. As described in the following equation, this theory states that the total resistance to mass transfer between phases is equal to the sum of the individual liquid phase and vapor phase resistances, and the reciprocal of a mass transfer coefficient is the resistance to mass transfer.

$$K_L^{-1} = k_L^{-1} + Hk_G^{-1} \quad (1)$$

Where

- K_L = Overall liquid mass transfer coefficient (length * time^{-1})
- k_L = Individual liquid phase mass transfer coefficient (length * time^{-1})
- k_G = Individual gas phase mass transfer coefficient (length * time^{-1})
- H = Henry's constant at 1 atmosphere of total pressure on a volume of water to volume of air basis (water volume/air volume)

Performance of an air stripping system is calculated using the transfer unit approach. The overall height (Z) of packing required for a given performance is the product of the height of a transfer unit (HTU) and the number of transfer units (NTU) as follows:

$$Z = HTU * NTU \quad (2)$$

Where

$$HTU = L/K_L a \quad (3)$$

$$NTU = [S/(S-1)] * \ln\{[(C_{L(in)}/C_{L(out)})(S-1)+1]/S\} \quad \text{if } S \neq 1 \quad (4a)$$

$$NTU = (C_{L(in)}/C_{L(out)}) - 1 \text{ if } S = 1 \quad (4b)$$

$$S = H(G/L) \quad (5)$$

and

L = Liquid rate (volume * time^{-1} * area^{-1})
G = Gas rate (volume * time^{-1} * area^{-1})
a = Effective interfacial area for mass transfer per volume of liquid (area * volume^{-1})
S = Stripping factor (dimensionless)
$C_{L(in)}$ = Influent liquid concentration of target compound (mass * volume^{-1})
$C_{L(out)}$ = Effluent liquid concentration of target compound (mass * volume^{-1})

DESCRIPTION OF THE ONDA MASS TRANSFER CORRELATION

The Onda mass transfer correlation is widely held to be the most suitable model to estimate mass transfer coefficients in air stripping columns [*3*, *4*, *5*]. The correlation estimates individual liquid phase resistance, k_l, individual gas phase resistance, k_g, and interfacial area, a, for use in calculating the overall mass transfer coefficient. Onda's three equations are:

$$k_l = 0.0051(L_M/a_w\mu_L)^{2/3} * (\mu_L/\rho_L D_L)^{-1/2} * (a_t D_p)^{0.4} * (\rho_L/\mu_L g)^{-1/3}$$

$$k_g = a_t D_G * c * (G_M/a_t\mu_G)^{0.7} * (\mu_G/\rho_G D_G)^{1/3} * (a_t Dp)^{-2}$$

$$a_w = a_t * \{1 - \exp[-1.45(\sigma_c/\sigma_L)^{0.75} * (Re_L)^{0.1}(Fr_L)^{-0.05}(We_L)^{0.2}]\}$$

Where

a_w = Wetted specific surface area of the packing-assumed equal to interfacial area (area * volume^{-1})
a_t = Total specific surface area of packing (area * volume^{-1})
L_M = Liquid mass flux (mass * area^{-1} * time^{-1})
G_M = Gas mass flux (mass * area^{-1} * time^{-1})
μ_L = Viscosity of liquid (mass * length^{-1} * time^{-1})
μ_G = Viscosity of gas (mass * length^{-1} * time^{-1})
ρ_L = Density of liquid (mass * volume^{-1})
ρ_G = Density of gas (mass * volume^{-1})
D_L = Liquid diffusion coefficient (length^2 * time^{-1})
D_G = Gas diffusion coefficient (length^2 * time^{-1})
Dp = Average size of packing (length)
g = Gravitational constant (length * time^{-2})
c = 2 if dp < 15 mm or 5.23 if dp > 15 mm (dimensionless)
σ_c = Surface tension of packing material (force * length^{-1})
σ_L = Surface tension of liquid (force * length^{-1})
Re_L = $(L_M)/(a_t\mu_L)$ = Liquid phase Reynolds number (dimensionless)
Fr_L = $(L_M^2 a_t)/(\rho_L^2 g)$ = Liquid phase Froude number (dimensionless)
We_L = $(L_M^2)/(\rho_L \sigma_L a_t)$ = Liquid phase Weber number (dimensionless)

LIMITATIONS OF THE MODEL

The Onda model is known to have limitations. These include a set of assumptions inherent in the transfer unit construction represented by equations 2 through 5 above. Limitations are also presented by the range of data with which the model has been verified, most particularly packing types and sizes. In addition, practical experience advises against use of the model at stripping factors below 1.5 [*4*]. Other parameters such as liquid loading rate, air:water ratio, and VOC properties have been tested against the model over quite wide ranges, and the model has performed suitably.

TRANSFER UNIT MODEL ASSUMPTIONS

Equations 2 through 5 have certain implicit assumptions that limit the model's range of application. Generally referred to as the "dilute solution, Henry's Law" condition [*1*], the assumptions include:

- Ratio of $(1 + X1)/(1 + X2)$ is essentially unity-dilute solution ($X1$ and $X2$ are the influent and effluent liquid concentrations of target compound)
- Constant L/G
- Henry's Law applies (equilibrium gas-phase concentration proportional to liquid-phase concentration)
- Isothermal operation

These assumptions are generally met for ambient temperature air stripping of VOCs.

ONDA CORRELATION—RANGE OF PACKING TYPES AND SIZES

The original Onda work included mostly data taken using 1-inch size and smaller Raschig rings, Berl saddles, Pall rings, spheres, and rods. Subsequent work in VOC stripping has shown that the model performs equally well for 1- and 2-inch Pall rings, saddles, and Tri-Packs [*4*, *6*].

ACCURACY OF THE MODEL

When used within the above limitations, the model has been shown to perform with an accuracy of ±30 percent with 90 percent confidence [*4*]. This result is based on analysis of a total data base of 449 points. After removing 12 data points that did not meet the model limitations described above, the Onda model overestimated mass transfer rates 192 times (with a corresponding + 16 percent average) and underestimated the values 239 times (with a corresponding − 11 percent average). Relative standard deviation computed was 17 percent.

PRACTICAL USE OF THE MODEL

A comparative review of air stripper performance in practice with that reported in research presents a paradox. Although researchers report the Onda model to be a good predictor of air stripper performance, practitioners relying on the model are occasionally disappointed with the performance of their air stripping columns. A recent review of 90 pilot and full-scale air strippers reported that "the correlation overestimated the mass transfer coefficient 75 percent of the time with an average overestimate of 37 percent. Some individual overestimates were more than 100 percent" [*7*].

The question that this paradox poses for the practitioner is, "how much deviation in practice is random variation within the model, and how much is controllable through careful attention in design and construction?"

It is important to remember that a mass transfer model will only predict the performance of an air stripper if the design of that air stripper is similar to those upon which the model was correlated. A host of variables under the control of the air stripper designer and constructor are not incorporated into or anticipated by the Onda model. For most of these variables there are standards of practice for design and construction. Since deviation from these standards will typically result in degraded performance, it is possible that these deviations from standard practice are the cause of the paradox discussed above.

The variables available to the designer and constructor include:

- Liquid distribution
- Packing
- Various construction practices
- Henry's Law Data
- Fouling
- Chemical reactions
- End effects

Of these, experience shows liquid distribution and packing selection and installation to be the most common causes of underperformance of air stripping columns.

LIQUID DISTRIBUTION

"Proper liquid distribution is the key to achieving the desired performance from any modern, high-efficiency random or structured packing" [*8*]. The packed depth required to achieve a given removal efficiency can increase by 10 to 25 percent in a typical VOC air stripper if "distribution quality" is 65 percent compared to a desired 90 percent. Poorer distribution can result in up to a 75 percent increase in packed depth requirements [*9*].

Any model of a packed column will require uniform liquid distribution. Research columns on which the Onda model has been validated will generally be carefully designed to achieve this condition. It will be difficult to replicate the model's predicted results unless careful attention is paid to liquid distribution.

Distribution Quality

Distribution quality is measured by three basic parameters [*8*]:

1. Number of distribution points (distribution density)
2. Geometric uniformity of distribution points across tower cross section
3. Uniformity of liquid flow from the distribution points

Recommended distribution density varies depending on the degree of separation desired, the packing size, and the fouling tendency of the system. Generally higher degrees of separation will require a greater distribution density. For general service most authorities recommend 9 to 10 distribution points per square foot. For lighter duties 1 to 3 points per square foot may be suitable.

Geometric uniformity of distribution points has more effect on packing efficiency than the distribution density [*8, 9*]. Various techniques have been suggested for analyzing geometric uniformity. One technique, suggested by the Norton Company, divides the tower cross section into three radial zones of equal areas. The number of distribution points in each section should ideally be equal. This technique will highlight under-irrigation of the wall zone.

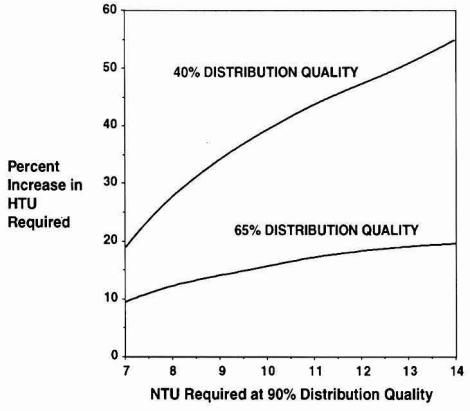

FIGURE 1. Effect of liquid distribution quality. [Adapted from Figure 9-6 (*9*).]

Uniform liquid flow can be one of the most difficult parameters to achieve and is an obvious source of poor distribution. Manufacturing limitations such as drill or punch reproducibility and construction factors such as levelness and fit-up tolerances can affect the uniformity of liquid flow. The necessity for uniform liquid distribution has often been thought to decrease as the liquid rate per square foot increases. However, it has been found that, regardless of the liquid rate, the necessity for uniform irrigation increases as the number of theoretical stages per packed bed is increased. For less than five theoretical stages per bed, the column is not as sensitive to the uniformity of liquid distribution. For over five theoretical stages per bed, the liquid distribution has a significant effect on packing efficiency, as shown in Figure 1.

Distributor Types

Distributors fall into two general categories: gravity-fed and pressure-fed. Of these, gravity-fed are more common and include orifice-riser and weir-trough types. Generally, orifice-riser distributors are preferred for smaller columns (3 feet and smaller) handling clean liquids. Weir troughs are most commonly used in larger towers [*10*]. Figure 2 shows an example design of an orifice-riser distributor. Figure 3 shows a traditional weir-trough distributor.

Pressure-fed distribution systems are generally of the orifice-pipe or "ladder" type. Figure 4 shows an example design of this type of distributor. The orifice-piper distributor is particularly suited for handling low liquid rates, and can be used in any diameter column [*10*].

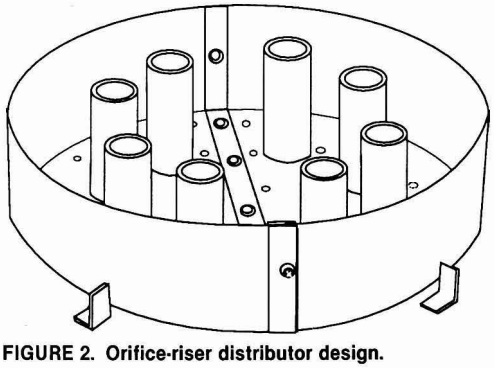

FIGURE 2. Orifice-riser distributor design.

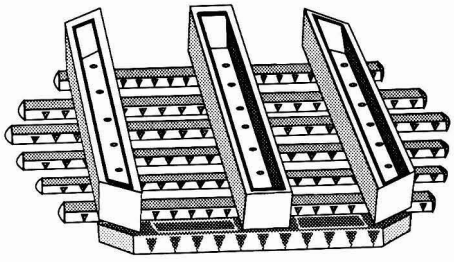

FIGURE 3. Weir-trough liquid distributor.

Spray-nozzle distributors have been used to irrigate packed beds, typically in heat transfer applications; however, they do not generate a uniformly distributed liquid flow pattern. A reasonably uniform liquid irrigation flow pattern requires 100 percent overlap, which is normally impractical to install [9]. For this reason, spray headers are not recommended for air strippers requiring high removal efficiencies.

Distributor Installation

The single most important detail for distributor installation, especially for gravity distributors, is that they be installed level within a very tight tolerance. For example, the flow through a V-notch weir is very sensitive to liquid level. This is a benefit because it gives good turndown performance, but a liability if the distributor is not installed level. A 60-degree V-notch weir that distributes 7 gallons per minute at 2 inches of head will pass almost 20 gpm at 3 inches of head. Thus, an inch differential height across a 14-foot-diameter column (0.6 percent deviation) can result in nearly three times the flow on the low side of the distributor.

In addition to level tolerances, gravity distributors require that the momentum of the influent liquid be low enough to avoid disrupting the gravity flow characteristics of the device. This commonly requires that the influent header split into multiple feeds that deliver liquid to the distributor at several points as opposed to a single stream impacting the distributor. Manufacturer's installation instructions generally address this issue.

Indications of Poor Liquid Distribution

An unusual relationship between mass transfer or removal efficiency and liquid flow rate in the tower may be a strong indication of poor liquid distribution. In one 14-foot-diameter tower a dramatic reduction in efficiency was observed as the flow rate increased from 1,500 gpm to 4,000 gpm. Figure 5 shows the performance of the tower compared to predictions of the Onda model.

The tower was taken out of service, and the operation of the weir trough distributor was observed. It was apparent from viewing the distributor that it was not performing adequately. The distributor was designed by an inexperienced contractor from textbook equations rather than purchased from an experienced designer of tower internals. The velocity of the liquid entering the troughs was too high, resulting in alternating shallow zones where minimal liquid was distributed onto the packing, and mounded zones where liquid was overflowing the trough onto the packing. This velocity problem was accentuated at higher liquid rates, resulting in a dramatic decrease in performance as the liquid rate increased. The owner is aware that the distributor will require replacement if increased tower performance is required. Fortunately, a safety factor used in the design of the tower compensated for the poor distribution.

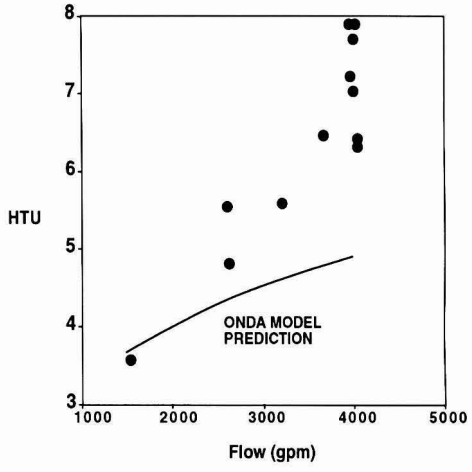

FIGURE 5. Tower performance with poor liquid distribution.

Liquid rate was the indicator in another instance involving a 12-inch-diameter pilot column. Review of the data showed the removal efficiency actually increased with increasing liquid rate. This is contrary to the relationship one would except from experience and mass transfer models. Investigation of the pilot unit showed that the orifice-pipe distributor had been partially plugged by sand from the newly developed well. At low flow conditions only a few of the orifices were observed to distribute water onto the packing, while at high flows the distribution appeared to be more complete. The distributor was replaced with an orifice riser type (gravity distributor), and performance improved significantly.

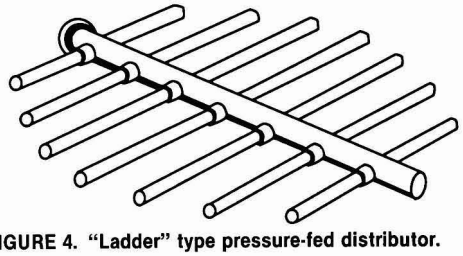

FIGURE 4. "Ladder" type pressure-fed distributor.

Packing

There are two basic types of packing used for mass transfer columns: random and structured. Random packing consists of individual pieces with unique shapes that are "dumped" into the column, resulting in a random orientation of the pieces. Structured packing is fabricated in blocks and stacked in the column, resulting in a uniform orientation of surfaces. Both types of packing provide large surface areas for mass transfer between air and water. While both have been used for air stripping services, random packing is the most common. Figure 6 shows several different types of random packing.

Appropriate Use of the Onda Model

The Onda model has only been verified for a limited set of packing types and may not be suitable for other types of packing. As given above, the packing types on which the correlation is based include: 1-inch size and smaller Raschig rings, Berl

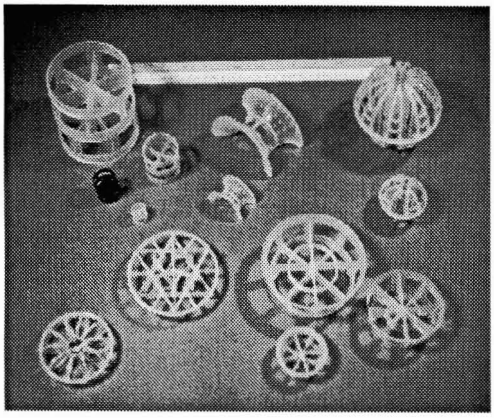

FIGURE 6. Types of random packing.

saddles, Pall Rings, spheres, and rods. Subsequent work in VOC stripping has shown that the model also performs well in predicting performance of Pall rings, saddles, and Tri-Packs in 1- or 2-inch sizes [*4*, *6*]. Although the model may adequately predict the performance of other packing types, the designer should apply them with caution. Representatives from LANTEC, INC., and Rauschert Industries have both indicated that the model fails to adequately predict the performance of their packing. The model has not been verified for packing larger than 2-inch size and may not perform well in this size range. It is also unlikely that the model would predict the performance of structured packing materials. When we consider that the Onda model predicts packing performance based on only three packing parameters (packing material, specific surface area, and characteristic diameter), it is surprising that the model adequately predicts the differences between the packings for which it does perform well.

For packing types where the model has not been verified, data are generally required to design an air stripping column. Data can be obtained from pilot testing if reliable comparative data are not available. Comparative data that might be used in lieu of pilot data might include: data comparing the performance of the desired packing to predictions of the Onda model, or pilot data taken by others under conditions similar to the designer's application. In some cases, manufacturer's representatives may be able to provide verifiable performance data suitable for tower design.

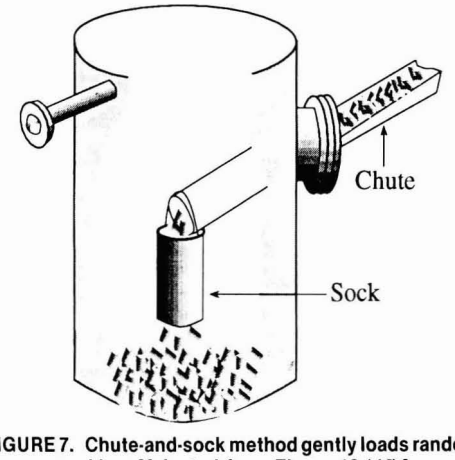

FIGURE 7. Chute-and-sock method gently loads random packing. [Adapted from Figure 13 (*10*).]

Packing Installation

Proper installation of the packing is important to achieve predictable results. For loading large quantities of packing for a large-diameter tower, or when the loading manway is greater than 20 feet above the support plate, a chute-and-sock arrangement is recommended (Figure 7). In large-diameter towers where workers may need to be on top of the bed to distribute and level the packing during loading, plywood or another rigid material having an area of 4 square feet or more should be used to stand on [*10*].

The tower packing should be installed after erection of the tower. In some cases, packing has been installed in the shop prior to shipping. During shipping the packing can shift in the tower, resulting in the packing binding together and bridging, thus leaving gaps in the packing section. There may be instances where costs are saved by shipping the packing within the tower, but the tower should always be repacked in the field to ensure appropriate random distribution of the packing.

It should be obvious, but leaving foreign materials in the packed bed can seriously degrade stripper performance. For example, if workers stand on plywood during installation, it is important that the plywood be removed. In one installation, a plastic film, that was intended to be removed before packing was installed, was inadvertently left on the interior wall of an FRP tower. A tower identical in all other respects was installed at the same site. The tower without the plastic film achieved the 92 percent design removal efficiency. The adjacent tower was achieving only 89 to 90 percent removal at the same flow rates. It appeared from observing the problem tower that liquid might be trapped behind this film and run down the wall without contacting air, resulting in the poor removal efficiency. Subsequent analysis indicated that only 5 percent of the flow trapped behind the plastic film would have given the measured result. The result appeared to be a 60 percent error in the model's prediction of HTU, but it was actually an error made during installation of the tower.

Other Tower Performance Factors

There are other factors that can cause an air stripping tower to perform below anticipated results. These include:

- Henry's Law Data
- Fouling
- Chemical reactions
- End effects

In general, these factors are believed to be either less frequent problems or to have lesser effects than the distribution and packing considerations discussed above. However, in some cases, they may turn out to be the cause of unexpected performance problems in field installations.

Henry's Law Data

The model as presented in equations 2 through 5 assumes that Henry's Law applies. This means that the equilibrium curve is linear and extends through the origin. For most of the VOCs in common air stripping applications, this condition is met. Occasionally ketones or ethers are encountered for air stripping that do not meet this criteria and require extra care in predicting performance.

It is also important that accurate Henry's constant data be available for modeling the air stripping system. For many of the commonly encountered VOCs, a significant data base of values is available from recent literature [*6*, *11*, *12*, *13*]. However, coverage is not complete for all VOCs encountered. When data are absent or data reliability is in question, modeling results will be of limited value. In these cases, pilot testing or

laboratory measurement of the Henry's constant is recommended.

Temperature affects the Henry's constant by an Arrhenius-type relationship (log H is proportional to $1/T$). Data are less commonly available for temperature variations of VOCs, but since most air strippers operate near the ambient temperatures at which data are taken, temperature effects can generally be accounted for in design. If air stripping is intended to operate at elevated temperatures, predicting Henry's constants for the VOCs may be difficult. Also, at elevated temperatures, some of the other assumptions inherent in equations 2 through 5, such as constant L/G and isothermal operation, may be violated.

When stripping VOCs from water or wastewater containing dissolved organic concentrations, there may be concern about interactive or cosolvency effects that reduce the volatility of the VOCs being stripped. Researchers have traditionally assumed there are no interactions or effects of Henry's constants. Other researchers have reported no significant effect on experimental data with the addition of methanol to the mixture [6].

Fouling

Fouling problems may cause towers to perform below the expectations of the designer. However, it would be unlikely that these problems would be present immediately after startup; typically, tower performance degrades over time. An exception may be distributor plugging with a high solids load as discussed in the distributor section above.

Fouling may be caused by solids in the feed liquid or chemical or bacterial deposition on the column internal surfaces. If fouling is anticipated to be a problem, the designer should make provisions by selecting larger packings, specifying larger openings in distributors, and providing for chemical addition or cleaning facilities to periodically remove accumulated solids.

Chemical Reaction

The Onda model does not account for chemical reactions occurring during the stripping application. Most of the commonly encountered VOCs are very stable and are resistant to chemical reactions under the conditions encountered in a stripping tower. However, if a chemical reaction were to occur, its effect would be significant. In one case, an air stripping column was designed to remove trihalomethanes (THM) from chlorinated water. Most of the THMs were removed as predicted by the Onda model. However, chloroform seemed to approach an asymptotic removal efficiency of about 80 percent, irrespective of the air flow rate used. The conclusion was that chloroform was being formed by reaction of the residual chlorine with organics present in the water. While chemical reactions may be rare in occurrence, they can cause significant problems.

End Effects

There is sometimes concern that column "end effects," the mass transfer that occurs above and below the packed bed, may distort the interpretation of pilot data. Most have found that this effect is negligible in all but the shortest of pilot columns (less than six feet) and can generally be disregarded [4].

CONCLUSIONS

Researchers and practitioners report different results regarding the Onda model's accuracy in predicting the performance of air strippers. Under the controlled environment of the research laboratory or in pilot testing, where careful attention is paid to all the aspects of a stripping column design, construction, and operation, predictions of the Onda model closely match operating data. In practice, however, where design and construction details vary, reports continue of significantly different results between field performance and model predictions. Careful attention to design and construction details on the part of the practitioner can minimize these discrepancies.

The most important details of design and construction include: liquid distribution, packing materials, and adherence to the limitations and restrictions of the air stripping model used. Other factors, which can be equally important in achieving adequate performance but are less often the cause of performance problems, include: Henry's Law data, fouling, chemical reactions, and end effects.

The Onda model has been found to be the best available mass transfer model for estimating air stripper performance at this time. An understanding of its limitations is essential to properly use the model for estimating air stripper performance. Adherence to good design and construction standards is essential for providing the best opportunity for the full-scale or pilot stripping column's performance to match the predicted results.

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Modeling the Effects of Plants on the Bioremediation of Contaminated Soil and Ground Water

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Plants have the potential for aiding in situ remediation of contaminated soil and groundwater by promoting microbial growth in the rhizosphere. Microbial populations vary in response to the presence of oxygen, water and metabolizable carbon sources. Plants are able to provide a favorable environment for microbe growth by providing a plant pathway for oxygen transfer to the soil, transferring water from saturated to unsaturated soil, and supplying supplemental substrate in the form of root exudates and decaying root hairs. Models of the physical, chemical, and biological relationships in the rhizosphere are reported. Simulation results are presented for a hypothetical vegetative buffer zone over a shallow aquifer. The fate of atrazine is simulated in order to investigate the effects of rainfall, evapotranspiration, atrazine uptake by plants, and atrazine adsorption to root surfaces on atrazine concentration at the downstream edge of the vegetative buffer zone.

INTRODUCTION

The rhizosphere, the root-zone of a plant, has an enhanced microbe population that is capable of degrading various compounds. For instance, Aprill and Sims (1990) reported that the degradation of polycyclic aromatic hydrocarbons was higher in a site vegetated with prairie grasses as compared to a non-vegetated site. While considerable literature is cited in this paper [*1–40*], the authors [*31, 32*] have reviewed the literature on remediation processes associated with the rhizosphere.

Plants with appropriate selection and spacing offer a cost effective bioremediation technology. Schnoor and Licht [*30*] planted a buffer zone of deep-rooted poplar trees which successfully intercepted and metabolized contaminant runoff from an agricultural field. For such a non-point source, with a wide distribution of contaminants in the soil, the use of plants in bioremediation is not only economical, but also it appears to be an efficient method of restoring contaminated sites. Nair [*24*] and Nair and Schnoor [*25*] have modeled the movement of alachlor and atrazine and compared the results with experimental field data. The PRZM (Pesticide Root Zone Model) was used. Paterson and Schnoor [*26*] reported that their model was most sensitive with respect to pesticide half-life, transpiration, root fraction, and pesticide concentration.

This paper addresses two factors in the role of the rhizosphere in bioremediation. The first is the movement of contaminants in the soil and their fate as they move past the root zone. Contaminants may be either degraded by the rhizosphere microbial community or taken up as part of the plant's transpiration stream. The second factor is the growth kinetics of the rhizosphere microbes including the rate of degradation, limiting factors associated with microbe growth, and how the appropriate plants provide a beneficial environment for biodegradation.

TRANSPORT MODEL DEVELOPMENT

There are a number of mathematical models to describe the movement of water and solutes in soil [*25, 26, 32, 33, 38*]. The model which the authors have selected can be used to model water movement in the soil and the plant in both the unsaturated and saturated zones. It is especially appropriate where the emphasis is on plant uptake and evapotranspiration.

In previous studies by Tracy and Mariño [*21, 35, 36*] root-soil water flow and contaminant transport models were developed to simulate the movement of water and a conservative solute through a root-soil environment as a continuous process. In two dimensions the root-soil water flow model can be written as a pair of coupled equations [*36*]

$$\frac{\partial}{\partial x}\left[K_{s_x}\frac{\partial \psi_s}{\partial x}\right]+\frac{\partial}{\partial z}\left[K_{s_z}\frac{\partial(\psi_s+z)}{\partial z}\right] - q=\left[\beta S_s+S_y\frac{dS_e}{d\psi_s}\right]\frac{\partial \psi_s}{\partial t} \quad (1)$$

$$\frac{\partial}{\partial x}\left[K_{r_x}\frac{\partial \psi_r}{\partial x}\right]+\frac{\partial}{\partial z}\left[K_{r_z}\frac{\partial(\psi_r+z)}{\partial z}\right] + q=R_d\frac{\partial WC_r}{\partial t}+WC_r\frac{\partial R_d}{\partial t} \quad (2)$$

in which: x, z = the horizontal and vertical directions of the simulation environment in meters (m), respectively; K_s = the hydraulic conductivity of the soil (m/d); K_r = the hydraulic conductivity of the root (m/d); ψ_s = the soil-water pressure head (m); ψ_r = the root-water pressure head (m); S_y = the specific yield of the soil (m^3/m^3); S_s = the specific storage of the soil (m^{-1}); S_e = the effective saturation of the soil (m^3/m^3); $\beta = 0$ if $\psi_s < 0$ and $\beta = 1$ elsewhere; R_d = the root density in the soil (m^3/m^3); WC_r = the root-water content (m^3/m^3); t = time (d); and q = the rate of extraction of soil-water by a plant's root system (d^{-1}). The term q is defined in Mariño and Tracy (1988) as

$$q = S_e R_d \Gamma(\psi_s - \psi_r) \quad (3)$$

where Γ = a lumped parameter describing the permeability of a plant's root system ($m^{-1} \cdot d^{-1}$).

To solve the coupled root-soil water flow model described by Eqs. 1 and 2, the root parameters, the initial and boundary conditions, and the relationships between the water content, hydraulic conductivity, and water pressure head of the soil, referred to as the soil characteristics, must be known. The initial and boundary conditions that are required to solve Eqs. 1 and 2 are discussed in detail in Tracy and Mariño [36]. The root parameters, K_r and Γ, are typically estimated using the results of field or laboratory studies and are thus obtained for specific plants growing in specific locations. The soil characteristics must be obtained from either laboratory experiments or mathematical relationships proposed in a variety of studies, e.g. Brutseart [9]. The method chosen to simulate the soil characteristics should be based on the type of soil that is being modeled and the amount of information available on the required relationships.

The solution of Eqs. 1 and 2, subject to the initial and boundary conditions, produces a spatial and temporal distribution of the soil and root-water pressure heads. The soil-water pressure head distribution is then used to determine the flux of water in the horizontal and vertical directions of the soil using Darcy's law as

$$V_x = -K_{s_x}\frac{\partial \psi_s}{\partial x} \quad (4)$$

$$V_z = -K_{s_z}\frac{\partial(\psi_s+z)}{\partial z} \quad (5)$$

in which V = the Darcy Flux (m/d). The Darcy's flux terms can then be used as the convective transport parameters in the Convective-Dispersive mass transport equation to describe the movement of a conservative contaminant through a root-soil environment as [36]

$$\frac{\partial}{\partial x}\left[\theta\left(D_{xx}\frac{\partial C}{\partial x}+D_{xz}\frac{\partial C}{\partial z}\right)-V_x C\right] + \frac{\partial}{\partial z}\left[\theta\left(D_{zx}\frac{\partial C}{\partial x}+D_{zz}\frac{\partial C}{\partial z}\right)-V_z C\right]=\frac{\partial(C\theta)}{\partial t} \quad (6)$$

in which: C = the solute concentration (kg/m^3); D = the dispersion coefficient (m^2/d); and θ = the soil-water content (m^3/m^3) which is related to the effective saturation as $S_e = \theta/n$ where n = the soil porosity (m^3/m^3). The effective saturation is a function of the soil-water pressure head; one such relationship is [9]

$$S_e = \frac{A}{[A+(-\psi_s)^c]} \quad (7)$$

The hydraulic conductivity in unsaturated soil depends on the effective saturation; for example, the model of Brooks and Corey [8]

$$K_s = K_{sat}(S_e)^d \quad (8)$$

is used in this work.

However, Eq. 6 does not account for the uptake of a solute into a transpiring plant's root system or the adsorption of the contaminant onto the root mass. Briggs *et al.* [7] proposed that the uptake of an organic contaminant into the transpiration stream of a plant could be described for dilute solutions as a linear function of the rate of soil-water extraction by the plant's root system, such that

$$C_{ts} = T_{scf} C \quad (9)$$

in which C_{ts} = the contaminant concentration in the plant's transpiration stream (kg/m^3) and T_{scf} = the plant's transpiration stream concentration factor (dimensionless); Briggs *et al.* [7] showed T_{scf} to be a function of the contaminant's octonal-water partition coefficient (dimensionless), K_{ow}, in the following relationship:

$$T_{scf} = 0.784\exp\left\{\frac{-(\log K_{ow}-1.78)^2}{2.44}\right\} \quad (10)$$

Thus, Eq. 6 may be modified to contain a contaminant sink term that is simply a product of the rate of soil-water extraction by the plant's root system, the soil-water contaminant concentration, and the plant's transpiration stream concentration factor, such that

$$S = -qT_{scf}C = -T_{scf}[S_e R_d \Gamma(\psi_s - \psi_r)]C \quad (11)$$

where S = the contaminant sink due to plant uptake ($kg/m^3 \cdot d$).

Briggs *et al.* [7] also demonstrated that the adsorption of a contaminant onto a plant's root mass could be expressed as a linear function of soil-water contaminant concentration

$$q_r = R_{cf} C \quad (12)$$

where q_r = the contaminant concentration adsorbed to the root mass (kg/m^3) and R_{cf} = the plant's root concentration factor (dimensionless), which was also shown to be a function of the contaminant octanol-water partition coefficient as

$$R_{cf} = 0.82 + 10^{(0.77\log K_{ow}-1.52)} \quad (13)$$

A contaminant may also adsorb to soil: this relationship is often written in the form

$$q_s = K_d C \quad (14)$$

where the value of K_d (m^3/kg) depends on the organic matter content of the soil, and q_s is the amount of adsorbed contaminant per unit mass of soil (kg/kg). As roots and root hairs die, organic matter is added to the soil; thus, the value of K_d

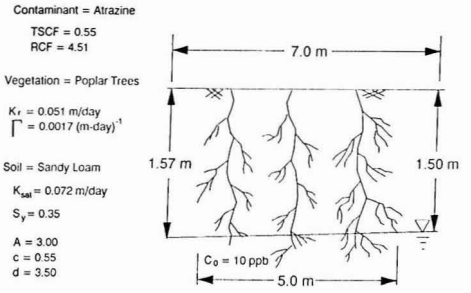

FIGURE 1. Example problem for atrazine movement through a shallow aquifer.

is expected to be larger in the rhizosphere and it may increase with time after the planting of a vegetative buffer.

Thus, the total mass of contaminant in the root-soil environment would have to be expressed as

$$M = C(R_d R_{cf} + \rho K_d + \theta) \tag{15}$$

where M = the mass of contaminant per unit volume of root-soil environment; R_d is root density in the soil (m^3/m^3) and ρ is the bulk density of the soil (kg/m^3). Other terms are as described above.

The study of Briggs *et al.* [7] used barley to develop the relationships given in Eqs. 10 and 13, but subsequent work by McFarlane *et al.* [22] has demonstrated that the relationships are valid for a wide variety of plant species.

The model to simulate the transport of a hazardous organic chemical through a root-soil environment can now be rewritten to include both the uptake of contaminants by a transpiring plant's root system and the adsorption of contaminants onto the plant's root mass as

$$\frac{\partial}{\partial x}\left[\theta\left(D_{xx}\frac{\partial C}{\partial x}+D_{xz}\frac{\partial C}{\partial z}\right)-V_x C\right] + \frac{\partial}{\partial z}\left[\theta\left(D_{zx}\frac{\partial C}{\partial x}+D_{zz}\frac{\partial C}{\partial z}\right)-V_z C\right]-qT_{SCF}C = \frac{\partial[C(\theta+R_d R_{cf}+\rho K_d)]}{\partial t} \tag{16}$$

The initial and boundary conditions and estimates of the dispersion coefficients that are required to solve Eq. 16 are discussed in detail in Tracy and Mariño [36].

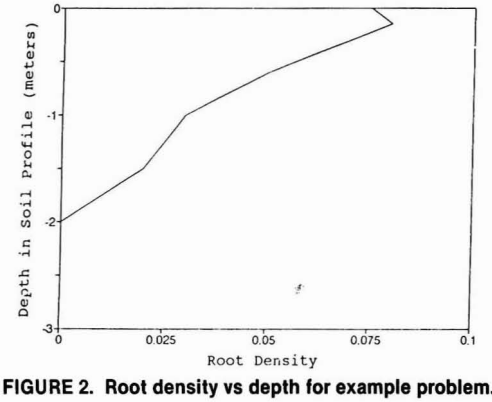

FIGURE 2. Root density vs depth for example problem.

The model described in Eqs. 1, 2 and 16 is solved using a Galerkin finite element method using isoparameteric quadratic elements and a Crank-Nicolson difference method for the time derivative. A more complete description of the general solution technique used to solve these equations can be found in Tracy and Mariño [35].

HYPOTHETICAL STUDY AREA

Figure 1 shows a hypothetical soil system with a proposed vegetative buffer width that is representative of soil conditions found in northeast Kansas where crops are grown near streams. The soil is assumed to be a sandy loam that has a saturated hydraulic conductivity of 0.072 m/day and a specific yield of 0.35. Brutseart's [9] relationship is used to simulate the relationship between soil-water pressure head and soil-water content, with the soil characteristic parameters taken as $A = 3.0$ and $c = 0.55$. The Brooks and Corey [8] model is then used to simulate the relationship between the soil-water hydraulic conductivity and the soil-water content, where the soil characteristic parameter, d, is taken as 3.5. The initial water table is taken to be approximately 1.5 meters below the soil surface and is sloping towards the stream with a natural gradient of 0.01 m/m. The contaminant to be used in the simulations is atrazine, which has an octanol-water partition coefficient of $K_{ow} = 2.71$. This yields a transpiration stream concentration factor of $T_{scf} = 0.55$ and a root concentration factor of $R_{cf} = 4.51$, using the relationships given in Eqs. 10 and 13 respectively. Atrazine adsorption to the soil is neglected in the simulation in order to better observe the effects of the plants and their roots on the fate of the atrazine. The initial concentration of atrazine in the groundwater beneath the plant buffer zone is taken as $C_0 = 10$ mg/m^3 = 10 ppb. The only input of atrazine is via ground water as would be the case if a buffer strip is next to a treated area but is itself untreated. Many other organic chemicals have similar parameter values. The method of solution and the characteristics of the results are more general than this specific example.

The plant used in the simulation is the Poplar tree; a constant root density is assumed over the simulation period, with the root density profile and root parameters shown in Figure 2; that is, the trees are rapidly established at the beginning of the simulation. It is also assumed that there will be very little variation in the root water content during the simulation, so that the right hand side of Eq. 2 used to simulate the movement of water through the poplar tree's root system is set to zero. The average monthly evapotranspiration and precipitation amounts for an area in northeast Kansas are shown in Figure 3, and are used as the boundary conditions for Eqs. 1 and 2 during the simulation period.

The above described root-soil system was then simulated over a period of 8 years, where the upgradient contaminant concentration was set to 10 ppb for the first 5 years of the simulation, and then reduced to 0 ppb for the remaining 3 years. This represents a case where usage is discontinued, or where leaching to ground water upgradient is prevented.

Figure 4 depicts the predicted atrazine concentration at the ground water surface for the upstream and downstream edges of the poplar tree buffer zone. As can be seen in Figure 4, the concentration of atrazine at the down gradient edge of the buffer zone is dramatically decreased within the first year of planting. This is a reflection of the great deal of adsorption of atrazine to the poplar tree roots in the early stages of simulation. However, after the second year of simulation the atrazine concentration begins to rise, and continues to rise in a somewhat cyclical fashion for the remainder of the simulation period.

The continuing rise in the atrazine concentration level is a reflection that the poplar tree roots exclude some of the atrazine from the soil-water solution when it is taken up into the root system. Thus, a greater proportion of water is taken up than

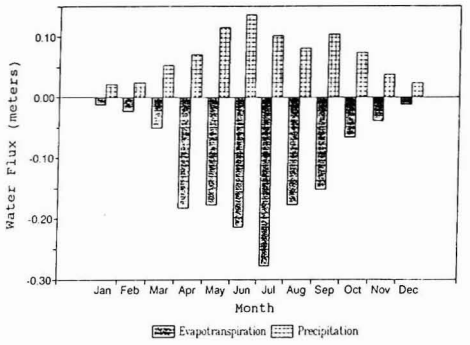

FIGURE 3. Typical monthly water fluxes for example problem.

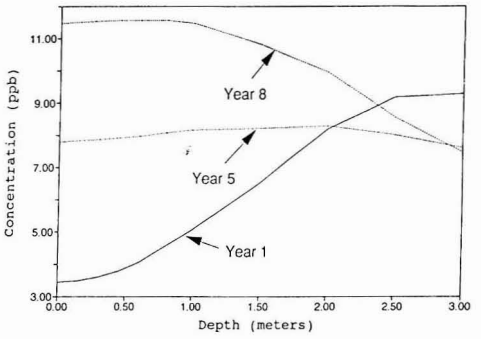

FIGURE 5. Concentration vs. depth at middle of root system at the end of July.

the atrazine and the concentration will rise if the water consumed by the poplar trees is not replaced by infiltration into the soil profile. As shown in Figure 3 the overall evapotranspiration is much greater than the total precipitation for the particular region being simulated, and thus the atrazine concentration would be expected to rise. The cyclical nature of the rise in concentration is a reflection of the yearly evapotranspiration and precipitation cycle. The summer months have significantly higher evapotranspiration than precipitation, and thus a rapid rise in atrazine concentration in the soil occurs during these months. In the winter however, there is considerably more precipitation than evapotranspiration, and the atrazine concentration tends to decrease slightly.

Profiles of the atrazine concentration versus the depth in the soil profile in the middle and down gradient edge of the buffer planting zone during several periods of time are shown in Figure 5 through 8. Figure 5 depicts the predicted atrazine concentration versus depth at the middle of the buffer zone for the month of July during years 1, 5, and 8 of the simulation. The model predictions suggest that atrazine levels would gradually increase in the upper 1 meter of the soil profile during the summer months, but would decrease below the ground water table over time. Figure 6 shows the predicted atrazine concentration versus depth at the middle of the buffer zone for the month of December during years 1, 5, and 8 of the simulation. Again the model predictions demonstrate the increased atrazine levels in the middle of the buffer zone in the upper 1 meter of soil over time. However, due to the leaching effects of the late fall rain and reduced evapotranspiration rate, the atrazine concentration beneath the ground water table remains relatively constant from year to year.

Figures 7 and 8 depict the predicted atrazine concentration versus depth at the down gradient edge of the buffer zone for years 1, 5, and 8 of the simulation during the months of July and December, respectively. The model predictions shown in Figure 7 demonstrate the initial reduction in atrazine concentration during the summer months at the down gradient edge of the ground water table from Year 1 to Year 5, but a significant build up from Year 5 to Year 8. However, Figure 8 shows that the atrazine concentration at the down gradient edge of the buffer zone during the winter months would show more of a consistent yearly increase, with a relatively large increase from years 5 to 8 in the simulation period. Mass balance calculations indicate that the amount of atrazine going out of the buffer strip is markedly reduced even though atrazine concentration increases within the strip (unpublished observation). This is because of decreased water outflow in the presence of the trees.

THE BASIS FOR IN SITU BIODEGRADATION IN THE RHIZOSPHERE

Equation (16) does not contain a term for microbial biodegradation of the contaminant. We need to add this to the model and repeat the simulation in order to show the effects of biodegradation. The remainder of this contribution is concerned with microbial biodegradation in the rhizosphere and the transport of oxygen to the rhizosphere since oxygen can limit the rate of biodegradation in contaminated soil.

The following chemical balance for microbial growth, with the organic contaminant and root exudates as the substrates, defines the primary nutritional requirements for aerobic biodegradation as it may occur in the root zone of plants.

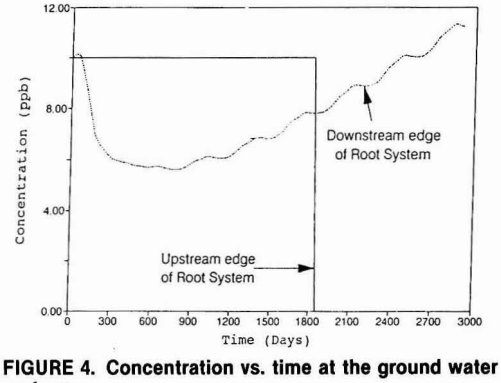

FIGURE 4. Concentration vs. time at the ground water surface.

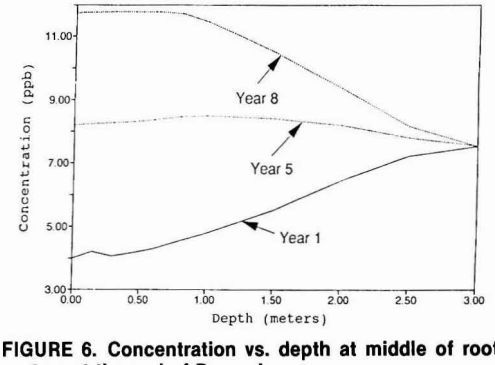

FIGURE 6. Concentration vs. depth at middle of root system at the end of December.

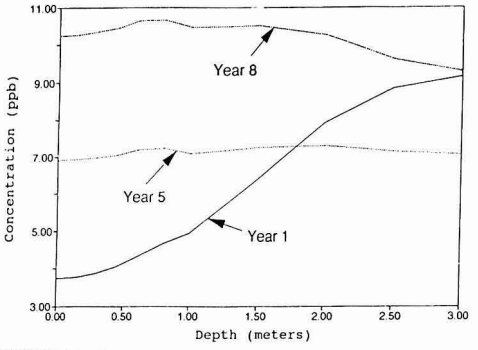

FIGURE 7. Concentration vs. depth at down gradient edge of root system at the end of July.

$$CH_mO_l + aNH_3 + bO_2 + zCH_iO_sN_t \Rightarrow y_cCH_pO_nN_q + cH_2O + dCO_2$$

Contaminant (substrate) | Root Exudates | Biomass

The stoichiometric coefficients a, b, c, d, y_c, and z can be found from measured quantities of reactants and products for well defined experiments. The subscripts l, m, n, p, q, r, s, and t are found from the elemental composition of the contaminants, root exudates, and microbial biomass. The soil temperature, the presence of an aqueous environment, phosphorous and trace minerals affect microbial growth and biodegradation. The microorganisms that degrade contaminants at low concentration levels in the soil or ground water may be limited by any one or a combination of these factors. Often microbial growth is carbon limited in the rhizosphere. The following sections discuss how plants are able to provide a favorable environment for rhizosphere microbes.

Root Exudates and Enhanced Microbial Activity

Rhizodeposition and root exudation are two means by which substrate is provided to the rhizosphere. Rhizodeposition is the addition of the organic substances resulting from the decay of dead root hairs. Exudates are classified as carbohydrates, amino acids/amides, organic acids, anions and cations. They are secreted over the entire length of the root, but the primary area of release is at the root tip [*34*].

Smith [*34*] presents reviews that estimate the annual amount of exudate added to the soil for various crop and tree species on per plant, dry root weight and hectare basis. A study of grassland and forest ecosystems in south-central Wisconsin showed that forests added 184 metric tons per hectare

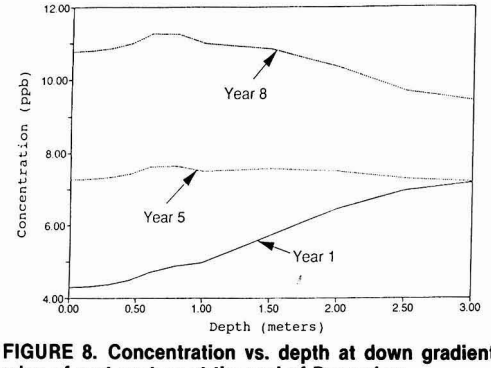

FIGURE 8. Concentration vs. depth at down gradient edge of root system at the end of December.

(~ 18 g/m^2) of organic material to the top 105 cm of soil while grassland prairie added 345 metric tons per hectare (~ 34.5 g/m^2).

Nitrogen Fixation by Rhizosphere

Although nitrogen is abundant in the atmosphere, it is generally the limiting factor in plant growth. Biological dinitrogen fixation is the process whereby atmospheric nitrogen is converted to ammonia and then into organic forms that are usable by plants and microbes. The largest contributor of nitrogen is probably through symbiotic or nonsymbiotic biological processes. Legume plants provide the rhizosphere environment for symbiotic nitrogen fixation with the bacteria of the tribe *Rhizobiaceae*. Soybeans, clover, and alfalfa when grown as cover crops can provide 50 to 200 kilograms nitrogen per hectare per year. Some nonlegume plants such as the red alder, *Ceanothus* species, and *Eleagnus* are capable of fixing more nitrogen in natural ecosystems than legumes used in agricultural fields. The bacteria *Azotobacter* and *Clostridium* are two of several dozen genera capable of nonsymbiotic nitrogen fixation in temperate zones. However both bacteria are usually limited by lack of carbon substrate and contribute little nitrogen to cultivated fields [*13*].

Often chemical spills and leaking underground storage tanks lead to organic contaminants in soil and ground water that have low concentrations of nitrogen. Plants which provide nitrogen fixing environments can contribute an enhanced microbial population and nitrogen for their growth.

Phosphorus Accessibility

Phosphorus in bulk soil is sometimes unavailable for plant uptake or microbe consumption. The rhizosphere is able to solubilize phosphorus by chemical activity of root exudates, and biological activity of rhizosphere bacteria and mycorrhizal fungi. Bacteria such as *Bacillus*, *Pseudomonas*, and *Agrobacterium* improve phosphorus uptake by plants. Mycorrhizal roots are often more efficient than nonmycorrhizal roots in plant uptake of phosphorus [*34*].

Oxygen Transfer

Since microbial biodegradation of organic contaminants usually is enhanced by an aerobic environment, oxygen transfer is an important consideration. Oxygen diffuses through the vadose zone and it is also transported within plants to the root zone. The simulation above dealt only with a relatively dry environment but bioremediation is often needed in wet riparian zones and in wetland areas.

The pathways of oxygen transport in plants through the roots and into the soil are not well understood; however plants and trees seem to fall into three general categories with respect to their varying oxygen ventilating efficiencies. These consist of 1) non-wetland herbaceous and woody plants with poor ventilating capabilities and 2) wetland woody plants with moderate ventilating capacities and 3) wetland herbaceous plants with good ventilating capacities [*3*].

Non-Wetland Plants

Non-wetland plants use a soil pathway and a plant pathway to move oxygen to their roots. Upon soil flooding fine root growth is reduced or stopped below the water line for flood intolerant plants. When soil is flooded the water fills the soil pores previously occupied by air. Any remaining oxygen is quickly consumed by aerobic microbes and any oxygen transport is limited to aqueous phase diffusion. Aerobic organisms

are replaced by anaerobic organisms whose heterogenous by-products are often harmful to non-wetland plants and trees. Most non-wetland trees and plants will die when subjected to an oxygen depleted, chemically hostile root environment [20].

The movement of oxygen within the plant appears to be diffusion controlled under some conditions. The simplest model assumes diffusion in a tubular structure

$$\text{Diffusion Rate } (gs^{-1}) = \frac{DA(C_2 - C_1)}{L} \qquad (17)$$

where D = the diffusion coefficient (cm^2/s)
A = cross-sectional area (cm^2)
C_2 = gas source concentration (g/cm^3)
C_1 = gas sink concentration (g/cm^3)
L = length of tube or diffusion path (cm)

As the gas spaces in plants are not simple tubes but follow irregular pathways, the diffusional impedance is rewritten to include the porosity and tortuosity [2].

Wetland Plants

Flood tolerant or wetland plants and trees have adaptations which enable them to maintain an aerobic environment in the rhizosphere and detoxify the soil. Wetland plants growing in unsaturated soil use the two oxygen pathways previously described. However, upon flooding several physiological changes occur and more oxygen is transferred through the plant pathway. In addition, many flood-tolerant plants adapt by forming lenticels and adventitious roots. These adaptations increase the oxygen supply to the soil [19, 20].

The various adaptive processes of tree species to flooding are summarized by Hook and Scholtens [19] in a flow chart format. It is important to note that different tree species within a genus may show wide differences in adaptation and flooding tolerance.

Due to several adaptations wetland herbaceous plants have a more efficient air transport system than do non-wetland plants. For example, the yellow water lily, *Nuphar luteum*, and the white water lily, *Nympaea alba*, have air flows of 260 ml/hr per leaf to the rhizosphere by thermoosmosis and Knudsen diffusion of gases [15]. Armstrong *et al.* [4, 5] report evidence of convective flows in plants. Temperature differences and humidity induced diffusion appear to create pressure differences which cause convective gas flow in plants.

Trees, which transpire large volumes of water, may also increase degradation by improving soil oxygenation in non-flooded areas. If sufficient numbers of trees are planted, the ground water level may be lowered, which increases the amount of unsaturated soil and the oxygen supply by gas phase diffusion through the soil. As a result trees can increase microbial numbers and activity. Many trees in a closed canopy stand will transpire more than a meter of water per year if it is available. Their effect on the water table may thus be considerable in sub-humid and semiarid climates.

An important effect of plant roots on the growth of microbes is that they may increase the oxygen availability as well as solute transport by increasing the hydraulic conductivity and diffusivity in soil [14]. The continuously dying root hairs produce tiny channels and pores in the soil which facilitate the diffusion of oxygen from the top surface. In addition, various nutrients move more rapidly due to the increased soil porosity so that the growth of microbes is enhanced.

Mitsch and Gosselink [23] reviewed wetlands as an ecosystem and Hammer [17] presents a broad overview of the use of wetlands for treatment of municipal, agricultural and industrial wastes. While most studies to date [11, 17, 27] have examined herbaceous wetland species such as reeds, rushes and cattails, there are some forested swamps used for nutrient removal of municipal wastewater discharges [28, 29].

Since wetland trees have been shown to oxidize the rhizosphere, it appears that contaminated soil that is oxygen deficient can be remediated. Instead of water being the planting medium as for wetland herbaceous plants, soil is the planting medium for wetland trees. Therefore, the potential use of wetland or flood tolerant upland trees as a means of decontaminating soil is worthy of further investigation.

Water and Solute Transfer among Roots

Trees can also change the soil and surface environment. In dry climates most of the tree's feeder roots are deep in the soil. As water is drawn up to nourish the tree, water is also transported to the oxygen-rich, dry soil near the surface where it is more accessible to biodegradation. Water and mineral transfer between *Populus* seedlings has been observed [18]. The transfer of water has been seen from deep-rooted alfalfa to shallow rooted maize [12]. Habben and Blevins [16] showed that alfalfa is also able to transfer non-N-minerals to shallower rooted plants. Desert plants use "hydraulic lift" at night to increase daytime water availability [39]. These transport processes may enhance the environment for in situ bioremediation.

Temperature

The relationship between bacterial growth and temperature is described by the Arrhenius equation [6] where:

$$k = Ae^{(-E_a/RT)} \qquad (18)$$

k = reaction rate constant (d^{-1})
E_a = activation energy (J/mol)
R = gas law constant (J/mol•K)
A = frequency factor (d^{-1})
T = absolute temperature (K)

While different microbes can grow at temperatures between −5 and 95 degrees Celsius (23–203 degrees F.) the typical growth rate shows a rapid decline as the temperature decreases. The optimum temperature for mesophile growth is 30–45 degrees C. (86–113 degrees F.) and for obligate psychrophiles it is 15–18 degrees C (59–64.4 degrees F.) [6].

At the surface, microbial growth is enhanced by solar radiation and soil temperature regimes in the top meter have been classified [13]. However growth is reduced in deeper regions as soil temperature drops dramatically with depth. In eastern Kansas where the annual air temperature variation is 92 degrees Fahrenheit, under grass cover at one foot the variation in soil temperature was 48 degrees F; at three feet, 38 degrees F; at six feet, 28 degrees F [40]. At some depth the soil temperature will not be affected by heating from the surface. This ambient soil temperature might be equated with ground water temperatures. Ground water temperatures from wells 50 to 150 feet deep, range from 80 degrees Fahrenheit in south Texas to 56 degrees F. in Kansas to 44 degrees F. in North Dakota [37]. It is expected that rates of microbial metabolism will decrease with depth during the warm season and conversely may be greater at depth than on the surface in the cold season.

Microbial Degradation Models

Conley *et al.* [10] have modeled the reduction in biological oxygen demand (BOD) of wastewater treated by the root zone method which employs wetland plants to oxidize organic contaminants in the rhizosphere and to promote microbe growth. First-order kinetics and plug flow were assumed. The authors plan to investigate growth and degradation models which follow the Monod kinetic model and depend on the concentration

(kg/m^3) of oxygen (C_0), biomass (C_b), organic contaminants (C) and root exudates (C_r). The microbes live in the pore spaces, on soil particles, and on root surfaces.

The rate of microbial growth is given by

$$r_b = (\theta + R_d R_b + \rho K_b) C_b \left[\frac{\mu_m (C + C_r)}{(K_{rs} + C + C_r)} \left(\frac{C_0}{K_0 + C_0} \right) - k_d \right] \tag{19}$$

while the rate of contaminant consumption is

$$r_s = -\frac{\mu_m}{Y_s} (\theta + R_d R_b + \rho K_b) C_b \left[\frac{C}{(K_{rs} + C + C_r)} \left(\frac{C_0}{K_0 + C_0} \right) \right] \tag{20}$$

where μ_m is the maximum specific growth rate (d^{-1}), R_b is the phase equilibrium parameter associated with the adsorption of microorganisms to the root surfaces (m^3/m^3), K_b is a similar phase equilibrium partition coefficient for the adsorption of microorganisms to soil surfaces, (m^3/kg) Y_s is a yield coefficient for microbial growth on the organic contaminant (kg/kg), k_d is the reaction rate constant for decay of microbial biomass (d^{-1}), K_{rs} is the saturation constant associated with the organic substrates (kg/m^3), and K_0 is the saturation constant associated with the dissolved oxygen (kg/m^3). The maximum specific growth rate depends on temperature as indicated earlier in Equation (18).

In order to simulate microbial degradation of the contaminants in the rhizosphere, mass balances must be developed for the contaminant, microbial biomass, root exudates, and dissolved oxygen. If the volatility of the contaminant is considered, the following equations for the rhizosphere may be used to model the process. The contaminant balance is

$$\frac{\partial}{\partial t}\left[C\left(\theta + R_d R_{cf} + \rho K_d + \frac{\theta_A}{H}\right)\right] = \frac{\partial}{\partial x}\left[\theta\left(D_{xx}\frac{\partial C}{\partial x} + D_{xz}\frac{\partial C}{\partial z}\right) + \frac{\theta_A}{H}\left(D_A\frac{\partial C}{\partial x} + D_A\frac{\partial C}{\partial z}\right) - V_x C\right] + \frac{\partial}{\partial z}\left[\theta\left(D_{zx}\frac{\partial C}{\partial x} + D_{zz}\frac{\partial C}{\partial z}\right) + \frac{\theta_A}{H}\left(D_A\frac{\partial C}{\partial x} + D_A\frac{\partial C}{\partial z}\right) - V_z C\right] - qT_{SCF}C - \frac{\mu_m}{Y_s}(\theta + R_d R_b + \rho K_b) C_b \left[\frac{C}{(K_{rs} + C + C_r)}\left(\frac{C_0}{K_0 + C_0}\right)\right] \tag{21}$$

The balance for the microbial biomass is

$$\frac{\partial}{\partial t}[C_b(\theta + R_d R_b + \rho K_b)] = \frac{\partial}{\partial x}\left[\theta\left(D_b\frac{\partial C_b}{\partial x} + D_b\frac{\partial C_b}{\partial z}\right) - V_x C_b\right] + \frac{\partial}{\partial z}\left[\theta\left(D_b\frac{\partial C_b}{\partial x} + D_b\frac{\partial C_b}{\partial z}\right) - V_z C_b\right] + \mu_m(\theta + R_d R_b + \rho K_b) C_b \left[\left(\frac{C + C_r}{K_{rs} + C + C_r}\right)\left(\frac{C_0}{K_0 + C_0}\right)\right] - k_d(\theta + R_d R_b + \rho K_b) C_b \tag{22}$$

The balance for the root exudates is

$$\frac{\partial}{\partial t}\left[C_r\left(\theta + R_d R_r + \rho K_r + \frac{\theta_A}{H_r}\right)\right] = \frac{\partial}{\partial x}\left[\theta\left(D_r\frac{\partial C_r}{\partial x} + D_r\frac{\partial C_r}{\partial z}\right) + \frac{\theta_A}{H_r}\left(D_{Ar}\frac{\partial C_r}{\partial x} + D_{Ar}\frac{\partial C_r}{\partial z}\right) - V_x C_r\right] + \frac{\partial}{\partial z}\left[\theta\left(D_r\frac{\partial C_r}{\partial x} + D_r\frac{\partial C_r}{\partial z}\right) + \frac{\theta_A}{H_r}\left(D_{Ar}\frac{\partial C_r}{\partial x} + D_{Ar}\frac{\partial C_r}{\partial z}\right) - V_z C_r\right] + qC_{rr} - qT_{SCFr}C_r - \frac{\mu_m}{Y_r}(\theta + R_d R_b + \rho K_b) C_b \times \left[\frac{C_r}{(K_{rs} + C + C_r)}\left(\frac{C_0}{K_0 + C_0}\right)\right] \tag{23}$$

The balance for dissolved oxygen is

$$\frac{\partial}{\partial t}\left[C_0\left(\theta + \frac{\theta_A}{H_0}\right)\right] = \frac{\partial}{\partial x}\left[\theta\left(D_0\frac{\partial C_0}{\partial x} + D_0\frac{\partial C_0}{\partial z}\right) + \frac{\theta_A}{H_0}\left(D_{Ao}\frac{\partial C_0}{\partial x} + D_{Ao}\frac{\partial C_0}{\partial z}\right) - V_x C_0\right] + \frac{\partial}{\partial z}\left[\theta\left(D_0\frac{\partial C_0}{\partial x} + D_0\frac{\partial C_0}{\partial z}\right) + \frac{\theta_A}{H_0}\left(D_{Ao}\frac{\partial C_0}{\partial x} + D_{Ao}\frac{\partial C_0}{\partial z}\right) - V_z C_0\right] + q_0 C_{or} - qT_{SCFo}C_0 - \frac{\mu_m}{Y_0}(\theta + R_d R_b + \rho K_b) C_b \times \left[\frac{C + C_r}{(K_{rs} + C + C_r)}\left(\frac{C_0}{K_0 + C_0}\right)\right] \tag{24}$$

In these equations the tortuosity is included in the dispersion coefficients. The subscript A refers to the gas phase and

$$\theta_A = n - \theta \tag{25}$$

is the volume fraction occupied by the gas phase and n is the porosity of the soil. The parameter H (dimensionless) is the gas-liquid phase equilibrium parameter or Henry's law coefficient. In Equation (23) the subscript r refers to root exudates and q_r is the volumetric rate of secretion of fluid from the roots. In Equation (24) the term $q_0 C_{or}$ accounts for oxygen transport from the plants to the soil-water.

The microbial processes in the soil depend on the organic carbon which is present. The model attributes this to contamination and root exudates; however, there are other sources of organic carbon such as that which is due to the death of microorganisms and other species. Experimental studies are needed to determine the utility of this model and the modifications that are desirable.

CONCLUDING REMARKS

Vegetation can enhance the rate of bioremediation through plant uptake and through microbial biodegradation in the rhizosphere. Models which can be employed to simulate contaminant fate have been presented. Simulation results with atrazine show that the contaminant concentration in the aquifer may increase because of evapotranspiration and the plants transpiration stream concentration factor for atrazine which depends on the octanol-water partition coefficient. The total quantity of atrazine in the aquifer is reduced.

Further work is needed in model development (particularly in coupling the water flow, plant biochemistry, and microbial degradation), simulation and validation. These preliminary results are presented to stimulate communication and interaction with others.

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Comparison of a Steady-State and Dynamic Model for Predicting Priority Pollutant Removal

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A dynamic model successfully predicted the effluent concentrations of both volatile and non-volatile priority pollutants from a large industrial wastewater treatment plant. A steady-state model, which was formulated with the identical rate equations and variable influent data, was inadequate for dynamic predictions. The dynamic model is the first developed for predicting the fate of priority pollutants in the PACT® process.

INTRODUCTION

Federal guidelines limit the effluent concentrations of 57 organic, priority pollutants in wastewaters from the organic chemicals, plastics and synthetic fibers (OCPSF) industries. Predictive models are needed to design and optimize wastewater treatment plants (WWTP) for priority pollutant removal. A number of steady-state models have been developed to predict the transport and fate of priority pollutants in the activated sludge process [*1-5*]. Steady-state models assume constant influent concentrations and flow. When the influent varies with time, a dynamic model is required. Melcer *et al.* [*6*] developed a dynamic model to predict the fate of volatile organic compounds in an activated sludge WWTP. O'Brien [*7*] has developed a steady-state model for the PACT® process, which is an activated sludge process with powdered activated carbon (PAC). O'Brien and Teather [*8*] presented a dynamic model to predict the fate of both volatile and non-volatile priority pollutants in a WWTP which utilized the PACT® process.

REVIEW OF MODEL DEVELOPMENT

The development of a steady-state model for priority pollutant removal by the PACT® process was described previously [*7*]. Pilot plant studies were used to separate the three primary mechanisms of removal: biodegradation, stripping and PAC adsorption.

The kinetic coefficients for each mechanism were determined for nineteen compounds. The average long-term removals predicted by the model were satisfactory for fifteen of the compounds, but unsatisfactory for three compounds which were batch discharged. Furthermore, the removal obtained from an individual data point could deviate markedly from the long-term average. It was concluded that influent variability was the major source of error, and a dynamic model was needed for accurate predictions.

The same rate equations and kinetic coefficients were used in the dynamic model development [*8*]. The kinetic coefficients were verified under dynamic conditions in the pilot plants by introducing a two-hour, step change in the influent concentrations and measuring the effluent concentrations with time.

The flow distribution in each pilot plant and WWTP vessel was obtained by injecting impulses of lithium chloride solution and measuring the effluent lithium concentrations with time. The model was verified by comparing predicted and actual effluent concentrations. Figure 1 outlines the development and verification of the dynamic model.

WWTP DESCRIPTION

The dynamic model was verified on a full scale at Du Pont's Chambers Works facility in Deepwater, NJ. This 1.26 m^2/sec (20,000 gpm) WWTP has only a few hours of equalization; hence, influent variability is not appreciably dampened before entering the WWTP. There are numerous on-site processes which utilize OCPSF compounds as raw materials in chemical manufacture. Many of these processes are batch or campaigned, consequently their wastewater discharges are intermittent. Additionally several OCPSF compounds are received from off-site sources from Du Pont's large outside waste business. Most of these wastewaters are discharged directly into the WWTP, which also contributes to the variability of the influent concentrations and composition.

Chambers Works WWTP consists of three stages as shown in the simplified schematic (Figure 2). The wastewater is neutralized and solids are removed in the Primary section. The Secondary and Tertiary sections utilize the PACT® process to remove dissolved organics for which the dynamic model was formulated. The Secondary consists of three, parallel, 15 km^3 (4 million gallon), aeration tanks which are followed by three, parallel 9.5 km^3 (2.5 million gallon) clarifiers. The solids from the clarifiers are recycled to the aeration tanks. A purge stream is sent to a carbon regeneration furnace, where the organics

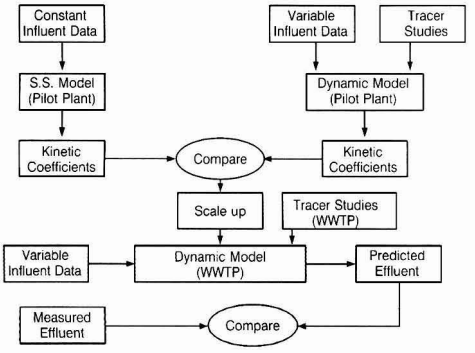

FIGURE 1. Experimental strategy to build and test the model.

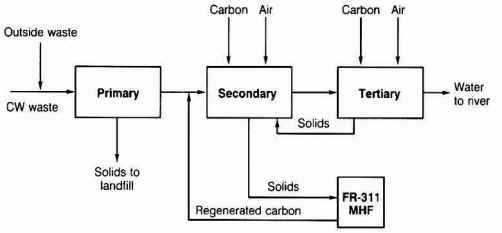

FIGURE 2. Chambers Works wastewater treatment plant.

are incinerated and the activated carbon is regenerated and recycled. The Teritary consists of a 22.7 km^3 (6 million gallon), axial-flow, aeration tank, which is followed by two, parallel, 14.2 km^3 (3.75 million gallon) clarifiers. The solids from the clarifiers are returned to the aeration tank, and a small slip stream recycled back to the Secondary aeration tanks.

WWTP DYNAMIC AND STEADY-STATE MODELS

The lithium tracer studies showed that each vessel in the pilot plant and WWTP could be characterized either as a completely mixed vessel (CSTR) or as a combination of complete mixing and plug flow [8]. The three, parallel, Secondary aeration tanks were lumped together as a single CSTR (equation 1). The three, parallel, Secondary clarifiers were treated as a single CSTR but without the PACT® removal mechanisms. The tracer studies showed that the Tertiary aeration tank could be represented with 55% of the volume as a plug flow reactor with no backmixing (equation 2) and the remaining volume as two, sequential CSTR's of equal size. Dividing the axial flow reactor into a pure plug flow section (no backmixing) and completely mix sections simplified the predictive calculations. Alternatively the Tertiary aeration tank could have been represented by a dispersion model, but the resulting equation is both time and position dependent. Roffel and Rijnsdorp [9] have show that the time-dependent, dispersion equation reduces to the steady-state equation 2, when the dispersion coefficient is negligible (no backmixing). A third approach which was used by Melcer *et al.* [6], is to approximate a plug flow reactor by 10 CSTR's of equal volume in series. Finally, the two, parallel, Tertiary clarifiers were modeled as a single CSTR without removal. Thus, the two general equations used to formulate the dynamic model for each compound were those for a CSTR and a plug flow reactor.

CSTR

$$\frac{\text{Rate In by Convection}}{FS_i} - \frac{\text{Rate Out by Convection}}{FS_e} - \frac{\text{Rate Out by Stripping}}{K_s S_e V} - \frac{\text{Rate Out by Biodegradation}}{K_B S_e X V} - \frac{\text{Rate Out by PAC Adsorption}}{K_A S_c S_e V} = \frac{\text{Rate of Accumulation}}{\frac{dVS_e}{dt}} \quad (1)$$

where:

F = flow rate
K = rate coefficient
S = concentration
S_c = aeration tank PAC concentration
t = time
V = aeration tank volume
X = biomass concentration in aeration tank

subscripts:

A = adsorption
B = biodegradation
e = effluent
i = influent
s = stripping

These equations were modified by adding recycle terms. Equation 1 was used to model the clarifiers by deleting the stripping, adsorption and biodegradation terms. Both biomass and PAC concentrations were assumed to be constant in equations 1 and 2. The relatively small concentrations of the priority pollutants allowed the rate expressions to be first order in substrate concentrations [7]. An unsteady-state material balance equation(s) was written for each WWTP vessel modeled, and the set of these differential equations comprised the dynamic model for a specific compound, which was defined by its unique rate coefficients.

PLUG FLOW REACTOR

$$\frac{\text{Rate Out by Stripping}}{K_s S V} + \frac{\text{Rate Out by Biodegradation}}{K_B S X V} + \frac{\text{Rate Out by PAC Adsorption}}{K_A S_c S V} = \frac{\text{Net Rate by Convection}}{\frac{dFS}{dV}} \quad (2)$$

The model was verified by comparing measured effluent concentrations with the dynamic predictions. Grab samples of the variable influent and effluent were taken over a period of time and analyzed for pollutant concentrations. The dynamic response was calculated from the model by treating each influent data point as step change. The calculated effluent concentration profile was then used as the influent to the next vessel in series. The plug flow equation 2 is independent of time and reflects only the change in concentration with respect to position. The variability with time was introduced by solving equation (2) with the secondary clarifier concentration profile as the influent. Additionally, the plug flow effluent concentration profile was delayed by a time interval equal to the hydraulic detention time. Initial conditions for equations (1) and (2) were based upon measured values. The calculated

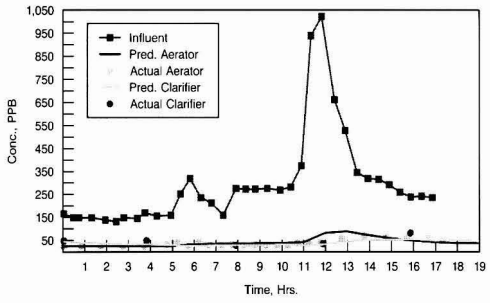

FIGURE 3. Methylene chloride dynamic prediction for WWTP.

steady-state concentrations were used when the initial concentrations of the downstream vessels were below analytical detection limits.

The steady-state model utilized the same set of equations, but with the CSTR accumulation terms set to zero. Again each influent concentration data point was treated as a step change in order to calculate the steady-state effluent concentrations from each vessel. At steady-state the influent and effluent clarifier concentrations were equal, since no removal occurred in the clarifiers. The plug flow effluent profile was calculated from equation 2. The calculated Secondary effluent concentration profile was used as the influent, and the effluent profile was delayed by time interval equal to the hydraulic resonance time. Hence, the calculational approach was identical to that used for the dynamic case except no accumulation terms were present when equation 1 was used to describe either the clarifiers or the Secondary aeration tanks.

DYNAMIC AND STEADY STATE PREDICTIONS VS. MEASURED

Grab samples of the influent, Secondary and Tertiary aeration and clarifier effluents were taken periodically for seventeen hours. The flow rate was relatively constant at 1.26 m^3/sec. Effluent concentrations of the Tertiary section were below detection limits, but Secondary effluents for six compounds were measurable. Figures 3 to 7 compare the data with predicted values for methylene chloride. The influent concentration was relatively constant until the eleventh hour of sampling when a "spike" occurred (Figure 3). Good agreement was obtained between the dynamic predictions and the actual

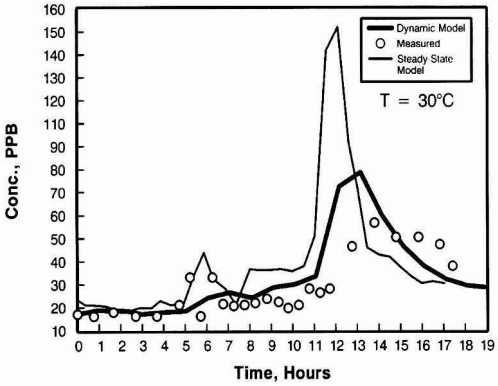

FIGURE 4. Dynamic vs. steady-state prediction for methylene chloride effluent from secondary aeration tanks.

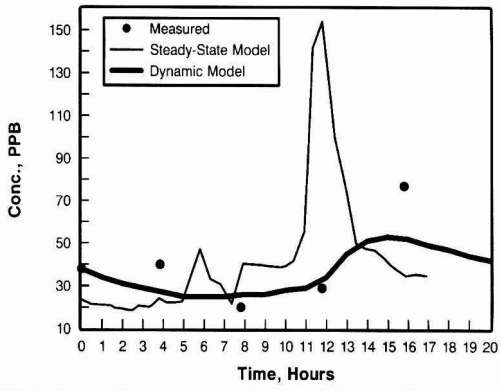

FIGURE 5. Dynamic vs. steady-state prediction for methylene chloride effluent from secondary clarifiers.

data for both the Secondary aeration tanks and clarifier effluents (Figures 3-5). However, the steady-state predictions for the aeration tank effluent concentrations were too high as the influent perturbation increased and too low as it decreased (Figure 4). The steady-state curve also peaked before the data. The same type of behavior was seen in the clarifier effluent (Figure 5), except the overshoot and the lead time were more pronounced, whereas the dynamic response closely followed the data both in amplitude and shape. (The last data point on Figure 5 was evidently erroneously high in concentration, because it was greater in magnitude than the data points from the aeration tanks which was physically impossible.) The disparity in the overshoot and lead time between the steady-state and dynamic predictions increased as the perturbation progressed through the Tertiary aeration tanks and clarifiers (Figures 6 and 7).

The model predictions were markedly different even though both models used identical rate expressions, kinetic coefficients and influent concentrations. The influent perturbation was dampened as it entered each CSTR and was mixed with the vessel contents. As the influent perturbation decreased, the effluent from a given CSTR did not decrease as rapidly, because the accumulation of methylene chloride within the vessel volume required time to be displaced. Each CSTR flattened the perturbation and delayed the response further. Mathematically these effects were taken into account by the accumulation term in equation 1, which was the only difference between the two models. Without the accumulation term, the steady-state curves retained the shape of the influent concentration profile.

Figures 8 to 12 illustrate a similar series of graphs for 1,2-dichlorobenzene. The influent concentration was not at steady-

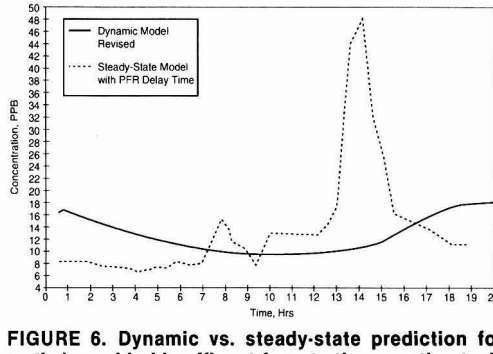

FIGURE 6. Dynamic vs. steady-state prediction for methylene chloride effluent from tertiary aeration tank.

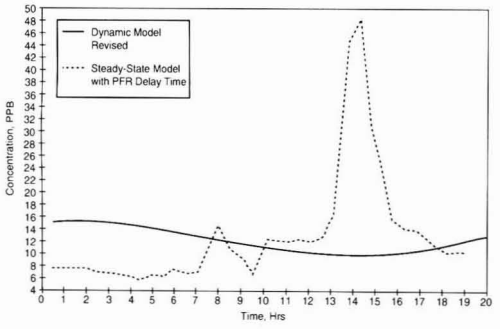

FIGURE 7. Dynamic vs. steady-state prediction for methylene chloride effluent from tertiary clarifiers.

state initially, which condition is assumed in the dynamic model, but the agreement between the dynamic model predictions and measured values was satisfactory (Figure 8). A large disparity did not exist between either models and the measured Sec-

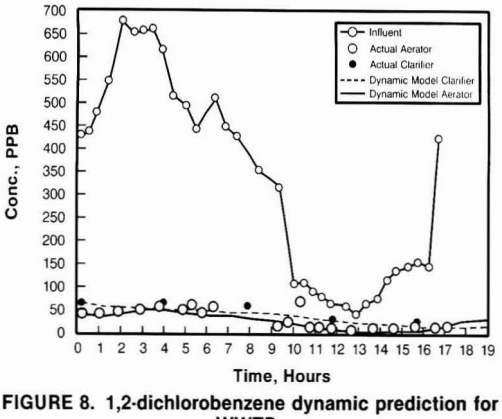

FIGURE 8. 1,2-dichlorobenzene dynamic prediction for WWTP.

ondary aeration tank effluent (Figure 9), but the steady-state calculations deviated markedly from the Secondary clarifier data and the dynamic predictions (Figure 10). Overshoot, undershoot and differences in the shapes of the effluent curves

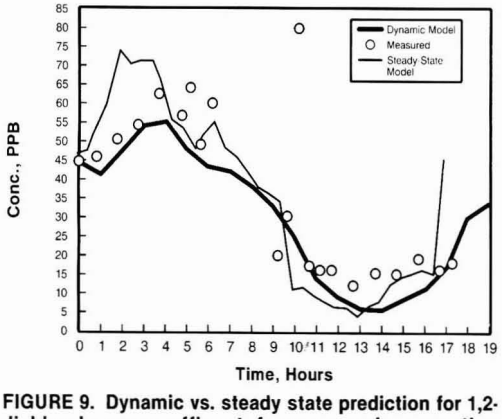

FIGURE 9. Dynamic vs. steady state prediction for 1,2-dichlorobenzene effluent from secondary aeration tanks.

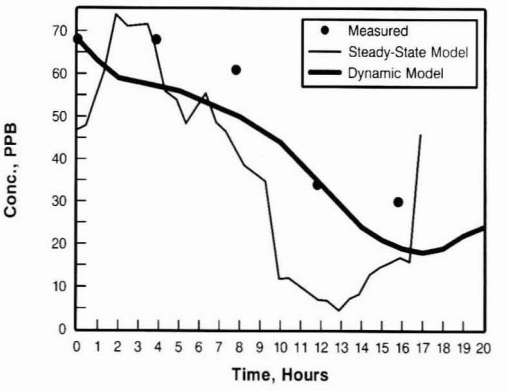

FIGURE 10. Dynamic vs. steady state prediction for 1,2-dichlorobenzene effluent from secondary clarifiers.

were observable. The disparity between the model simulations progressively increased in the Tertiary aeration tank and clarifiers as expected (Figures 11 and 12).

Data was also obtained for chloroform, monochlorobenzene, dichloroethane and dinitrotoluene with similar results.

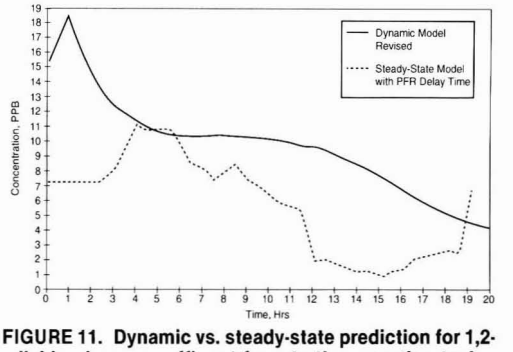

FIGURE 11. Dynamic vs. steady-state prediction for 1,2-dichlorobenzene effluent from tertiary aeration tank.

SUMMARY AND CONCLUSIONS

- The assumption of steady-state conditions should be questioned if a steady-state model fails to predict effluent concentrations.

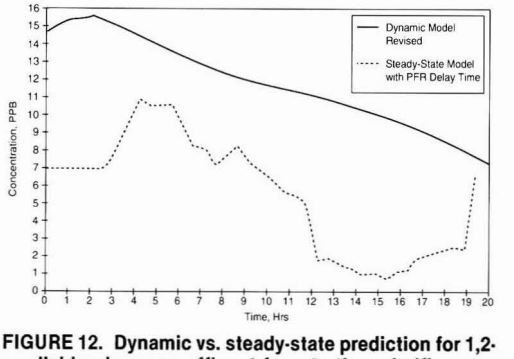

FIGURE 12. Dynamic vs. steady-state prediction for 1,2-dichlorobenzene effluent from tertiary clarifiers.

- A dynamic model has been developed for the PACT® process which successfully predicted effluent concentrations for both volatile and non-volatile priority pollutants.

- A steady-state model did not accurately predict the effluent concentrations of six priority pollutants when the influent concentrations varied with time even though identical influent data, rate expressions and kinetic coefficients were used in both models.

- The failure of the steady-state model under dynamic conditions was due to the lack of an accumulation term in the CSTR equation, which reflects the change in vessel concentration with time.

- Flow distribution characterization of each vessel was essential to accurately formulate the steady-state and dynamic models.

- Continuous analysers or frequent grab samples are needed for dynamic models. Lacking a continuous analyzer for the priority pollutants, grab samples every half hour were sufficient to characterize the influent and effluent concentration profiles in this study.

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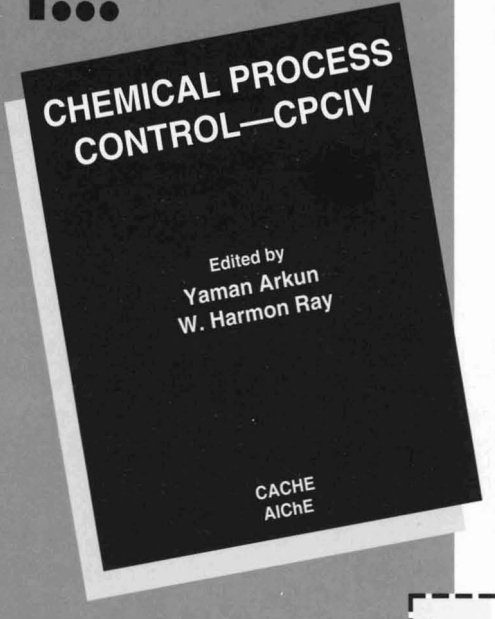

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