

# waste management *Research* **Report**



News from State University of New York at Buffalo and Stony Brook, and Cornell University

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Focus On  
Remediation



Waste Management  
Research  
**Report**

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## About This Newsletter

*Waste Management Research Report* appears three times a year in order to share research from the publication's contributing institutions. Each issue focuses on one major area of waste management and highlights the contributing institution where researchers concentrate on the featured topic. The New York State Center for Hazardous Waste Management at State University of New York at Buffalo is responsible for this Report, with the emphasis on remediation. The Cornell Waste Management Institute and the New York State Solid Waste Combustion Institute at Cornell University will be responsible for the next issue. The focus will be on source reduction.

### On the Cover

*Height of bar in each county is proportional to number of listed sites (number of sites in Erie County = 105, Albany County, 23). Data from New York State Department of Environmental Conservation Quarterly Status Report of Inactive Hazardous Waste Disposal Sites, April, 1990.*

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## Director's Comment

# Workshop Provides Environment For Exchange of Ideas and Concerns About Use of Alternative Technologies

By Ralph R. Rumer

In January, 1990, the New York State Center for Hazardous Waste Management, in collaboration with the New York State Department of Environmental Conservation, brought together representatives from state and federal agencies, public interest groups, and industry, as well as engineering consultants, lawyers, technology vendors, and legislative staff to:

- Identify obstacles and impediments that require resolution in order to facilitate the implementation of appropriate alternative technologies and methods in the state's remediation program, and
- Recommend measures that might be taken to address the identified obstacles and impediments so that the state's remediation program can move forward with implementation of appropriate alternative technologies and methods.

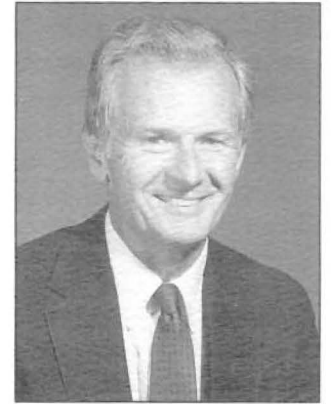
The workshop provided participants with the opportunity to break into three task groups, each of which focused on a particular aspect of the issue, namely:

- Regulatory impediments
- Societal concerns
- Administrative and other impediments

Task group moderators guided the discussions and provided draft summary reports of the views and recommendations emanating from their groups. These group reports were then incorporated into a workshop summary report published by the New York State Center for Hazardous Waste Management. Readers who wish to read the full report may request copies from the Center by writing or calling the address shown on the following page.

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*Dr. Ralph R. Rumer is executive director of the New York State Center for Hazardous Waste Management at State University of New York at Buffalo.*



Ralph R. Rumer

*Workshop on alternative technologies and methods for hazardous waste remediation drew participants from industry, government, and academia. Photo by John Goerg, NYS DEC.*



## Scope of Remediation Problem

More than 1,100 inactive hazardous waste sites are listed in New York, according to the Quarterly Status Report of the New York State Department of Environmental Conservation, July, 1990. More than 500 chemicals have been encountered at these sites. Many of these chemicals are considered to pose risks to human health and to the environment. The sites include open dumps, storage structures, lagoons, landfills, and treatment ponds.

Sites requiring remediation have in common contaminated soils, sediments, and groundwater. Each site, however, has unique hydrogeological characteristics, mix of chemical compounds, and degree of contamination. Because of the diversity of site-specific conditions, a variety of remediation technologies and methods have evolved and continue to be developed.

Both the public and the parties responsible for creating the disposal sites are anxious for permanent cleanup that will remove any significant threat to human health or the environment. All involved also are anxious that the permanent cleanup be accomplished as expediently as possible. The selection and implementation of specific methods and technologies is, however, complicated by numerous factors, many of which the January workshop participants discussed.

## Findings and Recommendations

Highlights from workshop recommendations include the following needs:

- Standard setting
- Streamlining of permitting
- Public participation
- Development of a process for independent, third-party review of alternative/innovative technologies and methods for remediation to establish effectiveness and applicability

Many findings and recommendations from the workshop deal specifically with New York Department of Environmental Conservation and federal Environmental Protection Agency regulations and procedures that apply to the remediation program, e.g., permit modifications, modifying estimates of risk under certain circumstances, classification of treated environmental media, the need for treatability studies before a record of decision is issued for a site, review of bonding requirements for cleanup contractors, and development of strategies that will provide incentives for the implementation of appropriate alternative technologies and methods.

The participants addressed a broad range of complex issues involving regulatory agency initiatives, public understanding, and technology vendor concerns and developed findings and recommendations that deal with more generic issues:

- What is meant by "permanent" in the context of permanent remedy?
- What is an appropriate level of "acceptable risk"?
- What are the best ways to inform the public and technology vendors of site-specific conditions?
- How should cleanup standards for contaminated soil be established?

The format for the workshop proved to be very successful because it allowed for open discussion (in a neutral setting) of issues and problems that are less easily considered in the everyday workplace. The discussions, findings, and recommendations emanating from the two-day workshop provide a basis for new and constructive approaches to the use of appropriate alternative technologies and methods in the state's cleanup of inactive hazardous waste disposal sites.

*To order a copy of the workshop report, "Impediments to the Implementation of Alternative Technologies," write the New York State Center for Hazardous Waste Management, State University of New York at Buffalo, 207 Jarvis Hall, Buffalo, NY 14260, or call (716) 636-3446.*

# Mathematical Models Useful In Design Of Systems For Subsurface Remediation

By Stewart W. Taylor

The future remediation of soils and groundwater contaminated by hazardous wastes will rely on processes borrowed from the treatment of water and waste water and upon processes used by the chemical and petroleum industries. Many of these processes are well understood, and tools exist that allow them to be designed for optimum performance, e.g., reactor vessel size, loading rates, and retention times. Industrial applications are characterized by regular and well-defined boundaries and controlled loading rates. Many treatment processes are designed to operate under fully mixed conditions. Once treatment is underway, process performance is easily evaluated by sampling the reactor or the reactor effluent directly.

The application of these technologies to soil and groundwater remediation, particularly *in-situ* remediation, raises new considerations. In contrast to natural surface water systems or engineered water treatment systems, the boundaries in the subsurface are poorly defined, and we can observe the response of a system at only a limited number of points, e.g., wells. In a river or lake, we have almost complete freedom to choose where we sample water quality, and sites are chosen to ensure that the samples are representative of the system. In soils or aquifers, we cannot observe the entire system synoptically, and we are never sure that the information derived from wells is representative. Therefore, assessment of soil and groundwater remediation is a difficult task, given that we can observe physical and chemical changes in subsurface water at only a limited number of points, or "holes," which may or may not be representative.

Fortunately, a rich body of information exists that deals with the theory of fluid flow and chemical movement in media comprised of a solid and one or more fluids, *i.e.*, porous media. This body of knowledge, primarily from geology, agronomy, and civil, petroleum reservoir, and chemical engineering, allows us to look between the "holes" and predict how water and chemicals will move underground.

The theories of porous media flow and chemical transport form the basis of all soil and groundwater models and provide us with tools

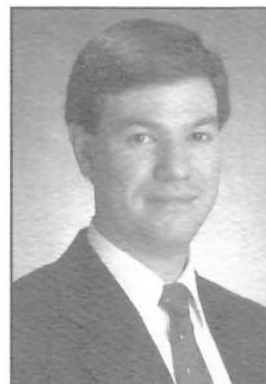
that enable us to predict and assess the performance of subsurface remediation systems. The objective of this article is to explore the nature and utility of such models.

## What Is a Model?

A model is a mathematical representation of the physical, chemical, and biological processes in any system. In the subsurface, we typically concern ourselves with two principal phenomena: the motion or flow of water, and the migration and transformation of chemicals. Hydrogeologists generally refer to these processes as "subsurface flow" and "chemical transport," or, in the case of aquifer contamination, "groundwater flow" and "contaminant transport." The mathematical representation of these two processes consists of a set of partial differential equations and a set of auxiliary conditions, both of which are applied to a specified domain. For hazardous waste applications, the domain might consist of a soil column when soil contamination is the issue, or an aquifer or aquifer-aquitard system when groundwater contamination is the subject.

The auxiliary conditions include both initial and boundary conditions. Initial conditions specify the initial state of the domain, e.g., initial groundwater levels and contaminant concentrations. Boundary conditions specify the state of the surface bounding the domain. When modeling groundwater flow, boundary conditions might include the specification of water surface elevation in a surface water body to which the groundwater is discharging. Modeling contaminant transport in groundwater might include specifying contaminant source concentration as a boundary condition.

Once the differential equations, auxiliary conditions, and geometry of the domain have been defined, a solution to the governing equations must be obtained to complete the model. Solutions may be sought analytically or numerically. Analytical solutions represent the closed-form solution to the governing differential equations. Analytical solutions typically are easy to compute and exact, but they often oversimplify a given problem by placing restrictions on the shape of the domain, auxiliary conditions,



Stewart W. Taylor

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specification of material properties, and the types of problems that can be solved. The last restriction is particularly troublesome. Many subsurface flow problems, (e.g., unconfined groundwater flow and unsaturated flow in soil), and chemical transport problems involving transformation (e.g., biodegradation) are so-called non-linear problems that cannot be solved analytically.

Numerical solutions represent an approximate solution to the governing equations, obtained by using a finite series to approximate the derivatives in the differential equation (finite difference method), or the solution of the differential equation (finite element method). In either case, the governing differential equations are replaced by a system of algebraic equations which are easily solved. In contrast to analytical solutions, numerical solutions are computationally intensive and sometimes inaccurate for certain problems. They often require personnel formally trained in their application. On the other hand, numerical solutions can be applied to fully general geometries, accommodate all possible auxiliary conditions, allow material properties to vary in space, and allow a solution to any problem one might normally encounter in the subsurface.

#### What Can a Model Do?

For remediation, a model is best viewed as a predictive tool to determine if natural processes, such as volatilization or biodegradation, will reduce contamination to acceptable levels, and as an assessment tool to evaluate the performance of a remedial system when required. It must also be kept in mind that different levels of analysis are possible for any given remedial strategy and that the more sophisticated the re-

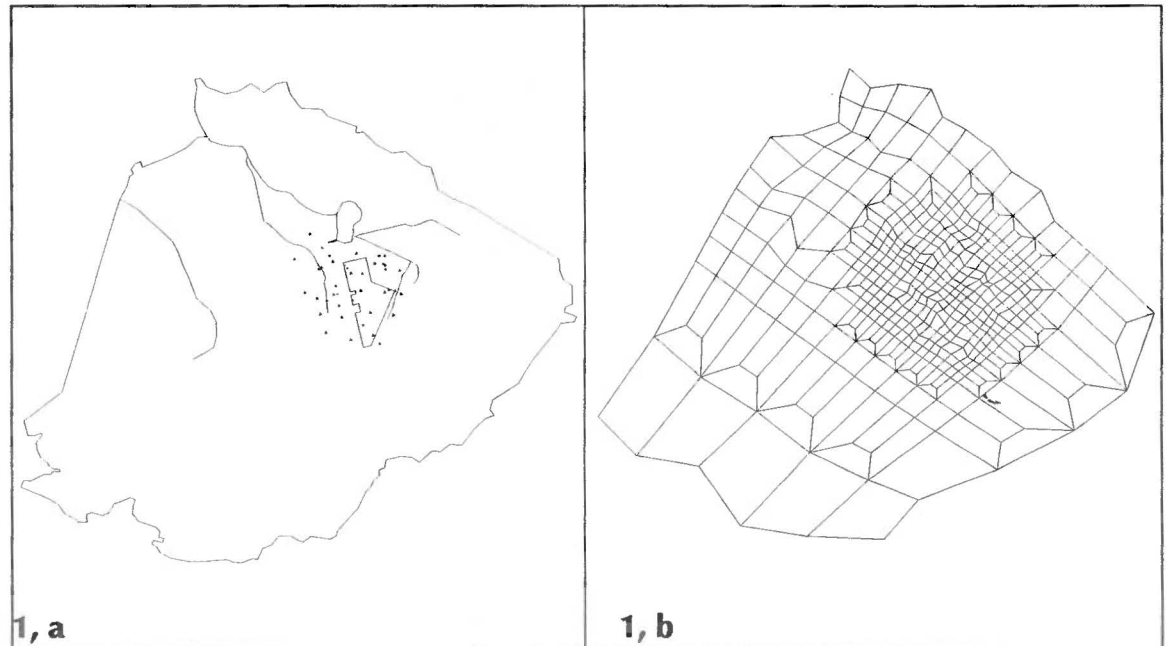
mediation the more complex and computationally intensive the model. These two points are best illustrated by the following examples.

Example 1: Consider an aquifer that has been contaminated by leakage of a petroleum hydrocarbon from an underground storage tank. Let us assume that the remediation system consists of withdrawal wells for the extraction of contaminated groundwater, some type of surface treatment, (e.g., air stripping followed by carbon adsorption), and injection wells for the re-injection of treated groundwater, otherwise known as pump-and-treat.

The first and second levels of analysis consist of modeling groundwater flow only and flow and transport simultaneously. At the first level, one could, by running the model several times, determine the location and number of wells needed to contain the groundwater hydraulically in the vicinity of the contamination plume. At the second level, where both flow and transport are modeled, one could locate wells, determine if any of the plume escapes extraction, and estimate how long pumping must continue to meet a water quality criteria.

The third level of analysis would involve modeling groundwater flow and contaminant transport under uncertainty. In today's regulatory environment, it is becoming increasingly necessary to report not only an answer but also the probability of that answer's being correct. Uncertainty in modeling subsurface processes arises primarily from imperfect knowledge of the subsurface material properties (e.g., permeability), which vary randomly in porous media. Given that the material properties can be defined in a probabilistic sense, multiple simulations that sample these probability distributions can gener-

*(a) Groundwater flow modeling requires location of bounding streams and lakes and groundwater drainage divides. Both determine size and shape of domain. (b) Numerical solutions divide domain into mesh of cells or elements. Finite element method accommodates very general boundaries and allows refinement of mesh for more detailed information.*



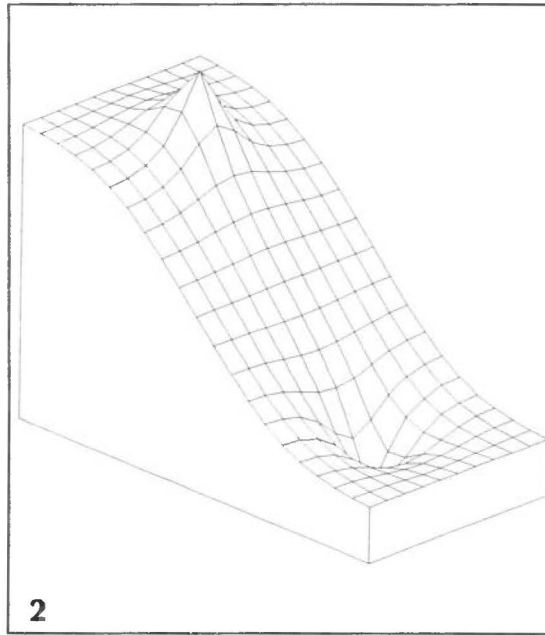
ate a probability distribution for the model output, such as concentration at the end of some time horizon. Modelers call this "Monte Carlo analysis."

The fourth level of analysis consists of combining the simulation of groundwater flow and contaminant transport with optimization theory to determine the best or optimal locations of wells and pumping rates that satisfy some project objective. For example, the objective might be to meet a water quality criteria at least cost in a given time, or to minimize the level of contamination without regard for cost. This approach is well suited for large, complex subsurface systems that are too complicated to design using trial and error methods for locating wells and determining pumping rates. Simulation-optimization analysis also can show whether it is possible to meet regulatory criteria with the chosen means of remediation.

**Example 2:** Consider an aquifer contaminated with an industrial solvent (trichloroethylene), and assume that *in-situ* biological treatment, a technology showing considerable promise but not yet in widespread use, will be used for remediation. The enhanced biodegradation of trichloroethylene is a relatively complex, biochemical reaction involving introduced nutrients, naturally-occurring or introduced bacteria, and the contaminant itself. Aerobically-based remediation might consist of injecting methane and oxygen and possibly methanotrophic bacteria into the groundwater through injection wells. As bacteria utilize the methane and oxygen for cell maintenance and growth, enzymes produced during this primary biochemical reaction degrade trichloroethylene.

The mathematical modeling of this process requires the simulation of chemical transport for each species involved in the reaction, *i.e.*, trichloroethylene, methane, oxygen, and bacteria, in addition to groundwater flow. Since biological growth is enhanced within the pores of the aquifer, some blockage of the pore space occurs and material properties like porosity and permeability are reduced in magnitude as bacteria accumulate over time in the media. Therefore, material properties vary not only with space but also with time, which complicates model formulation.

This model could be used to design an *in-situ* bioremediation system, including the location and operation of nutrient injection wells which maximize contaminant biodegradation. The application of the model would indicate the levels of remediation which are achievable by *in-situ* treatment. Relative to transport of a single, non-reactive chemical, the computational time to simulate this problem is 100-to-1,000 times



*Pump-and-treat remediation, left, consists of extraction and injection wells that contain contamination hydraulically. Groundwater flow models allow computation of hydraulic head distribution associated with extraction of water (hole) and injection of water (mound).*

greater, even for small systems. In theory, such a model also could be used to assess the remediation performance under conditions of uncertainty, or could be coupled with optimization theory for bioremediation design. In practice, however, the computationally intensive nature of these tasks exceeds the capabilities of available personal and mainframe computers.

The examples presented above demonstrate how mathematical models can be used in the design stage of pump-and-treat remediation systems, which are in widespread use now, and *in-situ* biological remediation systems, which will see more application in the 1990s. In both cases, the types of models and modeling approaches are not hypothetical; the software has been developed and is currently in use.

Of course, not all subsurface contamination occurs in dissolved form in groundwater. At many hazardous waste sites, soils that are only partly saturated with water are contaminated, and non-aqueous phase liquids (NAPLs) contaminate both soils and groundwater. These are examples of multiphase fluid systems. A body of literature is devoted to formulating the mathematics that describes the flow and chemical transport within the separate phases. Accordingly, numerically-based models are available for simulating these processes and can be used to assess the performance of dissolved or separate phase extraction processes.

#### **Limitations of Models**

A primary limitation of mathematical models for subsurface flow and chemical transport results from our inability to describe mathematically some physical, chemical, and biological processes. Most flow and transport processes

are relatively well understood, but some, particularly transformation processes, are understood only in the qualitative sense. Unfortunately, from a remediation perspective, these transformation processes often are the basis of remediation. Consider *in-situ* bioremediation as an example. The microscale spatial distribution of bacteria in a pore determines how one formulates a mathematical model for describing contaminant biodegradation. Yet, this distribution has not been directly observed because manipulation of the media destroys the configuration of the bacteria. Therefore, biodegradation models make assumptions about the microscale distribution of bacteria that have not been validated.

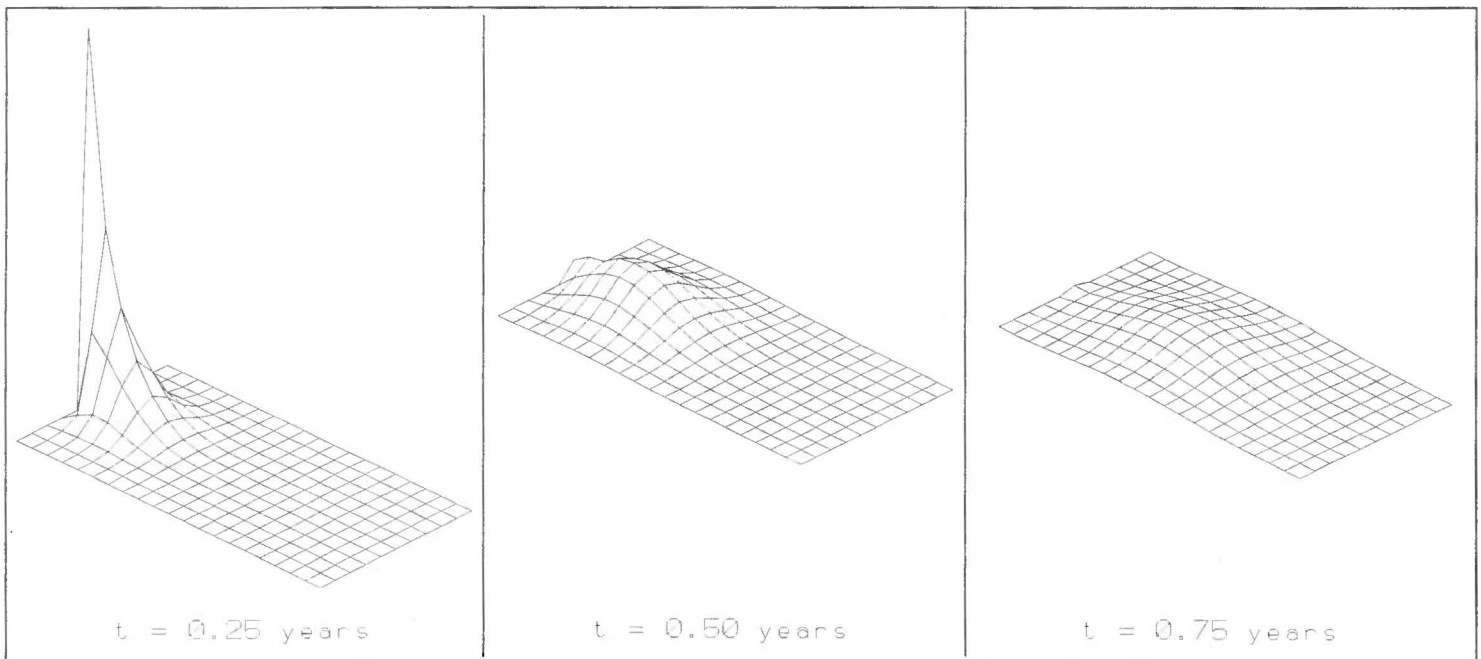
Another primary model limitation is insufficient data for establishing the parameters of a model. Models of subsurface flow and transport contain parameters that describe the physical characteristics of the soil or aquifer. Because of the way in which most soils and aquifers are formed geologically, these characteristics can vary over large ranges in relatively short distances. If one could log a very large number of borings, the spatial variability in parameters could be incorporated into a numerical model and simulations could be conducted with confidence. In reality, it is cost-prohibitive to characterize a site at such a fine level of detail, and therefore the modeler has less confidence in the simulated result. Simulation under uncertainty provides a means for formally quantifying the uncertainty in model output as a function of uncertainty in model parameterization. Uncertainty does not, however, detract from the utility

of models for remediation. It often can be shown, by simply varying parameters over likely ranges, that many model results are not overly sensitive to certain parameters.

#### Model Selection

Selecting a subsurface flow or chemical transport model to aid the implementation of site remediation requires a knowledge of the specific type of flow and transport problem to be solved. The first distinction to be made is whether flow is single phase (flow of groundwater) or multiphase (flow of soil water, flow of water and NAPLs). Secondly, a determination of whether subsurface flow alone is sufficient for remediation assessment, or whether both subsurface flow and chemical transport must be considered. For purposes of hydraulic containment, simulation of flow alone often is sufficient to design extraction well systems. If knowledge of containment migration and transformation is required, perhaps to demonstrate that the remediation would result in acceptable water quality, transport obviously should be modeled as well.

A knowledge of the dimensionality of the subsurface problem also needs to be considered prior to choosing a model. Models consider spatial dependence in one, two, or three dimensions. As a rule, one should select a model of the lowest dimensionality physically justifiable in order to minimize the data and computational requirements. Unsaturated flow in soils, for example, is predominantly downward, and a one-dimensional model might be perfectly adequate in many situations. Because of the tendency of aquifers and aquitards to be nearly horizontal



Contaminants in groundwater move with average groundwater velocity (advection) and with highly localized groundwater velocities (dispersion). Advection results in net movement of contamination plume; dispersion spreads and attenuates plume.



formations, groundwater flow in aquifers tends to be horizontal. A two-dimensional model would suffice. Many two-dimensional models can be turned on their sides to look at flow and transport in the vertical plane. Fully general applications require a three-dimensional model.

A choice also must be made between models using analytical solutions and those using numerical solutions. The choice should be made on the basis of data availability and level of study. While analytically-based models have severe limitations, a model is no better than the data used to develop parameters. In the absence of sufficient data, a numerical model usually is not justified unless a contaminant transformation process is the basis for remediation. In general, analytical models are best viewed as reconnaissance-level tools, while numerical models are best applied as design tools.

## Ordering Models

The best source for subsurface flow and chemical transport models is the International Ground Water Modeling Center, Holcomb Research Institute, Butler University, Indianapolis, IN 46208. The center serves as a groundwater software clearing house and distributes, at nominal cost, a wide variety of programs related to groundwater modeling. Programs are available for simulating two- and three-dimensional flow and transport under both saturated and unsaturated conditions. Included are models developed by the U.S. Geological Survey that are widely used in both the private and public sectors. In addition to these numerical models, many analytical models for simulating flow and transport in one, two, and three dimensions and to and from wells are available.

## New York State DEC Joins Effort To Implement New Technologies

By Edward O. Sullivan and Jack McKeon

The 1986 Superfund Amendments and Reauthorization Act (SARA) mandated that preference be given to permanent technologies in the selection of remedies for Superfund sites. A "permanent" remedy is defined as one that permanently and significantly reduces the mobility, toxicity, or volume of the hazardous waste present at the site. The New York State Legislature has not acted on Governor Mario Cuomo's proposed legislation which would include an explicit statutory preference for permanent remedies parallel to the federal law. However, the Commissioner of the Department of Environmental Conservation (DEC) has the statutory authority to select remedies, and Commissioner Thomas Jorling has established a policy that favors the use of permanent remedies wherever practicable.

During the last three years (fiscal years 1987-89 through 1989-90) 80 percent of the Records of Decision (RODs) issued for New York State projects included a permanent remedy or a combination of permanent and containment-oriented remedies. Federal Environmental Protection Agency (EPA) records show that RODs issued for NPL sites in federal fiscal year 1989, 75 percent included a permanent remedy of a combination of permanent and containment-oriented remedies.

Further, the EPA found that of the RODs containing treatment technologies issued during the last three years, 55 percent included incineration or solidification/stabilization. These tech-

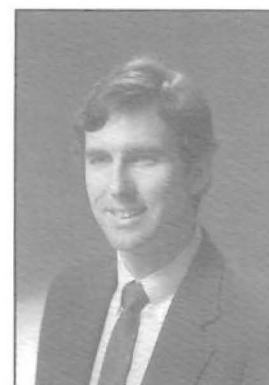
nologies have generally proven to be successful in meeting the SARA mandate. However, more innovative technologies are being recommended in RODs at an increasing rate. These newer technologies, including bioremediation, soil flushing, *in situ* vitrification, and chemical treatment, are considered innovative because they have not been widely used and their record of performance at Superfund sites is usually short or nonexistent. Many of these innovative technologies will be used to treat contaminated soil *in situ*, or without the need for excavation or transport.

Because of the newness of the technologies, there is uncertainty in the minds of those proposing the technology (the consultants), those undertaking the cleanup (the responsible party and the state or federal government), and those directly impacted (the community). Cost effectiveness must be considered because some permanent remedies may cost more without comparable increase in quality. Probably the most critical element affecting the wider use of innovative technologies is information exchange about what technologies can be successful.

Information exchange must cover a variety of areas:

A vendor must know what test data are needed to convince a prospective user that a process will meet performance standards.

Vendors and the investment community must know the characteristics of the universe of Superfund sites.



Edward O. Sullivan



Jack McKeon

*Edward O. Sullivan is deputy commissioner, New York State Department of Environmental Conservation Office of Environmental Remediation. Jack McKeon is director of the DEC's Bureau of Program Management.*

Government agencies, responsible parties, and consultants must know about successful (and unsuccessful) uses of technologies.

Citizens living near hazardous waste sites, who will be most affected by application of technologies, should have as much information as possible on the recommended technology.

A wide variety of groups have undertaken efforts to facilitate the exchange of information. The New York DEC has created a Technology Section in the agency's Division of Hazardous Waste Remediation with a mandate to increase applications of innovative treatment technology. The EPA has created a Technology Innovation Office (TIO) with similar goals in its Washington, DC, headquarters. In addition, the New York State Center for Hazardous Waste Management at State University of New York at Buffalo assists in the exchange of information concerning innovative technologies.

Last winter, the Center and the DEC sponsored a conference at which participants discussed impediments to the implementation of new technologies. Attending the meeting were people with responsibility in the hazardous waste remediation field, including technology vendors, developers, consultants, the legal community, and representatives of the New York DEC and the EPA. The conference focused on overcoming regulatory, procurement, and other administrative obstacles to the implementation of new technologies and, at the same time, served as a starting point for information dissemination.

Conference participants recommended the creation of standardized testing protocols for innovative technologies. The lack of standardized cost and performance information most often is the first obstacle to acceptance of and confidence in new technologies. A technology developer may possess seemingly successful test data, but the data may be insufficient to convince a prospective user of the validity of the developer's claims. To bridge the gap between developers' claims and potential users' need for precise data, the EPA's Technology Innovation Office plans to develop minimum criteria for collecting samples, carrying out tests, and evaluating the performance of new technologies.

Conference participants also addressed the need for additional dissemination of information about the universe of hazardous waste sites. The DEC provided some information to the people at last winter's conference, and the EPA's TIO has begun to provide profiles of the overall population of Superfund sites. The information will be particularly critical for members of the investment community who will want assurances that a large enough market for a particular technology exists before they invest.

Dissemination of information about successful use of a particular technology also is a necessity. The EPA's Alternative Treatment Technology Information Center (ATTIC) provides access to technical information in the form of abstracts and report summaries from numerous sources, including the EPA SITE Program, states, private industry, and the Department of Defense. The centrally-located body of information serves as a focal point for the exchange of information among users. The ATTIC database continues to grow as technical specialists abstract more information and enter it into the system. The EPA also maintains databases on records of decisions, treatability studies, and the costs of remedial actions.

The New York DEC has sponsored more than 20 staff seminars over the past two years at which technology vendors explained their systems in detail. The seminars give DEC project managers information about proven and developing technologies, making it possible for them to evaluate and recommend the most effective remedies. The DEC plans to expand seminar participation to include responsible parties, consulting engineers, impacted citizens, and the investment community.

The DEC is increasing its efforts to break down regulatory, procurement, and administrative barriers to the implementation of new technologies. The agency also has increased efforts to work with technology developers, consultants, responsible parties, affected citizens, the investment community, professional organizations, and universities, as evidenced by the DEC/New York State Center for Hazardous Waste Management conference last winter.

## Conference on Yard Wastes Set For March

Cornell University, the New York State Energy Research and Development Authority (NYSERDA), and the New York State Department of Environmental Conservation (NYSDEC) will sponsor a conference March 27 and 28, 1991, in Albany, NY, to focus on the beneficial use of municipal yard wastes. The conference will be of particular interest to government personnel and people in the private sector who produce yard wastes and land clearing debris and who use compost and wood chips. Interested persons may call Lauri Wellin at the Cornell Waste Management Institute, 466 Hollister Hall, Ithaca, NY, 14853, (607) 255-1187.



John W. Kalas

Theresa A. Walker

John E. Iannotti

Richard A. Poduska

## *NYS Center for Hazardous Waste Management* **New Members Named To Board, TAC**

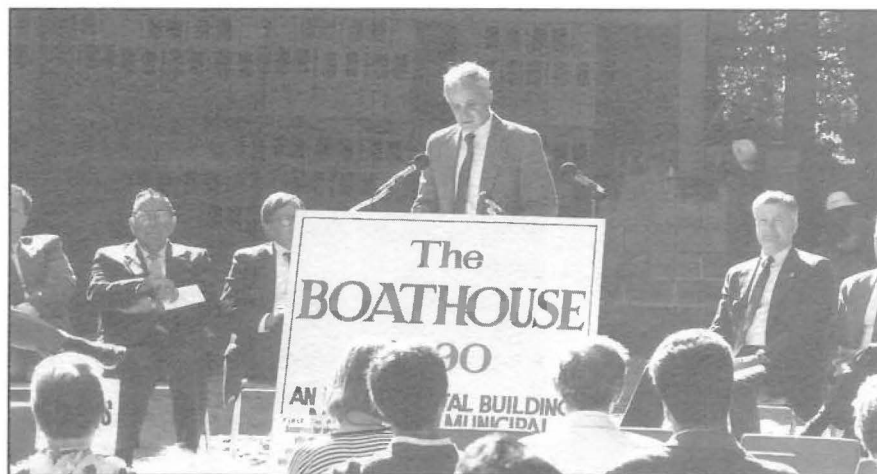
The New York Center for Hazardous Waste Management at State University of New York at Buffalo recently welcomed new members to its Executive Board and its Technical Advisory Committee (TAC). The TAC assists the Center in the development of its research agenda, in setting priorities, and in the review and selection of projects to be funded.

Dr. R. Bruce Johnstone, chancellor of the State University of New York (SUNY), named Dr. John W. Kalas his designee to the Center's Executive Board. Dr. Kalas, SUNY's associate provost for research and development, also serves on the boards of the New York State Institute on Superconductivity and the Great Lakes Research Consortium and as a member of the Governor's Council on High Technology. He was deputy director of the Washington, DC, office of the SUNY Research Foundation and director of research and development at the Foundation's Albany, NY, office. He earned a Ph. D. degree at Columbia University and has held academic and administrative positions at several colleges. He was director of special projects for VISTA/OEO in the late 1960s.

Vincent Tese, commissioner of the New York State Department of Economic Development, named Dr. Theresa A. Walker his designee on the Buffalo Center's Executive Board. She manages University/Industry Programs for the New York State Science and Technology Program, a public corporation formed to create and implement programs that support scientific and technical education, research, and development. Dr. Walker earned a Ph.D. in biochemistry at Yale University and taught at East Tennessee State University College of Medicine. She was a staff scientist for the Illinois State Legislature and director of the New York State Legislative Commission on Science and Technology. She joined the staff of the New York State Science and Technology Foundation in 1988.

John E. Iannotti and Dr. Richard A. Poduska are new appointees to the Buffalo Cen-

ter's Technical Advisory Committee. Iannotti is director of pollution prevention for the New York State Department of Environmental Conservation. He is a graduate of Clarkson University and earned a master's degree in environmental engineering at Rensselaer Polytechnic Institute. Poduska is director of environmental affairs for Manufacturing, Distribution and Support Services, Eastman Kodak Company. He has worked as a sanitary engineer with the U.S. Public Health Service and as an environmental engineer for the Tennessee Eastman Company. He was an adjunct professor at the University of Tennessee. Poduska earned a Ph.D. degree at Clemson University and completed undergraduate and graduate degrees at Cornell University and the University of Cincinnati.



**Dr. R. Lawrence Swanson, director of the Waste Management Institute of the Marine Sciences Research Center, SUNY Stony Brook, spoke in October at the dedication of a boathouse constructed with incinerator ash blocks on the Stony Brook campus. The boathouse construction follows years of research on the use of incinerator ash blocks in the marine environment and is the first such building in the United States. Air and soil around the experimental structure will be monitored for any release of heavy metals from the ash blocks. Pictured with Swanson are, from left, NYS Sen. James J. Lack, NYS Sen. Caesar Trunzo; Dr. J.R. Schubel, dean and director of the Center; Dr. John H. Marburger, president of SUNY Stony Brook, and NYS Sen. Kenneth P. LaValle.**

# Basic Approaches For Remediation Of Soils Contaminated By Metals

By Mark R. Matsumoto



M.R. Matsumoto

Modern society relies on the use of metals. In addition to the obvious dependence on metals in construction and the manufacture of automobiles, airplanes, and appliances, metals also are widely used in organic chemical production, agriculture, and the manufacture of pulp and paper products, inks, batteries, electrical and electronics components, and textiles.

The loosely-defined term, "heavy metals," refers to metal and metalloid elements (of which there are about 70) that are associated with pollution and considered toxic. In New York State, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, and zinc are the metals most often found in hazardous waste sites, according to data from the state health department.

Landfilling of metal wastes and sludges is the primary cause of metal contamination at hazardous waste sites, but other sources contribute to site contamination. Atmospheric fallout of metal particulates from smelters and incinerators, land application of wastewater and sludge, and the discharge of wastewater into a receiving stream are other possible sources of heavy metal contamination. Metal use is so widespread that it is impossible to identify one particular industrial sector as the principal source of metal contamination.

All heavy metals are potentially toxic at high enough concentrations. Heavy metals generally interfere with the normal enzyme production process of cells. The relative toxicity of heavy metals can be linked to two primary factors: 1) whether the metal is required as a micronutrient and 2) how easily cells can take up the metal. As a rule, heavy metals that are non-essential as micronutrients and that are readily taken up by cells are the most toxic. Cadmium, lead, and mercury have been called the "big three" heavy metals because they are common, highly toxic contaminants that bioaccumulate. None of the three is an essential micronutrient.

Heavy metals can migrate from a hazardous waste site in several ways: groundwater migration, sediment transport from precipitation run-off, plant uptake, and air transport. Migration

via any of the routes can produce severe impacts. Metal toxicity caused by inhalation of contaminated dusts and water vapor is enhanced significantly. Absorption of metals through the lungs bypasses the normal filtering organs (liver and kidneys), allowing the metals to reach sensitive organs (the central nervous system) more readily. Bioaccumulation of heavy metals occurs in both the aquatic and terrestrial food chains by as much as 1,000 times. Ingestion of metal-contaminated organisms often leads to severe chronic and acute toxicity effects. Leaching of heavy metals into groundwater may lead to violation of drinking water standards. (See Table 1.)

In the soil environment, heavy metals partition between the solid and liquid phases. The relative fraction of heavy metals that associates with either phase depends on the nature of the soil particles and the solution conditions in the liquid phase.

Principal factors that affect metal partitioning include pH, clay content, organic fraction, the soil, redox conditions, total dissolved solids concentration, and soluble total organic carbon, especially from organic acids.

Based on the partitioning behavior of heavy metals, two basic strategies are used in the remediation of contaminated soils: immobilization and soil washing/flushing. One of the two approaches should be included as part of the remedial treatment process for sites where heavy metals are the principal contaminants of concern.

## Immobilization

In very general terms, immobilization is a technology that employs chemical additives or a process to transform the soil into a less toxic form by physically and/or chemically immobilizing the waste constituents, limiting the mobility of the contaminant. The U.S. Environmental Protection Agency (EPA) is evaluating immobilization techniques as a best demonstrated technology available for treating contaminated soils on site.

There are three techniques for immobilization: solidification, stabilization, and vitrifi-

**Table 1: Quality Standards for Ground waters (NYSCRR, Title 6, Chapter X, Parts 700 - 705)**

Metal	Drinking Water Stds., mg/L	Effluent Discharge, mg/L
Arsenic	0.025	0.05
Cadmium	0.01	0.02
Chromium (+6)	0.05	0.10
Copper	1.0	1.0
Lead	0.025	0.05
Mercury	0.002	0.004
Nickel	No limits	No limits
Selenium	0.02	0.04
Zinc	5.0	5.0

cation. Each works in a different way to immobilize metals in a solid matrix.

In solidification, wastes that contain free water are solidified by reaction with a binder such as cement or lime. Solidified wastes meet the free water restriction on landfill disposal. In stabilization, binding agents, generally in larger quantities than used for solidification, are added to a waste to fix the hazardous constituents in a solid matrix. The process reduces the leachability of hazardous components as measured by the Toxicity Characteristic Leaching Procedure (TCLP). Hazardous constituents still remain in the waste or soil, but their mobility is greatly reduced by the stabilization process.

Vitrification is the fusing of solid materials into a glass-like substance by the application of electrical energy. For in situ remediation, contaminated soils are melted under controlled conditions by applying high voltage across electrodes inserted into the contaminated soil mass. Organic hazardous components are destroyed (thermal destruction), removed (volatilized), and/or permanently immobilized into glassified soil. Extremely high temperatures (> 1600° C) are employed in the vitrification process.

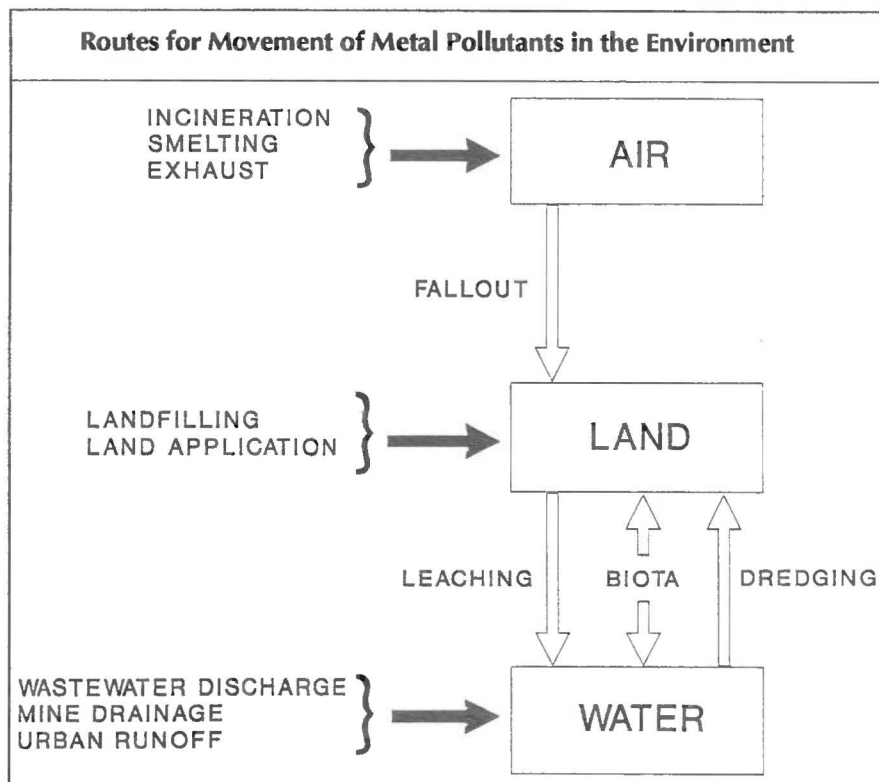
**Soil Washing/Flushing**

Soil washing/flushing, solvent, or chemical, extraction, and air stripping are the three major extraction techniques. In soil washing/flushing, water is the primary washing fluid. The water carries chemical additives to promote contaminant solubilization. Acids, bases, oxidizing/reducing agents, surfactants, and complexing (metal) agents are the typical chemical additives. Soil washing requires physical handling of contaminated soils, while soil flushing refers to in situ extraction of contaminants. The flushing agents are similar for both situations. Soil washing/flushing is used for the removal of non-volatile hydro-

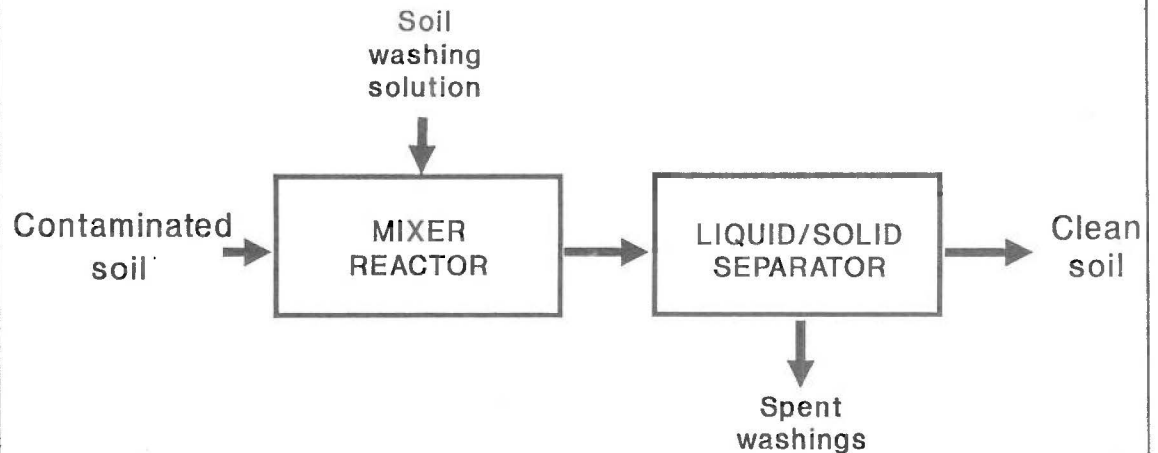
philic, and some hydrophobic, organic compounds as well as heavy metals.

The complete soil-washing process involves four primary steps: 1) contaminant solubilization by the wash fluid, 2) separation of the soil/wash mixture, 3) treatment of the spent wash water, and 4) disposal of treatment residuals.

After the initial washing step, additional treatment steps are necessary to complete the soil-washing process. Following the solubilization of metals by the soil washing fluid, the cleansed soil must be separated from the liquid wash before it can be returned to the site. The



### Schematic of Soil Washing Process



separated spent soil wash fluid then will require treatment for the removal of colloidal solids (clays), soluble metals, and complexants. In addition, the spent fluid may require pH adjustment. Treatment of wastewaters generally results in residual materials (sludges) that require disposal. Each of these additional steps must be addressed in assessing the feasibility of the over-

all soil washing process.

Separation of the soil and wash fluid can be accomplished using the conventional processes employed in water and wastewater treatment. Unit operations and processes used for solid/liquid separation include sedimentation, coagulation/flocculation, centrifugation, filtration, vacuum filtration, filter presses, belt presses, and dissolved air flotation.

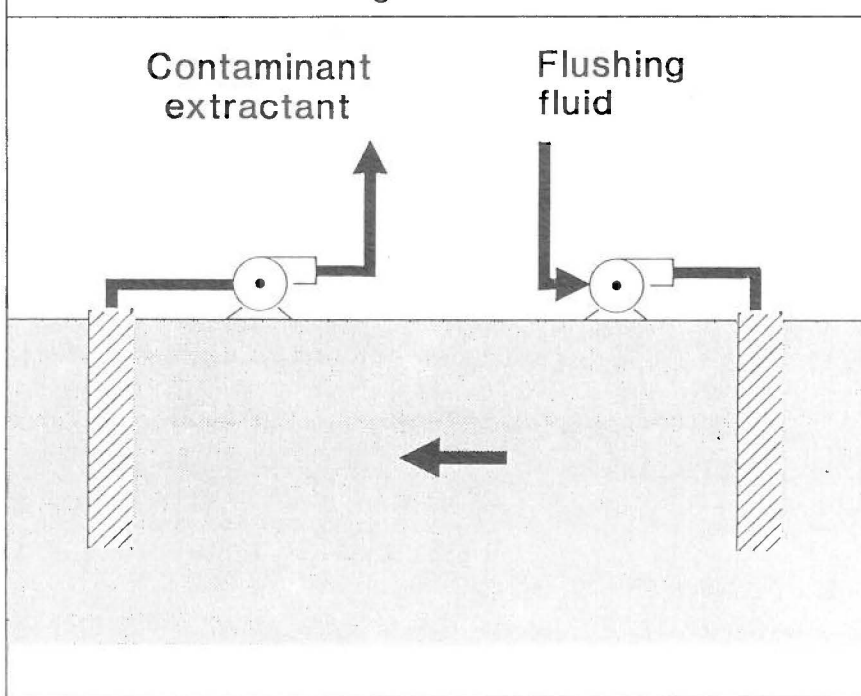
Hazardous metal contaminants in the separated wash fluid must be removed using normal wastewater treatment unit processes. After treatment, the wash fluid may be reused for further soil washing or discharged into a sewer or receiving body of water.

No matter what treatment process is used for removing heavy metal contaminants from spent soil washing fluid, some residual always will remain. The residual may be liquid, semi-solid, or solid. Land disposal is the only option for the ultimate disposal of these residuals. Thus, residuals must be treated to ensure that they meet all requirements for land disposal (40 CFR 268).

Immobilization technologies are now widely employed to make wastes compatible for land disposal. Residuals from the soil washing process must be immobilized by solidification/stabilization or vitrification before land disposal.

*Dr. Mark R. Matsumoto is an associate professor of civil engineering at State University of New York at Buffalo.*

### Schematic of Soil Flushing Process



# Combustion Simulation At Cornell Relies Upon Supercomputing For Solutions To Complex Equations

*By Frederick C. Gouldin*

Traditional practice in the design of combustors relies on the construction and testing of prototypes. For small systems, the testing of many different prototypes is feasible and allows for a vigorous "build'm and bust'm" approach to design refinement. For large combustors, such as the mass-burn incinerator, this approach is not feasible, and consequently designs have evolved slowly from one small modification to the next. A limited amount of small-scale prototype testing is done, especially on system components such as burners, but overall, the design is made cumbersome by the size of the system and its components and the consequent large scale and cost of physical testing.

In the Combustion Simulation Laboratory at Cornell, our primary goal is to develop computer-based design and analysis tools that improve the design process and reduce dependency on prototype testing. These tools will speed design, allow for more testing of new concepts because of simulation capability, reduce the cost of design, and lead to better designs.

The numerical simulation tools we are developing at Cornell will speed the design and development of municipal waste incinerators for cleaner and more efficient operation. Our work so far has dealt with the reduction of NO<sub>x</sub> emission by ammonia injection and the simulation of over-bed processes, with an emphasis on flow and mixing. Future work will include studies of the formation of toxic compounds during the combustion of plastics, and the fate of heavy metals, especially mercury.

Our approach is to express the physical and chemical processes of combustion in the form of mathematical equations—the combustion model—and then solve these equations on a digital computer. Thus the process of simulation development is composed of two distinct tasks: model development and numerical solution of the model equations. Each task presents unique and substantial challenges.

## **Developing and Solving Equations**

The study of combustion requires the study of several different rate processes: fluid

flow, heat and mass transfer, and chemical and physical transformation reactions.

Our present understanding of fluid flow and of heat and mass transfer is considered sufficient for writing a set of coupled, differential equations describing these processes. However, these equations are so complex that they have been solved for only a few problems. In the case of incinerator simulation, the primary factors that contribute to the difficulty of solution are flow turbulence (unsteady, chaotic flow), complex flow geometry, and the presence of multiple phases (solid, liquid, and gaseous). In addition, the equations have mathematical characteristics (nonlinearity and stiffness) that make their solution difficult. A major objective of researchers working on the flow and transport problems of combustion is to develop approximate, model equations that both provide an adequate description and are numerically tractable. With the continuing, rapid development of computational capacity, more and more complex model equations can be solved numerically, allowing for the development of increasingly accurate and general model equations.

In contrast, our understanding of chemical and physical transformation processes is not complete, and new investigations of combustion problems frequently lead to the discovery of new transformation paths and processes. A major reason for this state of affairs is that chemical reactions in combustion are chain reactions involving many different chemical species and reaction steps. The addition of new chemicals to a system introduces the possibility of new chemical compounds and reaction paths.

The necessity of keeping track of many different compounds and reactions increases the mathematical complexity of combustion simulation. For example, each chemical species considered adds a differential equation to the coupled set of equations that must be solved. The forms of



**Frederick C. Gouldin**

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*Dr. Frederick C. Gouldin is director of the Cornell Combustion Simulation Laboratory, a part of the New York State Solid Waste Combustion Institute at Cornell University.*

the chemical source terms are changed, as is the degree of coupling between the equations. Thus, when developing chemical and physical transformation models, one attempts first to determine all the important species and phases and the important transformation paths, and then to develop a transformation model that is, again, realistic and tractable.

From this brief discussion, it should be clear that one who would pursue combustion simulation faces a multifaceted problem requiring expertise in several areas — fluid flow, heat and mass transport, chemical reaction and phase change, and applied numerical analysis. And as the research proceeds, one must take care to assess the accuracy of both the combustion models used and the numerical solutions obtained.

### Combustion Simulation at Cornell

Over the last two decades, combustion simulation has undergone significant advancement and at present plays an important role in combustor design. Design applications of simulation are now made to gas-turbine and jet-engine combustors and to spark-ignition engines. Simulations are under development for coal-fired boilers and design applications are anticipated.

Our research team in Cornell's Sibley School of Mechanical and Aerospace Engineering is working on simulation methods for incinerators, using as a starting point the most recent developments in combustor design for furnaces and gas turbines. The work is supported by the

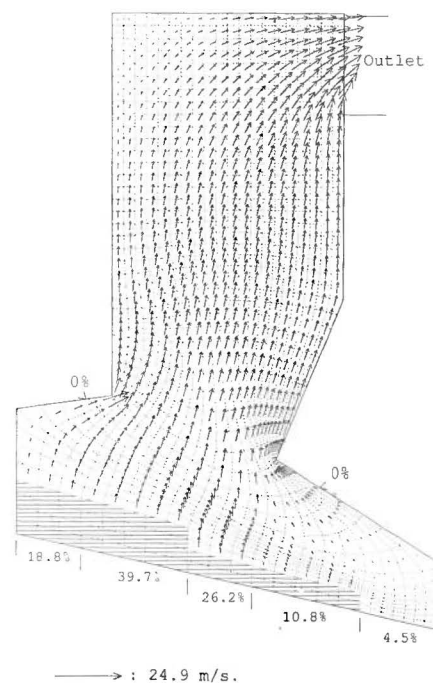
State of New York as part of the New York State Solid Waste Combustion Institute.

To develop an incinerator simulation, we broke down the problem into a series of component problems; each problem is solved separately and then the parts are integrated to form a whole. Examples of component problems are combustion in the waste bed, overfire air injection, radiative heat transfer,  $\text{NO}_x$  formation and control, heat-exchanger design, and gas-scrubber design.

We are now focusing on the simulation of above-bed processes in the incinerator: overfire air injection, radiative heat transfer, ammonia injection for  $\text{NO}_x$  reduction, turbulent mixing, and mixed forced and natural convection. On the basis of our past experience and our progress in other areas, we are optimistic that we can develop useful simulation tools that will incorporate our current understanding of the important physical and chemical processes and that can be readily modified to incorporate new findings about important processes affecting combustion and performance.

Specifically, our procedure is to pose a set of differential equations along with appropriate boundary and initial conditions, and then solve them numerically. Major challenges in posing these equations and conditions are to account for turbulence, important chemical reactions, the geometry of the incinerator, conditions of gases leaving the waste bed, and the addition of overfire air in small, high-velocity jets. Once the model equations are posed, they must be transformed into a form that can be

*Three-part figure represents test cases pertaining to 2-D numerical simulations of a solid waste incinerator. Examples show some results of changes in combustor geometry and rate of gas flow and the effect of overfire air in combustion chamber. So-called "k-ε" turbulence model was used. Images show velocity distribution. Grid is 20 x 47. Hatched sections accommodate code discretization constraints. Percentages indicate proportion of air entering different sections of combustor. Figure a pertains to configuration designated Geometry I. Conditions are: cold flow, no overfire air, Reynolds number =  $1.4 \times 10^5$ , average velocity = 4 m/sec. Figure b geometry is the same, but there is overfire air injection with initial jet velocity of 90 m/sec. In c, overfire air injection is same as b, but configuration is Geometry II.*





solved by large-scale computation.

In our case, a solution is sought on a set of discrete mesh points, and the differential equations are replaced by a set of algebraic difference equations. The solution of these difference equations is an approximation of the solution of the original differential equations; the difference between the solutions is referred to as numerical error. Factors that affect numerical error include the form of the transformation between the differential and difference equations — the differencing scheme — and the number of mesh points.

In general, the more mesh points the smaller the numerical error, but the larger the computer required for solution. That is why supercomputer facilities are essential to our work. We are fortunate to have access to the computers of the Cornell National Supercomputer Facility (CNSF).

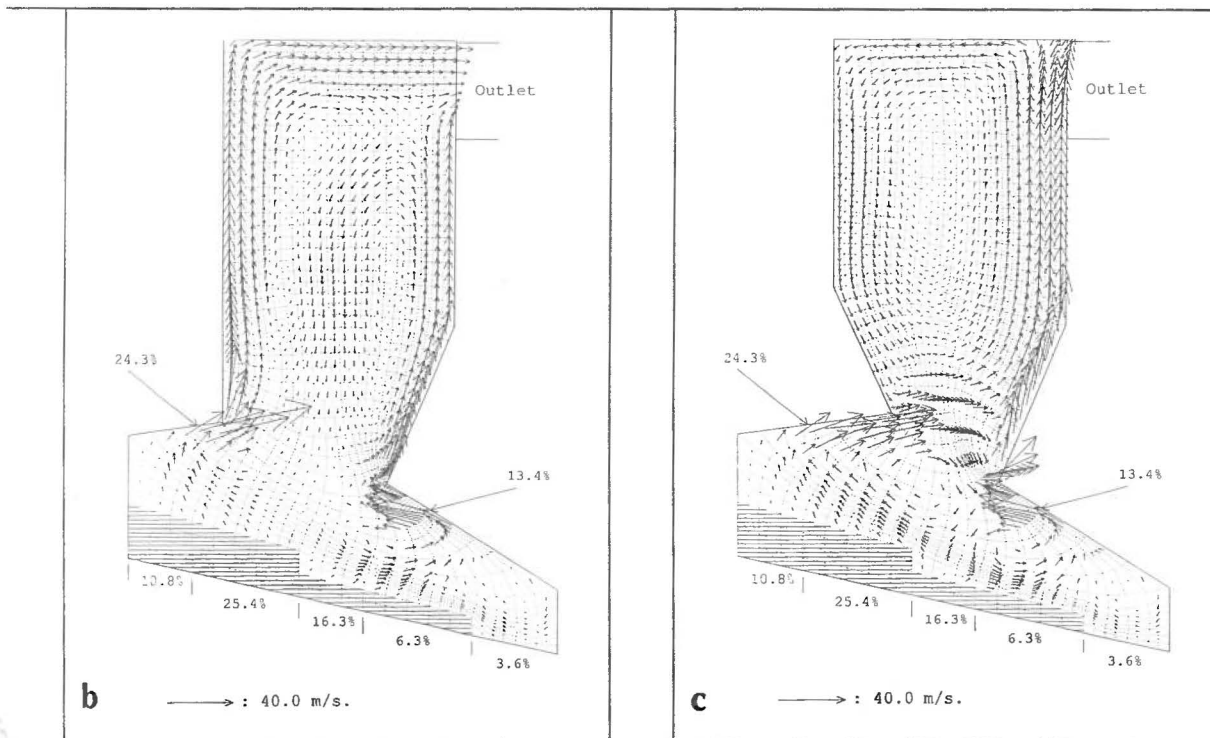
### Incinerator Simulation Problems

The geometry of an incinerator makes it difficult to simulate. For one thing, the flow is three-dimensional and a large number of mesh points are required for the numerical solution; for example, a 100x100x100 mesh has a million points. Also, the very large flow contraction just above the bed causes numerical problems, and it can cause flow separation that needs to be calculated accurately. An additional difficulty is encountered in simulating the overfire air jets along the front and back walls of the incinerator. The placement, direction of flow, and flow velocity of these jets are critical design decisions

that we plan to help make through simulation. The difficulty is that since the diameters of these jets are relatively small, it is necessary to have a fine enough mesh to obtain an accurate numerical solution of the jet flows and still avoid overdoing the mesh density elsewhere.

Turbulence modeling, which attempts to develop model equations for estimating the mixing and transport effects of turbulent velocity and property fluctuations without solving the full time-dependent equations, has been an area of active research for some time, and several models are available. We are using a well tested model (called the k- $\epsilon$  model) in which the expressions for the effects of turbulence on mass, momentum, and heat transfer are similar to those that are valid for laminar flow, except that the molecular diffusivity, viscosity, and conductivity are variables dependent on two turbulent quantities, k (the kinetic energy of turbulent velocity fluctuations) and  $\epsilon$  (the rate at which the energy is ultimately dissipated by viscosity.) Model equations for k and  $\epsilon$  are posed and solved. Since this model has been widely used, both its strengths and weaknesses are well known.

Most of the fuel is consumed by chemical reactions in the waste bed. With regard to the above-bed region, therefore, we are interested in a subset of reactions that are important for their influence on air emissions but do not affect the temperature significantly. Examples of such reactions include the oxidation of residual CO to CO<sub>2</sub>, the formation of NO, and the oxidation of residual hydrocarbons and chlorine-containing hydrocarbons that might contribute to toxic



emissions. The treatment of these and other important chemical reactions is hindered by a lack of knowledge of some of the important reaction steps and the difficulty of modeling the effects of turbulence on these reaction rates.

Given this situation, our objective is to determine what conditions of temperature and chemical mixture favor desirable reactions and then use simulation to determine how such conditions might be achieved in the incinerator.

Because the combustion processes in the waste bed are very complicated, we have decided not to attempt to model them during the initial phases of our work. Even so, to simulate the over-bed region, we must specify conditions in the gases flowing out of the bed. This problem is dealt with by performing a parametric study to determine how different bed exit conditions affect processes in the over-bed region.

### Two-Dimensional Incinerator

We are currently performing calculations on a two-dimensional incinerator (see figure). We are studying the quality of our numerical solutions and the effects of geometry changes and overfire air injection. Chemical reactions, heat transfer, and buoyancy effects are not accounted for in these calculations, but will be added to our simulation as progress is made.

The accompanying figure shows the velocity fields represented by velocity vectors located at the center of the mesh cells used for the calculations. The magnitudes of the velocities are indicated by the length of the vectors.

A noticeable feature of these results is the change in the recirculating flow patterns. The importance of such observations to designers is clear.

Since numerical simulation is built upon combustion models that are approximations, and because it is difficult to obtain accurate numerical solutions to these complex model equations, there is a need to verify results to the highest degree possible.

To this end we are building an experimental model that will allow us to test many aspects of our combustion simulations without lighting a match. In addition, we have established contacts with people in the incinerator industry and plan to discuss our results with them. In these ways, much can be done to test the simulations and our simulation methods.

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## Cornell Institute Provides Updates On Funded Projects

The New York State Solid Waste Combustion Institute supports eight research projects throughout New York State as part of its \$1.4 million research awards program. The research awards program is committed to fundamental combustion research leading to the development of combustion technologies and operating procedures that safeguard the environment. The Institute will report periodically on the progress of the funded research efforts. A brief update on two such research projects follows.

Accurate monitoring of potentially toxic emissions from incinerator facilities is an issue of public health concern in the management of municipal and hazardous wastes. In present practice, day-to-day process monitoring is based solely on indirect indicators of the efficiency of pollutant destruction. No reliable methods are available for direct, continuous, real-time monitoring of the concentrations of toxic emissions.

### REMPI Spectroscopy

Dr. Terrill A. Cool, a professor of applied and engineering physics at Cornell University, is exploring the possibility of monitoring toxic emissions from municipal and toxic waste incinerators using a new laser-based technique called "resonance-enhanced multiphoton ionization" (REMPI) spectroscopy. REMPI spectroscopy has the sensitivity and selectivity for real-time monitoring of a wide class of hazardous polycyclic aromatic hydrocarbons and chlorinated hydrocarbons.

REMPI detection of the chloroethylenes has been explored in a search for suitable surrogates for monitoring the formation of chlorinated hydrocarbons. Minimum concentrations for the mass-selected detection of REMPI fragments have been established for these species. In addition, quantitative estimates of the selectivity for the detection of two of these species indicate that they are readily detectable against thousand-fold larger background concentrations of chemically-similar interferant compounds.

The research effort continues with the design of prototype apparatus and procedures for field testing of this new approach to monitoring of potentially harmful emissions. Researchers hope that the demonstrated capabilities of this apparatus may help to address public health concerns and may ultimately improve proce-

dures for operating and regulating incinerator facilities.

### Dioxins and Furans

A second research project supported by the Combustion Institute seeks to identify the thermal conditions that favor formation and destruction of dioxins and furans in incinerators. This study involves a collaborative effort between Professor Elmar R. Altwicker of Rensselaer Polytechnic Institute and Professor Christoffer Rappe at the University of Umea in Sweden.

The researchers are conducting experiments that elucidate the role of potential precursors in dioxin/furan formation. This effort is also investigating further reactions on the surface of fly ash in the formation of dioxins and furans.

Since there is evidence that both homogeneous and heterogeneous pathways may play a role in dioxin/furan formation, two existing laboratory flow reactors are being used. The Swedish group is using a plug flow micro reactor while the RPI group is using a spouted bed reactor.

Experiments thus far indicate that dioxins and furans are formed at the beginning of the experiment when the fly ash is most active, followed by a much slower decomposition. Data also indicate that at a temperature of 250°C the decomposition rate may not be sufficient to compete with formation. In addition, it appears that dioxins and furans production is independent of precursor concentration.

The project is entering the second year of a three year effort to identify the major combustion variables involved in the formation and destruction of dioxins and furans during incineration. The project will also generate a database which can be tested against fundamental thermodynamic and kinetic considerations.

## Cornell Involved In Cooperative Project On Yard Waste Management

By Ellen Z. Harrison

Yard wastes represent about 20 percent of the solid waste stream in New York State. In deciding how to manage these wastes, communities need to consider significant economic, environmental, and energy costs and benefits. A major effort is underway at Cornell University to help promote efficient and beneficial use of these organic materials and to divert them from landfills and incinerators in New York State through composting and chipping.

Technical assistance to communities is the primary focus of a joint project that involves the Cornell Waste Management Institute (CWMI), Cornell Cooperative Extension, the Local Government Program at Cornell University, the university's Department of Agricultural and Biologic Engineering, the New York State Energy Research and Development Authority, and the New York State Department of Environmental Conservation (DEC). The cooperative effort develops and delivers information to local officials and community leaders to help them plan, initiate, and operate yard waste management programs.

The project began with a recently completed survey of more than 1,550 local governments in New York to determine how they deal with yard wastes now and provide other information necessary to develop the technical assistance program. Results of the survey show that



Ellen Z. Harrison



*Drop-off collection requires smaller investment, less effort, and fewer people than curbside collection.*

approximately 10 percent of yard wastes (primarily leaves) in the state is diverted from landfills and incinerators through 149 municipal composting programs. Economics and a desire to protect the environment are major incentives for the establishment of composting programs.

Municipalities identified a need for information on costs, equipment, and collection and processing methods. They also asked for educational programs on backyard composting and for suggestions on ways to encourage participation in municipal yard waste programs.

To help spread the word throughout the state and to develop local expertise, a key contact person has been recruited in each county in New York. In all but one county, the contact person is a Cornell Cooperative Extension Agent. Each has a copy of all materials developed under the joint program as well as a list of communities that have implemented yard waste management options. Each contact person serves as liaison between Cornell and the communities in his or her county. The contact people may also serve as local sources of information and organize educational events to serve local needs.

#### **Materials Available**

A database developed from the survey of local governments, together with detailed case studies of "scenario communities," will help

other communities understand their options and identify the size and level of sophistication that meets their needs.

Print and audio-visual educational materials on this and other Cornell projects are available. *Planning Guide for Municipal Yard Waste Management* may be obtained free from the DEC, the CWMI, and local offices of Cornell Cooperative Extension. In preparation are a book of *Case Studies*, a series of *Fact Sheets* for facilities operators, and a home study certificate course. Educational materials for young people, including *Composting: Waste to Resources*, a workbook for educators, complement the materials developed for local officials.

Two video tapes will be completed by the spring of 1991 to introduce communities to the benefits of composting and chipping. The videos build upon slide/tape sets available now.

Home composting, in addition to keeping yard wastes out of the collection system, helps to promote community acceptance of municipal composting facilities. A set of posters, a "how to" brochure, and numerous demonstration sites around the state introduce householders to the benefits of managing yard wastes at home.

Workshops took place last summer at eight locations in New York State, and a statewide conference is scheduled for March 27 and 28, 1991, in Albany. The meetings provide information to communities and give an opportunity to visit facilities where yard wastes are managed beneficially. The conference on establishing programs and promoting the beneficial use of yard wastes will include field demonstrations.

Research activities at Cornell help to ensure that advice to communities is environmentally sound. Concerns about potential contamination of yard wastes by pesticides prompted a Cornell study that showed composted yard wastes to be safe, with pesticides either undetectable or at very low concentrations. Research is underway to expand the range of materials acceptable for composting by investigating the potential for composting food wastes from restaurants and food processing facilities.

Interested persons may contact local Cornell Cooperative Extension offices or Ken Cobb, Ellen Harrison, or Lauri Wellin at the Cornell Waste Management Institute, 466 Hollister Hall, Ithaca, NY 14853, (607) 255-7535.

*Turning frequency depends on nature of raw waste and length of composting time. Fresh grass clippings may need twice-daily turning initially while windrows of all leaves may need turning only once a season.*



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*Ellen Z. Harrison is associate director of the Cornell Waste Management Institute.*

# Stony Brook Researchers Investigate Methods For On-Site Remediation of Groundwater

By Bruce J. Brownawell

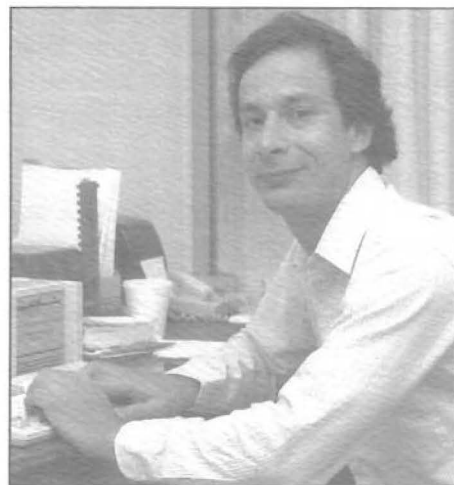
Groundwaters provide a precious source of clear and safe drinking water to many areas of the United States. The reliance on groundwater is greatest in regions of low precipitation (e.g., much of the Western Plains and the Southwest) and in areas where surface runoff does not result in rivers or large reservoirs (Long Island, for instance). Groundwater resources are threatened increasingly by numerous types of chemical contamination. The long list of problematic or potential groundwater contaminants includes: (i) chlorinated solvents such as trichloroethylene (TCE) used in a number of cleaning and degreasing applications; (ii) petroleum hydrocarbons leaking into the subsurface from corroded underground gasoline or fuel oil tanks; (iii) nitrate from fertilizers or landfill plumes; and (iv) persistent biocides used in agricultural applications. Microbial pathogens, trace metals, radioactive substances, as well as a myriad of organic chemicals are possible, but less frequently reported, groundwater pollutants. In Suffolk County on Long Island for example, there have been a number of closures of private and public wells contaminated by nitrate from fertilizer and by Aldicarb, a soluble pesticide formerly applied to potato crops.

Given the critical importance of groundwater supplies, there has been a large effort in recent years to develop effective methods to remediate contaminated groundwaters, as well as to protect aquifers from existing subsurface contamination. Geologic barriers, such as layers of low permeability clays have been used to isolate areas of contamination from critical water supplies and to line landfills and some hazardous waste disposal sites. Remediation of already contaminated aquifers is complicated by the slow rates of groundwater movement, the large volumes of water usually involved, and the tendency of many pollutants to associate with immobile aquifer solids. The last phenomenon retards not only the rate at which contaminants move within an aquifer but

also the rate at which contaminants can be removed by most remediation technologies.

A vast array of groundwater remediation strategies has been developed or proposed. These different approaches can be broadly generalized as "pump and treat" or *in-situ* methods. Pump-and-treat technologies involve destruction or removal of contaminants in water pumped from wells near, or down gradient from, the source of contamination. The treated water is usually used to recharge the groundwater at points upflow of the contaminations. Pump-and-treat methods can be expensive and may require years to decades of continuous operation to achieve effective cleanups. Examples of this type of clean-up include microbial degradation ("bioremediation") or vapor stripping of volatile organic chemicals. Many other methods are used for these and other contaminants; a review of even the most important technologies that have been employed or are under development is beyond the scope of this article. One point to bear in mind is that because groundwater remediation technologies are rather new on the scene, it is difficult to draw conclusions about the long-term effectiveness of various approaches that are now being used.

Treatment of subsurface contamination by *in situ* methodologies is



Bruce J. Brownawell

appealing because on-site treatments do not disrupt local hydrology and associated operating costs are lower. *In situ* technologies are largely in the research stage. Among promising strategies for dealing with recalcitrant organic pollutants are injection of short lived chemical oxidants that can degrade pollutants, and *in situ* bioremediation. The latter approach might involve stimulating indigenous populations of microorganisms to degrade toxic chemicals, or introducing into the subsurface microorganisms with ability to degrade the targeted pollutants. This is a difficult challenge for microbiologists who must address factors such as selecting bacte-

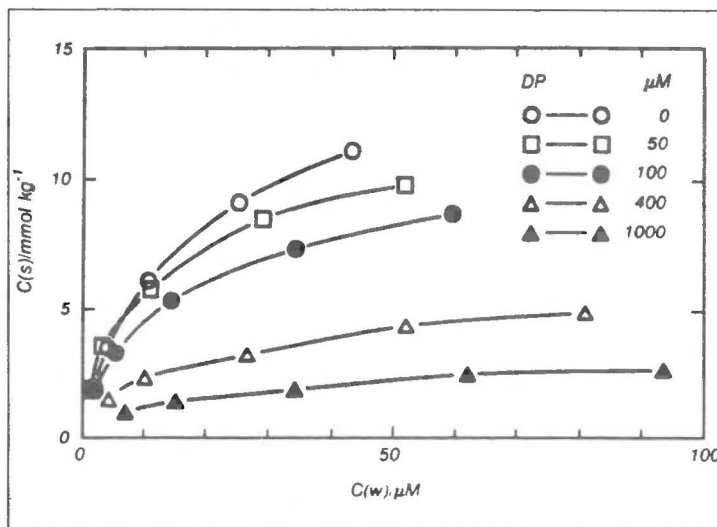


Figure 1. The effect of DP at various concentrations on adsorption of copper by Lula N6 Aquifer Material.  $C(s)$  and  $C(w)$  are sorbed and water phase concentration respectively. Batch experiments were conducted at  $\text{pH} = 4.9 - 5.5$  to ensure Cu solubility at these concentrations.

ria that can compete under a variety of environmental conditions, and more importantly, how to introduce the microorganisms through porous aquifer environments to where they are needed. Major research and contributions in the field of microbial degradation and bioremediation of organic contaminants has been conducted over the years by Martin Alexander and his colleagues at Cornell University.

### Organic Cations

As mentioned above, a large number of strategies are being examined as potential tools in protecting and remediating groundwater contamination. Research involves understanding of microscale chemical and biological processes, hydrological investigations and flow modeling, and engineering of operational technologies. John Westall from Oregon State University and I have conducted studies of organic cation adsorption on aquifer and subsurface materials. One major component of this research has been to examine the effects of organic cations on the adsorption and mobility of metals and nonpolar organic contaminants in subsurface environments. The driving force for this research was to examine, from a "microscale" chemical behavior perspective, the potential use of organic cations in remediation.

Large hydrophobic organic cations are positively charged chemicals. Due to favorable hydrophobic and electrostatic interactions, they are strongly adsorbed by negatively charged subsurface solids, with adsorption occurring primarily by cation exchange reactions. The presence of organic cations can have a number of effects on the mobility of chemical pollutants in subsurface environments: (i) they can effectively compete for adsorption sites with metal cations (e.g., copper, cadmium, and zinc), increasing the mobility of such metals in contaminated soils or aquifers; a displacement of metals in a pump and treat process with a nontoxic, biodegradable organic cation might be beneficial; (ii) adsorbed organic cations can dramatically increase the tendency of mineral surfaces to adsorb nonpolar organic contaminants (e.g., benzene, toluene, and TCE) that are otherwise sufficiently mobile that they have contaminated groundwater supplies; appli-

cation of organic cations in subsurface environments (e.g., clay liners) might be considered to retard diffusive or advective migration of contaminants from contaminated soils; and (iii) cationic surfactants at high concentrations form micellar phases that can act to solubilize organic pollutants and increase their mobility; surfactant flushing with a nontoxic, degradable surfactants might be useful in a pump and treat operation where organic contaminants are strongly adsorbed to mineral surfaces.

We have studied the effects that various concentrations of a large organic cation, dodecylpyridinium (DP), has on the distribution ratio ( $D_c$ ) of copper and a series of chlorinated benzenes. Batch adsorption experiments are used to measure distribution ratios and flow-through soil column experiments are run to study transport in porous media. Figure 1 shows that the concentration of copper adsorbed to the surface of Lula Aquifer Material is reduced in the presence of DP. This indicates that organic cations like DP would have the effect of facilitating transport of Cu from a contaminated site. Further work is being conducted to examine the effect of organic cation structure on adsorption of copper and other cationic metals.

The effect that DP has on adsorption of chlorinated benzenes is illustrated in Figure 2. Lula Aquifer Material is a low organic carbon sorbent and exhibits relatively weak binding behavior with nonpolar organic pollutants like the chlorobenzenes. Increased adsorption of DP on the surface makes the surface more hydrophobic and greatly increases the  $D_c$  of the chlorobenzenes. This increase in adsorption is reason-

ably well predicted by the amount of DP adsorbed and the hydrophobicity of the organic pollutant (e.g., its octanol-water partition coefficient). If an organic cation can be adsorbed to clay liner material that does not degrade or desorb readily, it would have the effect of greatly retarding diffusive migration of relatively soluble chemicals (e.g., benzene and toluene) through the low permeability barrier. The migration of such compounds through clay liners over decadal timescales is potentially a problem in that bentonite and other clays are not particularly strong adsorbents for nonpolar organic chemicals.

### Summary

A large number of remediation strategies for subsurface contamination and protection of groundwater are developing. Successful containment or clean up of subsurface contaminations with pump-and-treat technologies is difficult. Adequate site characterization is important, and complex chemical, geological and hydrologic processes which act to retard contaminant movement must be recognized and dealt with. As further research is conducted, the number of tools for addressing specific contamination problems will undoubtedly increase, but it is probably too early to predict how successful *in situ* methods will be in the fight to reclaim contaminated groundwaters for future use. Cost, and short and long term environmental risk assessment of various options should be factored into decisions regarding choice of remediation methods on a site by site basis.

*Dr. Bruce J. Brownawell is a chemist at the Waste Management Institute, Marine Sciences Research Center, State University of New York at Stony Brook.*

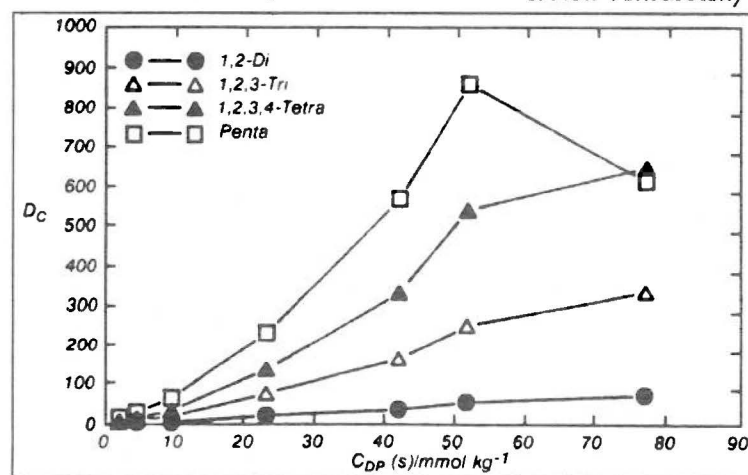


Figure 2. The effect of the amount of DP adsorbed to Lula Aquifer Material on the distribution ratio,  $D_c$  (mL/g)

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Guest Comment

# Law Mandates Waste Reduction

By John B. Daly

In 1978, New York State residents, as well as the rest of the nation, were shocked by the revelation that hazardous chemicals from an abandoned disposal site were seeping into the homes of the Love Canal area of the City of Niagara Falls. People soon realized that the Love Canal disaster was not an isolated incident, but the tip of an iceberg.

Over the last 12 years, the New York State Legislature has put into place an extensive array of hazardous waste regulatory programs that are designed to prevent future Love Canals. Despite the fact that these programs have been in place for well over a decade, the problems posed by the disposal of hazardous wastes continue to grow. In 1983, more than 800 suspected inactive hazardous waste sites had been identified in New York. By 1990, this number had grown to more than 1,200.

The advent of new waste management technologies, especially those being pursued by joint academic and industrial partnerships such as the New York State Center for Hazardous Waste Management, promise help in dealing effectively with the remediation of these inactive hazardous waste sites. In order to address the source of the problem, however, we must get back to basics and reduce the amount of waste that we as a society produce.

In 1987, legislation was passed that made reduction the state's highest priority when dealing with hazardous waste. This past session, the Legislature enacted and the Governor signed into law S.5276-B, demonstrating the state's commitment to the goal of waste reduction. This legislation and other programs being implemented by the Department of Environmental Conservation are anticipated to reduce by as much as 50 percent the amount of waste generated in New York over the next decade.

I introduced S.5276 in the Senate after the issue was studied in detail by the Joint Legislative Commission on Toxic Substances and Hazardous Wastes, which I chair. One of the first things shown by the commission's research was that many industries already take it upon themselves to begin waste reduction programs. The motivation is simple: they can have more efficient chemical processes and cut their costs for disposal. Many changes were basic housekeeping measures that also increased safety in the work place; others led to the development of improved products. But all of these changes were responsible for reducing the amount of hazardous wastes sent to landfills, incinerators, water treatment plants, and other current forms of hazardous waste treatment or disposal.

If some industries undertake these measures voluntarily, why not mandate that all large producers of hazardous waste be required to reduce waste? There was no reasonable excuse for any industry to resist these measures, especially if we could phase in a law so that the largest producers are brought into compliance first.

Over a five-year period, the amount of waste that must be generated to trigger the waste reduction requirements would be reduced from 1,000 tons per year to 25 tons per year. Additionally, industries would be required to evaluate waste reduction programs for individual waste streams if they constitute 90 percent of their total hazardous waste generation, or if they exceed 5 tons annually.

Under the provisions of the bill, hazardous waste generators will be required to certify to the Department of Environmental Conservation that they have a program in place to reduce the volume and toxicity of their waste streams. The plans must also certify that their waste management method minimized potential present and future threats to human health and the environment. Facilities that fail to meet the requirements of the law will be prohibited from generating hazardous waste in New York State.

If we produce less now, there will be less to manage in the future. Waste management has improved greatly in the past decade, but we are still in need of permanent solutions for hazardous waste. Waste reduction is a permanent solution.

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John B. Daly (R, Niagara Falls) represents the 61st District in the New York State Senate. He is chairman of the Joint Legislative Commission on Toxic Substances and Hazardous Wastes.



John B. Daly

## Back Cover

*Field test of surfactant flushing process for aquifer reclamation now underway at test site near Alliston, Ontario, uses process developed by Drs. John Fountain and Dennis Hodge, SUNY Buffalo Department of Geology, funded by the New York Center for Hazardous Waste Management. In photo, four extraction wells and several multi-level monitoring wells can be seen. Test is conducted in 3-by-3 meter cell constructed in 4m thick surficial aquifer by the University of Waterloo. Organic pollutants (tetrachloroethylene in test) are extracted from contaminated aquifer by injecting aqueous surfactant solution on one side of contaminated zone and extracting it on the other side.*

Waste Management  
Research  
**Report**

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