Groundwater Contamination in Latin America
Proceedings of a SCOPE/UNEP Workshop
San Jose, Costa Rica

Editors
Hugo A. Loaiciga
Christine Shoemaker
Michael Barcelona
Groundwater Contamination in Latin America

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July 26 to July 30, 1993
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From July 26 through July 30, 1993, ground water experts and practitioners met in San Jose, Costa Rica, to participate in the First International Workshop on Ground Water Pollution Problems in Latin America. This event was sponsored by the United Nations Environment Program (UNEP), by the Scientific Committee on Problems of the Environment (SCOPE), and by the Costa Rican Association on Water Resources. Primary funding for the workshop was provided by UNEP.

In 1987 SCOPE initiated an international project, co-chaired by C. Shoemaker and A Zehnder, to address scientific aspects of ground water contamination. Ground water pollution is a potentially serious problem throughout much of the world, but its importance has not been recognized in many countries. The purpose of the international SCOPE Project on Groundwater Contamination is to facilitate interaction among scientists to advance our knowledge of chemical, biological, and hydrologic processes important in preventing and removing ground water contamination. Workshops in this international project have also been held in U.S.A. (1989), Thailand (1992), Australia (1994), Czech Republic (1994), and China (1995).

The main objective of the Latin American Workshop was to synthesize scientific and technical knowledge on ground water pollution and its prevention, emphasizing problems and conditions peculiar to Latin America. The format of the Workshop consisted of a series of lectures presented by invited ground water experts to an audience of close to 100 ground water professionals from Latin America. Round tables and panel discussions were held throughout the workshop to exchange ideas, questions and answers, and delineate strategies for cooperation between all attendees to the event. Ground water experts represented a wide cross-section of countries: Canada, Chile, Costa Rica, France, Germany, Israel, Italy, Mexico, Spain, United Kingdom, United States, and Venezuela. Latin American ground water practitioners from Costa Rica, Chile, Colombia, Guatemala, Honduras, Mexico, Nicaragua, and Venezuela participated in the ground water workshop. State-of-the-art principles of ground water monitoring and remediation, theoretical aspects of ground water flow and contaminant migration analysis, and case studies focusing on Latin America's most pressing ground water contaminant problems were reviewed in San Jose.

The following eight papers are a representative sample of the scholarly work presented at the Workshop. The publication of this issue of *Ground Water and Remediation (GWMR)* containing proceedings of the San Jose Workshop represents the first such thematic issue focusing on regional ground water pollution problems. This gives the readership of *GWMR* a rare glimpse at ground water use and pollution problems typical in a large geographical area of the world comprising many countries linked by cultural, historical, and trade relationships. This publication was made possible by the foresight and entrepreneurial disposition of Dr. Michael Barcelona, editor of *GWMR* and one of the presenting experts at the workshop.

The financial support provided by the United Nations Environment Program was instrumental in organizing this workshop and is gratefully acknowledged. UNEP Program Officer Gerhart Schneider was an active and very welcome participant in the SCOPE workshops in Costa Rica, Czech Republic, and China. Oscar Jimenez and the Costa Rican Association on Water Resources (ACREH) were very helpful in making local arrangements and providing administrative assistance. This workshop was organized under the auspices of the Scientific Committee on Problems of the Environment, and without their organizational assistance the workshop never would have taken place.

Uptake of Dissolved and Oil Phase Organic Chemicals by Bacteria

by James R. Mihelcic, Annette Pritschow, and Donald R. Lueking

Introduction

Uncontrolled releases of hydrophobic organic chemicals (HOCs) to subsurface systems have resulted in environmental problems that are widespread throughout the world. Examples of these releases include leaking underground storage tanks, improper use of agricultural chemicals, and improper disposal of hazardous materials on land. Due to their cost effectiveness and potential for the complete elimination, or detoxification, of target pollutants, biological processes are receiving considerable attention for the treatment of contaminated subsurface systems. These processes can either occur naturally or be engineered. Engineered bioremediation can be conducted in situ and generally consists of procedures involving the application of nutrients and/or electron acceptors to the subsurface in an attempt to stimulate the growth of indigenous organisms capable of degrading the target pollutants.

Information on the presence of pollutant-degrading organisms in the environment suggests that many subsurface systems have the potential to support biodegradation of organic pollutants under the proper conditions (Song et al. 1990; Aelion and Bradley 1991). Soils may contain $10^5$ to $10^8$ viable bacterial cells per gram of dry soil and $10^5$ to $10^6$ fungi per gram of dry soil (Alexander 1977). Microorganisms have also been identified in ground water (Ghiorse and Wilson 1988), though at lower levels, and the majority of these organisms have been identi-
fied as gram-negative cells. For example, 60 to 90 percent of microbial isolates from ground water are typically gram negative (Chapelle 1993). Gram-positive organisms also occur in ground water, although to a more limited extent.

Although biological processes offer great potential for solving some environmental problems, the many complex biochemical mechanisms that influence the ultimate fate of many organic pollutants are still not well understood. This is complicated because, after discharge to the environment, organic chemicals will partition into gaseous, aqueous, oil, and solid phases. This phase partitioning can have a strong impact on the subsequent bacterial uptake of the organic chemical, which in turn influences its degradability. Accordingly, the objective of this manuscript is to provide information on how bacterial systems assimilate dissolved and separate-phase organic solutes prior to metabolism. It is hoped that this information will result in the design and operation of more efficient bioremediation systems.

Transport Through the Cell Envelope

Structure and Composition of the Bacterial Outer Envelope

Bacteria display variations in the structure, composition, and role of the cellular barriers that protect them from the environment. These barriers not only serve as physical barriers, but also determine the rate and route of substrate penetration into the interior of the cell. After penetration into the cell's interior, biochemical processes can transform a hazardous chemical into biomass and/or nontoxic substances. This penetration may or may not require an expenditure of cellular energy by the organism, and the mechanism of penetration appears to be different for hydrophilic and hydrophobic chemicals. Therefore, this section will provide a general description of the envelope structure of bacteria, the four known transport mechanisms for cellular uptake of substrates, and a discussion of how hydrophobic compounds are believed to enter bacterial cells.

Bacteria are generally classified as either gram positive or gram negative based upon their response to the differential Gram staining procedure. The differential nature of the Gram stain reflects significant structural differences in the cellular bounding layers possessed by gram-positive and gram-negative organisms. The cytoplasm of all bacterial cells is delimited by a structure termed the cytoplasmic membrane. This typical unit membrane is comprised of phospholipids arranged in a bilayer configuration and contains a variety of proteins that function in substrate transport, energy production, DNA replication, biosynthetic processes, and cellular excretion. Immediately apposed to the cytoplasmic membrane is a netlike polymer of N-acetylglucosamine and N-acetylmuramic acid subunits termed either the cell wall, murine sacculus, or peptidoglycan layer. This structure determines the shape of both gram-positive and gram-negative cells and also provides limited tolerance to fluctuations in osmotic pressure. The cell wall of gram-positive cells is the final bounding layer of the cell and is distinguished by being thick (30 to 40 nm) and containing distinctive components such as teichoic acids. The peptidoglycan layer of gram-negative cells is much thinner (2 to 4 nm), not as rigid, and devoid of teichoic acids.

In addition to the cytoplasmic membrane and peptidoglycan layer, gram-negative cells possess an additional bounding layer referred to as the outer membrane. This and other important features of the cell envelope in gram-negative bacteria are shown in Figure 1. Like the cytoplasmic membrane, this structure contains proteins and phospholipids; however, the lipopolysaccharides are the dominant distinctive component of the outer membrane. The lipopolysaccharides, or LPS components, of the outer membrane (discussed later) are exclusively localized in the outer leaflet of the outer membrane and, in association with phospholipids, produce a compositionally asymmetric bilayer-type structure containing membrane-spanning proteins. The integrity of the outer membrane is maintained, to a large extent, by the covalent attachment of an outer membrane lipoprotein component to the peptidoglycan layer. The outer membrane constitutes 80 percent of the dry weight of the gram-negative cellular envelope, while the peptidoglycan layer contributes around 10 percent (Schlegel 1992). Reviews on the structure of the gram-negative outer membrane have appeared elsewhere (Nikaido and Vaara 1985; Hancock 1991). Importantly, in contrast to gram-positive cells where the cytoplasmic membrane provides the only substantial barrier to the entry of environmental chemicals, the penetration of the outer membrane of gram-negative organisms is thought to be rate limiting for the transport of most nutrients and presents a formidable barrier to the uptake of hydrophobic compounds.

Finally, the structure of the gram-negative envelope also serves to delimit another important region of the gram-negative cell: the periplasmic space. This region, which encompasses the area between the inner leaflet

Figure 1. Important features of a gram-negative bacterial cell envelope. Adapted with permission Hancock (1991).
of the outer membrane and the outer leaflet of the inner cytoplasmic membrane, may constitute as much as 10 percent of the volume of the cell and possesses a variety of hydrolytic enzymes and binding proteins that participate in transport and other processes (Beveridge 1995).

Review of Basic Procaryotic Transport Mechanisms

Transport of chemicals into the interior of a bacterial cell may occur via passive or facilitated diffusion (transport) mechanisms, or the transport may be energy linked (Gottschalk 1986; Voet and Voet 1990). Nonmediated transport (i.e., simple diffusion not involving specific proteins) transports molecules from an area of high concentration to an area of lower concentration according to Fick’s Law of Diffusion. Cellular entry by passive diffusion is limited to a small group of substances, including water, oxygen, carbon dioxide, and possibly some hydrophobic compounds. Like passive diffusion, facilitated transport mechanisms derive their energy from a concentration gradient of the transported substrate; however, in this instance, a specific protein is involved in facilitating the arrival of the substrate at equilibrium across the cytoplasmic membrane. Neither passive diffusion nor facilitated transport require an additional source of metabolic energy. During facilitated transport, substrate molecules bind to transmembrane transport proteins at high substrate concentrations and then pass through the membrane to the lower concentration region in the cytoplasm, where the substrate dissociates from the protein. The transmembrane protein may be solute specific or it may display various degrees of substrate specificity. These diffusional mechanisms do not result in intracellular substrate concentrations higher than those that occur in the environment. Facilitated diffusion is common among multicellular organisms but rare in bacteria.

Energy-linked substrate transport (i.e., active transport and group translocation) uses metabolic energy to transport molecules against a concentration gradient and is typically substrate specific. Thus, energy-linked transport allows cells to thrive at the low nutrient conditions common in nature. The process of active transport does not chemically alter the substance being transported, while group translocation results in the chemical transformation (i.e., phosphorylation) of the substrate as the substrate enters the cell. In most bacteria, the energy source for active transport is the proton motive force, the combination of proton and electrical chemical gradients established across the cytoplasmic membrane as a result of respiratory and photosynthetic electron transport and other energy-linked processes (Haddock and Jones 1977). In this regard, the best described bacterial active transport system is the mechanism used by cells of Escherichia coli for the transport of lactose (Kaback 1989; Kaback et al. 1990).

The model system for cellular transport by group translocation is the phosphoenolpyruvate:glucose phosphotransferase system that has been extensively described for cells of E. coli (Meadow et al. 1990). This system is responsible for the transport of glucose and a variety of other sugars with the immediate energy source being the high-energy phosphorylated intermediate, phosphoenolpyruvate. However, since the sugar is phosphorylated, and thus chemically transformed as it enters the cell, transport against a concentration gradient does not occur and, technically, accumulation of the transported intermediate is not observed. This highly complex system is extremely efficient and allows bacterial cells to maintain maximum rates of growth in the face of dilute (μM) concentrations of sugars.

Transport of Hydrophobic Chemicals into the Cell Interior

Because the structure and properties of the gram-negative outer membrane have been extensively examined, and because gram-negative organisms constitute the majority of the organisms present in the subsurface, the following discussion will focus on these organisms. In addition, as mentioned previously, the cell wall of gram-positive organisms provides little selectivity in the initial contact with environmental substrates.

Figure 1 provides a detailed schematic of the gram-negative outer membrane. The outer membrane has an inner layer, comprised mainly of phospholipids and embedded proteins, and an outer layer of mostly lipopolysaccharide (LPS). The membrane is best visualized as a group of many types of proteins embedded in a phospholipid bilayer. For example, there are at least six major and 50 minor proteins in a gram-negative outer membrane. A phospholipid has a hydrophobic tail and a hydrophilic head. Surrounded by water, phospholipids form a lipid bilayer with the hydrophobic tails pointing inward and the hydrophilic head pointing outward. The lipid bilayer protects as a tight barrier, while the embedded proteins bind substrates for transport into the cell or serve to bond the outer membrane of the inner peptidoglycan layer.

The LPS consists of lipid A, rough core, and O-antigen regions. As shown in Figure 1, the lipid A region is embedded in the phospholipid layer, and the rough core is bound to the lipid A. Important to the ultimate fate of hydrophobic chemicals is the O-antigen units. These O-antigen units protrude into the external medium and are very hydrophilic, thus repelling hydrophobic compounds. Furthermore, the LPS has a significant excluding tendency due to strong attraction of neighboring LPS molecules and by cross bridging with divalent cations (e.g., magnesium).

The importance of LPS in excluding hydrophobic chemicals has been demonstrated numerous times. This may explain the low permeability of gram-negative membranes to hydrophobic antibiotics, dyes, and detergents. Further evidence of the importance of LPS in acting as a barrier to hydrophobic chemicals are experiments that destabilize the LPS region of the outer membrane. Disrupting the LPS or destabilizing the outer membrane with membrane-disorganization agents like EDTA can increase solute uptake as well. For example, it has been shown in P. aeruginosa that an increase in uptake of the hydrophobic fluorophor N-phenylnaphtyl-
amine occurs with an increase in EDTA concentration. The LPS also serves to provide resistance to enzyme attack from the external medium. The outer membrane is resistant to the movement of hydrophobic chemicals into the hydrophobic region of the outer membrane due to the tight bridging of the LPS layer and the outer leaflet, which lacks phospholipid. However, very hydrophobic chemicals may partition into the outer membrane because the driving force of a hydrophobic chemical to partition into the hydrophobic region will overcome the resistance of the LPS layer.

The permeability of gram-negative organisms is different as well. For example, the permeability of *P. aeruginosa* has been found to be ten- to hundredfold lower in magnitude than *E. coli* (Nikaido and Hancock 1986). This is perhaps due to different composition of the outer membrane. Transport of molecules across this selective membrane is thought to occur through porin and non-porin paths (Nikaido and Saier 1992). Porins are proteins spanning the outer membrane of gram-negative cells that provide a pathway for diffusion. It has been estimated that transport through porins is slower than through the membrane because porins make up a much smaller percentage of the total surface area in bacteria (Koch and Wang 1982). One type of porin forms nonselective water-filled channels through which hydrophilic molecules of a certain size range can readily diffuse. Thus, the porin's size is one factor that determines its selectivity. Specific porins have a specific affinity for substrate and selectively allow facilitated transport of that substrate through the porin. The penetration rate for this process will typically be faster than in the nonspecific porin. No hydrophobic porins have been identified to date that suggest they are used for hydrophilic compound transport only. Lastly, not all porins in biological cells are similar. For example, *P. fluorescens*, *P. putida*, and *P. stutzeri* are sensitive to some antibiotics, while *P. aeruginosa* is not. This suggests that their porins may be more active in the transport of some compounds than *P. aeruginosa*.

Most biological membranes allow diffusion of small hydrophobic molecules to some degree. Diffusion rates are fastest with smaller molecules. The steps for solute uptake in a gram-negative organism are thought to be dissolution in the hydrophobic interior of the membrane, diffusion through the hydrocarbon layer, and then partitioning to the other side of the membrane in the periplasmic space. The molecule will continue to partition into the cytoplasmic membrane where it finally becomes available for catabolism. For hydrophobic molecules, the membrane's low permeability may be due to the tightly bridged LPS (Nikaido and Vaara 1985). However, in deep, rough mutants, the surface of the outer membrane contains more phospholipid and LPS with very short saccharide chains (the protruding hydrophilic region of LPS). In this case, penetration is believed to be increased through either the increased phospholipid domains or LPS domains that are now more permeable due to an alteration in their structure (less compact cross bridging). No studies to our knowledge have focused on identifying the role deep, rough mutants play in uptake and degradation of HOCs.

Because the rate of diffusion of a solute initially entering into the outer membrane through diffusion is dependent on the solute concentration in the aqueous phase, it is reasonable to assume that the rate of cellular transport of pollutants with low water solubilities may limit the rate and/or the extent of pollution degradation. In fact, this may be one reason that biological processes are believed to be less effective in removing low concentrations of chemicals.

Alternatively, a protein-mediated active transport system used in the transport of hydrophobic chemicals would potentially allow an organism to degrade a solute to much lower levels than proposed by diffusion. From the microorganism's standpoint, it seems plausible that the evolution of a catabolic pathway that uses a carbon source with limited water solubility would include a mechanism to ensure a growth-sustaining level of the pollutant within the microorganism. This type of system may explain how cellular growth and metabolism are possible with the low aqueous concentrations encountered in the environment. Unfortunately, little evidence is available about the existence of these systems for uptake of hydrophobic environmental pollutants.

Our laboratories have recently completed a study supporting the existence of an active transport system for naphthalene assimilation of a *P. fluorescens* isolate (Whitman 1994). This system is energy linked and is competitively inhibited by structural analogs similar to naphthalene. This suggests the system is a protein-mediated active transport system. These results are significant because a few previous studies that have addressed this topic suggest that a simple diffusion process is responsible for the transport of organic pollutants into bacteria (e.g., Bateman et al. 1986).

It is important to identify the potential existence of an active transport system for a hydrophobic organic solute because a diffusional transport mechanism for hydrophobic compounds across the cellular membranes would be expected to be limited by the low aqueous concentration of these compounds in the environment. Furthermore, if microorganisms that have active transport systems for hydrophobic organic pollutants could be selected for bioremediating a contaminated site, the rate and/or extent of biodegradation may be enhanced. Further research is required to see if other microorganisms may have active transport systems for hydrophobic compounds and to see how these transport systems may affect biodegradation of environmental pollutants.

### Uptake of Oil Phase Pollutants

The extent of biodegradation of hydrophobic pollutants can be limited because sorbed phase and separate phase pollutants may not be bioavailable. This manuscript does not address the role that solid surfaces play in biodegradation because that topic has been discussed elsewhere (Mihelcic et al. 1993). In addition, the influence of synthetic surfactants on biodegradation is reviewed elsewhere (Mihelcic et al. 1995; Liu et al. 1995).
Microorganisms live in aqueous phase environments and are not able to live in the oil phase (Gottschalk 1986). Furthermore, the outer cell wall of gram-negative organisms is hydrophilic, which limits a microbe's ability to contact with a hydrophobic oil phase. This lack of contact makes degradation difficult because the enzymes responsible for degradation are typically located within the cytoplasmic membrane. Thus, specific uptake mechanisms of oil compounds are necessary if bacterial systems are to degrade oil phase contaminants. Three different mechanisms have been postulated: (1) uptake of monodispersed dissolved oil compounds; (2) contact with fine oil droplets (pseudosolubilized organic chemical); and (3) contact with large oil droplets (Haferburg et al. 1986; Hommel 1990).

Various microorganisms have developed the ability to overcome some of these difficulties by synthesizing surface active agents (i.e., biosurfactants). This process allows uptake and utilization of the hydrophobic compounds (for reviews refer to Haferburg et al. 1986 and Hommel 1990). Generally, surfactants are amphiphilic molecules (i.e., they have a hydrophilic and a hydrophobic moiety). They aggregate in micelles or at interfaces between two phases. Therefore, they can emulsify, disperse, and/or solubilize hydrophobic compounds. This leads to an increased surface area between the aqueous and the oil phases. Surfactants also decrease surface tension of aqueous environments and the interfacial tension of oil-water environments. At increasing concentrations of surfactant, interfacial or surface tension decreases rapidly until a certain surfactant concentration is reached. Above that concentration, termed the critical micelle concentration (CMC), the further decrease is very small. This is when interfaces have become saturated with surfactant, and additional surfactant appears as micelles in the bulk phase. The concentration of surfactant produced by bacteria has been reported to be greater than the CMC (Haferburg et al. 1986), which is important because CMC levels of surfactants are believed to be required in order to solubilize HOCs. Furthermore, in the subsurface surfactant, adsorption to soil may decrease the apparent surfactant concentration.

The hydrophobic portion of a biosurfactant is usually the hydrocarbon tail of one or more saturated/unsaturated, hydroxylated, and/or branched fatty acids. Biosurfactants can be grouped into five classes according to the hydrophilic moiety (Hamml 1990; Stache and Kosswig 1990): (1) neutral lipids such as alcohols and glycerols; (2) fatty acids; (3) glycolipids including trehalose-lipids from Arthrobacter, Corynebacteria, Rhodococcus, rhamnolipids from Pseudomonas species, and sophorolipids from Candida species DSM 2874 (Syladt et al. 1985) and sophorolipids produced by Rhodococcus et al. 1982). The second strategy (Figure 2b) is that extracellular surfactants can be excreted into the environment. These mostly anionic surfactants emulsify or disperse the oil phase. Examples of extracellular surfactants are rhamnolipids produced by Pseudomonas species DSM 2874 (Syladt et al. 1985) and sophorolipids produced by several species of Candida yeasts (Jones 1967).

In several publications (Cooper and Zajic 1980; Syladt and Wagner 1987), the presence of extracellular or cellbound surface active compounds was regarded as a prerequisite for initial oil-microbe contact. Various reports discuss the isolation of biosurfactants among oil-degrading microorganisms (Passeri et al. 1991; Schulz et al. 1991) or the formation of biosurfactants during growth on hydrocarbons (Hommel et al. 1987; Powalla et al. 1989; Koch et al. 1991). In some cases, it has been proven that surfactant production is a prerequisite for growth on hydrocarbons. For example, Koch et al. (1991) isolated P. aeruginosa mutants that were unable to produce rhamnolipid and did not grow on medium-containing hydrocarbons. Hydrocarbon utilization could only be restored by adding trace amounts of purified rhamnolipids. There are also reports on the addition of purified biosurfactants that promote growth of microorganisms on hydrocarbons (Zhang and Miller 1994).

Examples of anionic surfactants are rhamnolipids, acidic sophorolipids, and surfactin. Lactonic sophorolipid is known to be nonionic.

Figure 2 shows the two mechanisms by which biosurfactants are believed to assist microorganisms with the uptake of an oil phase. The first strategy (Figure 2a) is for an organism to produce cell-bound surfactants, which are mostly nonionic and have structures similar to existing cell wall compounds. They render the hydrophilic charged cell envelope hydrophobic and therefore facilitate contact with large oil droplets, an action which allows subsequent penetration of a solute through the cell wall. An example is trehalose mycolates produced by Rhodococcus (Kretschmer et al. 1982). The second strategy (Figure 2b) is that extracellular surfactants can be excreted into the environment. These mostly anionic surfactants emulsify or disperse the oil phase. Examples of extracellular surfactants are rhamnolipids produced by Pseudomonas species DSM 2874 (Syladt et al. 1985) and sophorolipids produced by several species of Candida yeasts (Jones 1967).
However, not all microorganisms that degrade organic pollutants in the subsurface, an individual should understand the composition of a bacterial cell envelope and how it influences the uptake of hydrophobic substrates into the cell prior to metabolism. The hydrophilic nature of gram-negative cell outer membranes and tight packing of the LPS in the membrane can act as a barrier for the penetration of hydrophobic molecules in the cell. Some microorganisms have developed methods to overcome these problems. One method is production of biosurfactants. Biosurfactants can be produced that either facilitate cell-oil droplet contact or solubilize the oil phase so that it can then be transported into the cell. Though system specific, it appears that a hydrophobic organic chemical that has partitioned to other phases besides the aqueous phase (e.g., oil, solid) may not be bioavailable. Accordingly, engineers and scientists must consider these items if they are to provide efficient remediation of hydrophobic contaminants in the subsurface.

Conclusions

In order to understand the biodegradation of organic pollutants in the subsurface, an individual should understand the composition of a bacterial cell envelope and how it influences the uptake of hydrophobic substrates into the cell prior to metabolism. The hydrophilic nature of gram-negative cell outer membranes and tight packing of the LPS in the membrane can act as a barrier for the penetration of hydrophobic molecules in the cell. Some microorganisms have developed methods to overcome these problems. One method is production of biosurfactants. Biosurfactants can be produced that either facilitate cell-oil droplet contact or solubilize the oil phase so that it can then be transported into the cell. Though system specific, it appears that a hydrophobic organic chemical that has partitioned to other phases besides the aqueous phase (e.g., oil, solid) may not be bioavailable. Accordingly, engineers and scientists must consider these items if they are to provide efficient remediation of hydrophobic contaminants in the subsurface.

References


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Biographical Sketches

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Annette Prirschow is now employed as an International Standards Organization coordinator for a German food company (Ziegelhofstrasse 105B D-26121 Oldenburg, Germany). She holds a diploma degree in technical biology from the University of Stuttgart, where she specialized in biochemical engineering. She conducted her research on biosurfactants and wrote her diploma thesis while an exchange student with the Department of Civil and Environmental Engineering, Michigan Technological University.

Donald R. Lueking is an associate professor of biological sciences at Michigan Technological University (Department of Biological Sciences, Michigan Technological University, Houghton, MI 49931). He received his B.S. and Ph.D. degrees from Indiana University, Bloomington, Indiana, in the areas of microbiology and microbial biochemistry. He was an NIH postdoctoral fellow at the University of Pennsylvania and has held postdoctoral and/or faculty positions at the University of Illinois and Texas A&M University. His teaching and research interests are in the areas of biochemistry, environmental biochemistry, microbial physiology and biochemistry, bioremediation, bioleaching, and the purification and characterization of metal binding proteins.
Abstract

This paper presents results from a preliminary sampling strategy developed to track agricultural contaminants found in surface and subsurface media and used commonly in rice paddy cultivation in the dry, tropical forest coastal region of Guanacaste, Costa Rica. The emphasis is on the impact of eight indicator pesticides, five forms of nitrogen and phosphorus that are common nutrients found in fertilizers. After the field sampling strategy was developed, soil and water samples were collected twice: once during the beginning of the wet season and once during the initiation of the dry season. Hydrological parameters, soil classifications, agricultural product toxicology, irrigation and drainage networks, cultivated areas, land ownership, and pristine environments have been studied, mapped, and entered into a database in order to understand the spatial and temporal distribution of potential contaminants and their pending ecological degradation.

Alternative crops and agricultural practices are suggested to reduce or eliminate impacts on biological preserves. Database development and basin characteristics have been entered into a Geographic Information System (GIS) that is capable of fully integrating suggested site modeling. Field sampling results indicate that proposed rice paddy cultivation in a relatively undisturbed basin is likely to have minimal impact on downstream biological preserves.

Introduction

The large delta region of the Tempisque and Bebedero Rivers in the northwestern province of Guanacaste, Costa Rica, contains favorable soils and growing conditions for the cultivation of rice. A continuous and reliable water supply to support irrigation of this crop is lacking in this tropical latitude (10° N. 84° W; see Figure 1), characterized by a strong dry (December-April) and wet (May-November) seasonal, cyclic climatic pattern. The Costa Rican agency responsible for irrigation projects, the National Ground Water Irrigation and Drainage Services (SENARA), has submitted a proposal to the International Development Bank to construct an irrigation canal that will bring more than 25 m³/s of water from a Caribbean watershed across the central Cordillera by conduit and open canal to the region under study. The assessment of the construction of the irrigation canal, referred to as the Western Canal, is complete. This interbasin water transfer across the continental divide is part of Costa Rica’s largest irrigation undertaking to this date and is known as the Arenal-Tempisque Irrigation Project (Suarez et al. 1986). What follows is an analysis of the possible impact from the proposed development of 5163 hectares (1 hectare = 2.47 acres) located at Tamarindo Ranch, a province of Guanacaste, Costa Rica, which lie in the micro drainage of La Quebrada La Mula (La Mula Creek). SENARA hopes to develop the said area into rice paddies that would naturally discharge directly into the downstream
Palo Verde National Park, known for its wetland ecosystems and abundant waterfowl (Janzen 1983; Boza 1988). Major questions addressed by the study are (1) Can the development be done without negatively influencing the preserved lands of the Palo Verde National Park; and (2) If not, What would the likely impacts and possible alternatives be?

The evaluation of potential agrochemical contamination of these wetland ecosystems from the effluents of rice paddies requires a careful and comprehensive field sampling strategy for agrochemical concentrations in soils and effluent waters. Given the cyclical nature of pesticide and fertilizer application, it is difficult to acquire conclusive data through field sampling alone because contaminant peaks can be short and sporadic. By the construction of a Geographic Information System Database (ARC/INFO) (ESRI 1991), data generated by both field measurement and models can be archived, analyzed, and graphically displayed for high-quality output (Leipnik et al. 1993; Leipnik 1995). Field sampling was the primary focus of this study, but many of the input parameters for water quality modeling are provided and can be used with models of multiple component migration in future research efforts.

**Water Quality Contamination Potential and Site Geology**

**Potential Migration Paths**

The study area is situated just north and upslope from Palo Verde National Park and preserved wetland habitats in the northwestern region of Costa Rica (see Figure 1 for general location). The basin under study, La Quebrada La Mula, was an old cattle ranch that was once deforested for grazing but has lain fallow for many years, enabling second-growth forest to establish. If developed into rice paddies, the flat, central area of the basin will be terraced, making possible agricultural chemical migration from the paddies to the ecologically sensitive lagoons of the Park lands. The natural drainage of the La Quebrada La Mula Basin discharges stream effluent at the lower point in the region, El Bocano La Mula, a small ephemeral lake just inside the northern national park boundary. Once the lake has filled, water will overflow into the lower regions of the Tempisque River delta, the predominant regional hydrographic and fluvial feature. The receiving delta is parched with numerous perennial lagoons of various sizes. Estuarial marshlands also abound therein. This series of steps — namely, (i) effluent discharge from rice paddies, (ii) lake overflow, and (iii) fluvial transport through water bodies in the delta region — poses a potential contamination pathway to the wetland ecosystems.

**Regional Geology**

The geology of the study region is dominated by fluvial deposits throughout the upper reaches of the delta and marshy mangrove swamps near the river margins within 25 km of the confluence of the Bebedero and Tempisque Rivers and the Gulf of Nicoya, Pacific Ocean. The depositional basin of the Tempisque Depression is bordered to the north by the Bagaces Formation, described as fluvial and sedimentary deposits interwoven with columnar basalt lava flows, and denotes the beginning of the volcanic pediment of the Central Cordillera of Costa Rica (Dengo 1962). The depositional basin is bordered on the south by the Liberia Formation, a fluvio-lacustrine deposit with some interbedding of granular rhyolite and pumice. Abrupt limestone buttes composed of reef deposits of homogeneous texture, the Barra Honda and Brita Formations, bisect the delta plain and provide for a natural break between the preserved and agricultural lands, through a conspicuous drop in topographic elevation in the area. The Brita Formation is distinguished by fine-textured and well-stratified volcanic lenses appearing within the limestone (Bergoeing 1983).

Exact cross sections of the study area do not exist, and well logs for the area are rare. Hence, site-specific information was difficult to gather. Table 1 presents hydrogeologic data and was generated from geologic reviews, scattered well logs (compiled by SENARA 1976-1986; 1989), and well data presented in the master

---

**Table 1**

<table>
<thead>
<tr>
<th>Formation Name</th>
<th>Aquifer Thickness (m)</th>
<th>Transmissivity (m²/day)</th>
<th>Water Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alluvium</td>
<td>60</td>
<td>60-320</td>
<td>Good to Mediocre</td>
</tr>
<tr>
<td>Liberia</td>
<td>100</td>
<td>10</td>
<td>Low pH and low TDS</td>
</tr>
<tr>
<td>Bagaces</td>
<td>350</td>
<td>77</td>
<td>Excellent</td>
</tr>
<tr>
<td>Brita</td>
<td>600</td>
<td>No data</td>
<td>Limited Data</td>
</tr>
<tr>
<td>Barra Honda</td>
<td>300</td>
<td>No data</td>
<td>Limited Data</td>
</tr>
<tr>
<td>Nicoya Complex</td>
<td>No data</td>
<td>66</td>
<td>Good</td>
</tr>
</tbody>
</table>

TDS: Total Dissolved Solids.
plan (Bel Ingenieria and Bookman-Edmonston Engineering Inc. 1978) for the entire Arenal-Tempisque Irrigation Project, of which the study area is a part. In spite of inherent limitations, the data in Table 1 is valuable for understanding the general hydrogeology of the study area.

Major water bearing formations are shown in Table 1, including transmissivity, flow capacity, stratigraphy, and water quality generalized indicators. From well logs collected by SENARA (1989) and field observations, these aquifers are, for the most part, not affected by near-surface events such as agriculture and irrigation infiltration and are primarily recharged along basin margins where outcropping occurs. Aquifer vulnerability from vertical contaminant migration is strongly impaired by the thick, impermeable clay lenses of the surficial alluvium that are prevalent in the depositional basin of the desired agricultural area.

Basin Soil Characteristics

Particle Size Distribution

Basin soil hydrologic parameters were established by sampling along five transects, each perpendicular to the stream course and equally spaced throughout the basin, as shown in Figure 2. Particle size distribution analyses for soils from the study area were carried out by hydrometer (Gee and Bauder 1986; Klute 1986), based on Stoke's Law (see, e.g., Hillel 1982). Samples were extracted from each apparent soil horizon at three separate soil pits dug along each transect shown in Figure 2. Results showed an average of 16 percent sand, 26 percent silt, and 55 percent clay for the A horizon; 10 percent sand, 27 percent silt, and 61 percent clay for the B horizon; and 14 percent sand, 15 percent silt, and 71 percent clay for the C horizon. PH was near 7 in the upper horizons and slightly alkaline at depth. Mean horizon temperatures did not vary over 2°C from the surface horizons at mean 30°C to 28°C at depth measured during daylight hours. The mean biotemperature in this life zone, classified as dry tropical forest, according to Holdridge (1967), is approximately 25°C. Mean annual rainfall is close to 1200 mm/yr (Hartshorn 1983).

Soil Classification

Soil pits were dug out along the transects, shown in Figure 2, one per transect, to a depth of approximately 1 meter. Soil samples were taken for each apparent soil horizon. The soils were classified according to the U.S. Department of Agriculture (USDA) soil classification scheme (see, e.g., Brady 1990). Of the 11 soil orders described in the classification, undoubtedly these soils are vertisols (Dudal and Eswaram 1988). Field observations and laboratory analyses revealed that they have minimal to no B horizon, are average in carbon content, have a particle size distribution high in clays, and have a massive structure with low hydraulic conductivity, stable temperature regime, and typical geographical location and pedon color. Working through the various characteristics and descriptions in the USDA's soil taxonomy led to a classification of these soils as type pellusters: fine, mixed, and isohypothermic.

Bulk Density

Bulk density of soil samples, shown in Table 2 by soil horizon, was calculated through field testing using a 100 mL-sample coring device that extracted soil samples without disrupting in situ conditions. The samples were run through a Daiki DIK-1120 Three-Phase Meter (Daiki Rika Kogyo Co. 1990) to test for bulk density, i.e., grams of the extracted soil over the in situ (bulk) volume. The field results, shown in Table 2, had standard deviations on the order of ±10 percent of mean values. There appeared to be a general trend

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Transect I</th>
<th>Transect III</th>
<th>Transect IV</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.42</td>
<td>1.26</td>
<td>1.19</td>
<td>1.29</td>
<td>0.13</td>
</tr>
<tr>
<td>B</td>
<td>1.64</td>
<td>1.35</td>
<td>1.34</td>
<td>1.44</td>
<td>0.22</td>
</tr>
<tr>
<td>C</td>
<td>1.59</td>
<td>1.41</td>
<td>1.10</td>
<td>1.37</td>
<td>0.18</td>
</tr>
</tbody>
</table>

See figure 2 for location of transects I, III, and IV.
of increasing bulk density with increasing depth for all sites sampled. Prior to the field tests, Vazquez (1972) had reported mean bulk densities of 1.27 gr/cc, 1.22 gr/cc, and 1.18 gr/cc for the horizons A, B, and C, respectively, from soil pits dug out some 50 km to the northwest of the study area, but still in the Tempisque River flood plain. The differences between those prior values and the values presented in Table 2 are attributed to soil differentiation over such distance.

Infiltration

Infiltration was studied along the central longitudinal axis of the basin to assist in the characterization of the basin soils and vadose zone properties. However, the focus of this project was off-site environmental degradation. For this reason, infiltration and hydraulic conductivity were studied more intensely toward the end of the drainage basin along transect IV (see Figure 2), where contaminants are likely to be released. Infiltration was measured using a double-ring infiltrometer (Burgy and Luthin 1956; Bouwer 1986), and the results for dry and wet season testing are as shown in Table 3. Because of the length of each test, man-hours needed, and other logistical and seasonal difficulties associated with infiltrometer measurements of infiltration rates, it was possible to acquire only part of the desired data according to the overall sampling design. The latter consisted of preplanned field measurements at three sites evenly distributed along the transects shown in Figure 2. The infiltrometer measurements were attempted, but either flooded conditions or large macropore cracks made the test impossible at various of the preplanned measuring sites. The successful measurements, however, indicated that infiltration rates decreased with topography toward the center of the basin and downstream along its central longitudinal axis toward the Palo Verde biological preserve. The lowest measured values were found to be 0.1 cm/hr and 1.6 cm/hr for the wet and dry seasons, respectively (see Table 3).

Hydraulic Conductivity

Hydraulic conductivity (K) measurements were conducted in two different ways. The first was done in situ, using an Eijkelkamp Hydraulic Conductivity Test Kit. The reverse Hooghoudt Method was applied, as field measurements were conducted under unsaturated conditions. Because large soil cracks were widely found in the area, it was felt that there was high probability for error in the upper soil horizons, as the water placed in the auger hole rapidly traveled laterally in the cracked soil zone and substantially slowed down in the non-cracked zone below. The in situ measurements of hydraulic conductivity indeed turned out to be too high, as shown in Table 4. To avoid the effects of cracks on conductivity under unsaturated conditions (and remembering that soil under rice paddies is flooded and saturated), soil samples for different horizons along transects IV and V were taken and flown back to the Vadose Zone Monitoring Laboratory (VZML) of the University of California at Santa Barbara (UCSB). There soils were dried, ground, and repacked to field-measured bulk densities to best simulate in situ conditions. Laboratory values of hydraulic conductivity of the repacked samples for all three horizons were then measured with constant head permeameters (Klute and Dirksen 1986); mean values are reported in Table 5. These latter estimates of K appear to be more consistent with field hydraulic characteristics of soils under saturated conditions.

Summary of Basin Hydrogeologic Characteristics

Clay content increased with depth farther downslope in the Quebrada La Mula Basin, toward the Palo Verde National Park, and toward its center. This is naturally
occurring condition propitious for rice paddy water retention and for holding migratory contaminants onsite. The high clay percentage throughout the basin should produce slow migration of surface waters into the substrata and aquifers below. Low infiltration rates supported this conclusion, as contaminant migration into underlying aquifers would be negligible. The potential for aquifer vulnerability to surficial contamination in Quebrada La Mula Basin appears quite low when the soil is saturated.

Low hydraulic conductivity values indicated low ground water propensity to surficial contamination given the slow movement of any contaminant plume. Ground water vulnerability appears to be an issue only in localized areas where clay aquitards may not be present. Macropores from soil cracks, characteristics of vertisols, could enable rapid movement of surface contaminants both vertically and horizontally through the soil profile when the soils are not saturated. If agricultural practices were modified to restrict agrochemical applications to rice paddies only after the fields have been flooded, the chance of rapid migration via macropores would be reduced or eliminated. If this idea were to be put into practice, analytical sampling could be limited to surface water and surface soils only.

Rice Paddy Cultivation

The majority of rice grown in the province of Guanacaste, Costa Rica, is in flooded fields or paddies. In contrast, there is some upland rice grown on the flanks of the Central Cordillera, but the amount of acreage is insignificant in comparison. The species of rice cultivated in paddies is *oryza sativa communis*, a medium-to long-grained white rice. The varieties most popular in Costa Rica are CR-1821, CR-5772, and CR-113, with the former being the most common (Sanabria 1988). These are hybrid varieties developed for Costa Rica. Other specialty varieties are grown, although their acreage is relatively small in comparison.

There are two cropping cycles per year. The dry and wet season cropping periods run from January to May and from July to November, respectively, given fluctuations in the climate cycle. Periods in between are used for field preparations and machinery repairs. The interval from planting to harvest ranges from 110 to 140 days, depending on the rice variety and the amount of sunlight (Monge 1989). Yields of rice range from 3 to 4 tons per hectare for the wet season and 5 to 6 tons per hectare for the dry season (Sanabria 1991). On average, the dry season yields are quite high, indicating favorable growing conditions in Guanacaste and relatively high use of fertilizers (Yagi 1993).

Throughout the Arenal/Temisque Irrigation Project of Guanacaste there are hundreds of agrochemicals used for various crops at varying frequency. The following discussion focuses on the pesticides, herbicides, and fertilizers used in rice paddy cultivation, specifically in the area with the closest proximity to the microbasin La Quebrada La Mula and to three other basins cultivated with rice that were included in this study for comparative purposes. General agrochemical application amounts will set the background information for the ensuing sections on pesticide and nutrient characteristics. Agrochemical application exhibits a high variability from season to season and from farm to farm. The ensuing information was compiled from farm records kept at nearby Rancho Pelón de la Bajura (Loaiciga 1990) and from the rice paddy irrigation project managed by SENARA at the location of Bagatzi, adjacent to the study site (Ajun 1991).

Dry to wet seasonal variations in agrochemical application rates used for rice paddy cultivation are pronounced. During the summer or dry season crop, there are fewer incidents of plagues and blights. Therefore, fewer applications of fungicides and insecticides are needed. Many pervasive weeds such as *penoly mientor* grow vigorously in the paddies throughout these dry months because of the long hours of sunlight at these equatorial latitudes. Often they can be controlled by raising paddy water levels. Nevertheless, herbicide use in general is higher during the dry months of the year. Fertilizers are also applied at higher amounts during the summer to capitalize on favorable growing conditions. Farmers clean their drainage canals once a year. Cleaning is routinely done with machinery after application of a herbicide such as Paraquat, Round-Up, Giforato, or Tordon 101 (Ajun 1991).

Actual field applications of agrochemicals were difficult to obtain since they vary from farm to farm, year to year. It is the rare farm that actually records its agrochemical use per unit area (hectare), and, more often than not, the rule is “apply when needed” for any agrochemical. Each farm sampled in the study used approximately the same products and amounts of applied product per unit area. Limited variation came with some of the more expensive agrochemicals because of cost and local specialized pest or weed problems. Rice yields also vary from season to season. For the dry season, yields can be as high as 8.0 tons per hectare and average 5.3 tons per hectare. During the wet season, the greatest yields are 6.8 tons per hectare with an average of 4.8 tons per hectare. The difference in seasonal rice yields is due to seasonal variations in the amount of sunlight (higher in the dry season) (Sanabria 1991).

Methodology

Field Sampling

A field sampling strategy was developed to understand the potential environmental impacts to the national park land of Palo Verde from applied agricultural products upstream. La Quebrada La Mula drainage basin was used as the control since it is a relatively pristine basin used for very limited cattle grazing and is under consideration as a potential rice paddy irrigation project. In other words, the soil and water chemical composition at La Quebrada La Mula Basin was the basis to establish background levels against which to compare the field concentrations found in areas where past agrochemical applications have occurred. After
establishing a sampling protocol, samples taken from Quebrada La Mula Basin were compared to water and soil samples extracted from three morphologically similar basins. All three basins were under rice paddy cultivation. Basin contaminants in each case would be expected to reach off-site ecosystems via effluent drainage channels. Therefore, the focus of the sampling design was on water and soil in the pathways of the effluent releases. Laboratory analyses of the samples were conducted to characterize pesticide and fertilizer residual present in the water and soils of principal effluent canals, which drain the selected basins. Sampling these canals presented the best chance of identifying the highest concentration of agrochemicals present in the drainage system from cultivated lands because the drainage canals are the principal pathways for contaminants. A map of contaminant concentration was then produced to demonstrate the spatial decay of agrochemical concentrations as one moves away from identified contaminant sources. A discussion of Geographic Information Systems (GIS) mapping in this study follows.

The three sampling basins to be compared to the control basin were carefully chosen for similarity in the following: (1) number of hectares in paddy rice cultivation; (2) exclusive rice cropping since initiation of the cultivation in each basin; and (3) rice paddy effluent leaving the farm via a principal drainage canal of comparable length. The basin sites chosen for comparative sampling — Pelón de la Bajura, Rancho Horizonte, and Bagatzi — are all within 60 km of each other on the northern fringe of the floodplains of the Bebedero and Tempisque Rivers. By design, each basin site exhibited a wide variance in the number of years they have been under rice cultivation (i.e., 45, 15, and eight years for Pelón de la Bajura, Rancho Horizonte, and Bagatzi, respectively). The variation of years under exclusive paddy cultivation allows for any buildup of residuals over time. In addition, to get an idea of residual decay with distance along the drainage canals in each of the three basins, sampling was done in three locations along their main canals: (i) the starting point of the canal; (ii) halfway to the discharge point; and (iii) just up channel from any tidal influences at the canal’s termination. Vertical (paired) water samples of approximately 125 mL each were taken from 1 inch below the water surface to a few inches above the canal bottom, being careful not to take any surface water or saltating bedload sediment. The water samples were carefully handled to avoid extraneous contamination, packed in ice, and delivered for laboratory analysis within 24 hours of collection time. The purpose of this part of the sampling program was to catch contaminants wherever they might be traveling in the water column and mark the location of the water extractions for future study.

Soil samples were collected at the same channel cross sections as for the water samples using the same sample extraction protocol. Three partial extractions were taken in the soils forming the canal’s bed in each basin: (i) 1 foot below the canal water level; (ii) 1 foot above the water level; and (iii) directly at the canal water level.
boundaries, along with hydrographic maps, soil maps, and sampling location maps (to cite just a few) were digitized and downloaded into the ARC/INFO (ESRI 1991) GIS (these color maps could not be reproduced herein). Each of these maps, called thematic maps, can be brought in to similar scales, overlayed, and combined to produce a variety of spatial representations of the study area, such as combined site location/hydrographic maps, for example. In this study, the following maps were digitized and fed into ARC/INFO: boundary of area defined by major rivers, boundary of project site, boundaries of the three biological reserves of the region, major rivers and streams present on topographic map sheets, streams within river boundaries, mountains within project site and adjacent areas, lakes within the project site and adjacent areas, transportation road network, geology of the project site, soils, land ownership within the river boundary, present and proposed irrigation and drainage canals, irrigation subdistricts of the Arenal-Tempsique Irrigation Project, and contaminant concentration spatial distributions (Robinson 1993). This extensive database will be used in future studies to interface the soil and hydrogeologic database with multicomponent mathematical models of nonpoint source pollution (see, e.g., Jamieson and Clausen 1988; Bonazountas and Wagner 1984) into a SDSS for rice paddy contamination assessment. The objective of this work, insofar as GIS is concerned, was to develop the aforementioned database and download it into ARC/INFO for mapping of contaminant plumes, carrying out proximity analysis of those contaminant plumes to sensitive ecosystems, and initiating the more involved process of developing the SDSS that will interface the spatial database cited above to contaminant transport models.

### Laboratory Analysis for Pesticides

Having established a field sampling strategy, the next step was to identify the types of agrochemicals being used in the Cabuyo Irrigation Subdistrict (part of the greater Arenal/Tempsique Irrigation District) that encircles the project basin, La Quebrada La Mula. Identification of applied agrochemicals was essential to the subsequent establishment of a small group of indicator parameters on which to base contamination potential, rather than working with the entire set of analytes due to prohibitive costs, redundancy in terms of toxicity impacts, and relatively unequal potential impacts among the set of all applied agrochemicals. More than 175 agrochemicals (including pesticides, herbicides, and fertilizers) are regularly used throughout the Arenal/Tempsique Irrigation District according to a survey of SENARA records at their field office in the city of Cañas (Brizuela 1990; Sanabria 1988; SENARA 1989). Personal interviews with government extension agronomists and farmers in the areas immediately adjacent to the study basin resulted in a reduction of the most intensely used pesticides and herbicides in the specific area of interest at La Quebrada La Mula to 30. Pesticides/herbicides were originally singled out because of their toxicity. The list of these 30 agrochemicals was the cornerstone in contractual agreements with two separate government analytical laboratories located in San Jose, Costa Rica. One of these two laboratories, at the Ministry of Agriculture, would test for concentrations of the 30 agrochemicals in soil and water samples, with similar tests to be made for verification by INCIENSA, the second governmental analytical laboratory. Sampling protocols were agreed upon by the principal investigators and authors of this paper and chemists from the test laboratories (The U.S. Dept. of Agriculture's 1987 *Agrochemical Handbook* served as a guideline for this study sampling protocol). A team was sent to the field and (replicated) samples were collected according to the agreed upon sampling protocol at the sites, as previously determined in the overall field sampling program previously described. A third paired set of water and soil samples was sent to the University of California at Santa Barbara (UCSB) for analysis of chosen agrochemicals and further investigation of nitrate-nitrogen and phosphate-phosphorus fertilizer concentrations.

Standard sample preservation, transport, and chain of command protocols were followed to ensure integrity of the samples. Laboratory results obtained at the two independent government laboratories in Costa Rica and at UCSB indicated concentrations below detection levels for the 30 selected pesticides in the analyzed soil and water samples. The analytical results obtained at the two laboratories in Costa Rica were shrouded with uncertainty, as those laboratories did not have enough experience in conducting analytical testing for chemically complex pesticides/herbicides. The pesticide concentrations obtained at UCSB were also nondetects across the board for all 30 pesticides and herbicides. The first round of sampling, therefore, did not support the hypothesis that agricultural practices resulted in potential hazardous concentrations of chemicals in the downstream waters and soils of the cultivated acres.

A second round of field sampling was undertaken for verification of these initial results. It was determined, based on their environmental persistence, level of toxicity, and representativeness of groups of pesticides, that the list of 30 agrochemicals originally selected could be reduced to a more workable number of eight indicator agrochemicals. The decision analysis for the determination of key indicator agrochemicals was done in collaboration with researchers at the Department of Environmental Toxicology of the University of California at Davis, who have accumulated significant experience with rice paddy toxicologic studies conducted in the Sacramento River flood plain near Sacramento, California (Crosby 1991). The indicator list of eight selected pesticides/herbicides, shown in Table 6, was sent to various analytical laboratories in southern California for an estimate of the cost of laboratory analysis. Laboratory analysis for all the field samples for one round of sampling (i.e., either in dry or wet climate), and not including the analytical methodology development cost for two products that have never been tested before, amounted to nearly $80,000, according to the lowest bid received.
Table 6
Eight Indicator Pesticides/Herbicides

<table>
<thead>
<tr>
<th>Name</th>
<th>Alternate</th>
<th>Common</th>
<th>CostlSample</th>
<th>Water</th>
<th>Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insecticide</td>
<td>Carbofuran</td>
<td>Furadan</td>
<td>$150</td>
<td>$195</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cypermethrine</td>
<td>Ambush</td>
<td>175</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methamidophos</td>
<td>Monitor</td>
<td>150</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>Herbicide</td>
<td>2-4-D</td>
<td>Hedonal</td>
<td>150</td>
<td>175</td>
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<tr>
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<td>Oxadiazon</td>
<td>Ronstar</td>
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<td>200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thiobencarb</td>
<td>Bolero</td>
<td>150</td>
<td>175</td>
<td></td>
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<tr>
<td>Rodenticide</td>
<td>Brodifacoum</td>
<td>Klerat</td>
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<td></td>
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<tr>
<td>Fungicide</td>
<td>Mancozeb</td>
<td>Dithane-M-45</td>
<td>115</td>
<td>115</td>
<td></td>
</tr>
</tbody>
</table>

from analytical laboratories contacted. This included testing for the eight selected indicators in soil and water samples in each of the three cultivated test basins — Pelón de la Bajura, Rancho Horizonte, and Bagatzi — and at the control La Quebrada La Mula Basin. Sampling in dry and wet months, as called for in the original sampling strategy, would double the cost of analytical testing. The prohibitive cost of analytical testing required by focusing on pesticides/herbicides led the authors to redirect strategy and opt for the alternative of analyzing for selected nutrients (i.e., total nitrogen and phosphorus, nitrate-nitrogen, ammonium-nitrogen, and phosphate-phosphorus). This decision was not exclusively economically motivated, as pesticide/herbicide concentrations for the first samples were below detection level. It was recognized that eutrophication by nutrients and associated oxygen depletion of surface and soil water could pose the greatest risk to receiving waters. For the investment of resources needed in conducting additional environmental sampling and testing, fertilizer nutrients clearly offered the potential highest return in terms of significant impacts that could be discovered.

Laboratory Determination of Nutrients, Nitrogen, and Phosphorus

Agricultural fertilization introduces nutrients that can migrate to neighboring ecosystems. Fertilizers are known to promote excessive plant growth, thick algal mats, oxygen depletion by benthic organisms, and eutrophication. Farmers of the region use a variety of fertilizer formulas, usually referred to by percentage of weight of nitrogen (N), phosphorus (P), and potassium (K). Examples of typical formulas for N/P/K are 15-3-31, 10-30-10, and 26-0-26. The constituents with the highest potential impact are nitrogen and phosphorus. Hence, the analytical sampling focused on various forms of the two elements. These forms were nitrates (NO$_3$-N), ammonium nitrates (NH$_4$-N), total Kjeldahl nitrogen (TKN), phosphates (PO$_4$-P), and total phosphorus (TP). The sampling program for these five nutrients consisted of taking quadruple sets of soil and water samples (with replicates) at each of the sampling basins (each basin included four sampling locations along its main drainage channels: the first at the inlet, two intermediate ones, and the fourth at the outlet), in the cultivated areas (Pelón de la Bajura, Rancho Tamarindo, and Bagatzi), and at the control or background La Quebrada La Mula Basin. This was done during dry (December) and wet (August) months. Two sets of samples were sent to two independent analytical laboratories in Costa Rica (i.e., one set to each laboratory) and the other two sets of samples were analyzed at two different analytical laboratories at UCSB. This provided not only verification for consistency of analytical results, but also allowed us to average results obtained at each sampling cross section within each basin when analytical results were deemed consistent in terms of methodology, absence of systematic errors, and the like.

The laboratory procedure for analyzing NO$_3$-N in soils using an extract ratio of 10 gr wet soil to 25 mL of water was implemented before passing the extractant through a copperized cadmium reduction column. The nitrate was then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The resulting water solution has a magenta color, which is read at 520 nm. The PO$_4$-P extraction for soils used an acid digest of a KCl solution instead of water on a dry soil to a solution ratio of 5 gr to 25 mL followed by a modified molybdenum blue assay. Absorbances were read at 888 nm. Both soil water extracts were passed through a flow injection analyzer instrument applying spectrophotometry, where sample absorbances were matched to a concentration curve of standard samples of known amounts of NO$_3$-N and PO$_4$-P. Water analyses, the procedure was identical, with the exception of the extraction process. TKN follows the Kjeldahl Method of analysis for both water and soil. Soil extract is done through a digest of sulfuric acid. Through a series of dilutions and conversions between the ammonium cation and ammonia, water and soil samples are heated with salicylate and hypochlorite to produce a blue assay, at which point colorometric chemistry can be applied to identify sample
concentrations of total nitrogen (MacBeth Division of Kollmorgen Instruments Corp. 1988). Total phosphorus is determined by using an acid digest with soils where the extractant is then analyzed with colorimetric chemistry at a ratio of 0.5 g soil to 10 mL acid solution (usually 4 parts HNO$_3$ and 1 part HClO$_4$). The procedure is the same for water samples as for soils, minus the extraction step. NH$_4^+$-N is extracted from soil with a 2 M solution of KCl. The KCl extract is filtered, and the filtrate is analyzed for ammonia by the salicylate method. Ammonia is heated with salicylate and hypochlorite in an alkaline phosphate buffer, resulting in an emerald green solution. The intensity of color is proportional to the concentration of ammonia. The analysis for water samples is identical to that for soils with the extraction phase.

Results

The results for the first round of agrochemical sampling (30 pesticides/herbicides were considered) yielded nondetects across the board for all organic phosphates and chlorinated hydrocarbon pesticides and herbicides. As indicated previously, the reliability of laboratory results for this round of sampling was low, and, therefore, results were considered inconclusive as to the real environmental hazard of current agricultural practices in the study area. A verification of the first sampling results based on eight selected pesticides and herbicides was prevented by the high cost of associated analytical tests. Therefore, fertilizer concentrations became the focus of the study. These are easily categorized into phosphorus, nitrate, and ammonium compounds and prone to fairly straightforward chemical testing. Based on the negative results for pesticides/herbicides, it was realized that nutrients' potential for eutrophication of receiving waters as well as for creating anoxic conditions in soil water made these fertilizers the primary environmental risk associated with agrochemical application practices in the area.

Table 7 shows the complete analytical results for fertilizer sampling. These results indicate that the concentrations of fertilizers in soil and water in the cultivated acreages were not significantly different from those in the control basin. As was the case for pesticides, there does not seem to be an accumulation of agrochemicals in the soils or above-background agrochemical residuals in effluent waters, either for pesticides/herbicides or fertilizers. Table 7 is set up with the five nutrient constituents placed across the top with water and soil sample results in separate columns, and down the right side are the sampling location sites, the control basin, and the three active rice-growing basins. The intention was to demonstrate a decline in contaminant levels as one moves away from the rice paddy and down the drainage canal and an increase in the residual soil contamination with an increase in the number of years continuously cultivating rice. Irrigation water freshly arriving to the farm was also analyzed for the same constituents to provide a comparison and a baseline of water quality. These results are labeled with a “0” in the location column of Table 7.

Appearing in the columns under NO$_3^-$-N and PO$_4^-$-P for water are data arrays marked by the month during which the samples were taken. The August sampling (1992) was done one to two months into the wet season cropping cycle, and the December sampling (1991) was done in the early stages of the dry season.

To better understand the data presented, reference values have been provided for comparison as well as the results from irrigation inlet water samples taken during the 1992 sampling. There is only one U.S. EPA standard for the nutrients studied. Nitrates in drinking water have a maximum concentration of 714 µM (micro Molar) or 10 mg/L (U.S. EPA 1991). Evidently, the acquired data are several orders of magnitude lower than the standards. For ammonium nitrate (NH$_4^+$-N), the U.S. EPA health advisories or Suggested No-Adverse-Response Levels (SNARLS) have proposed a maximum concentration level of 126 µM NH$_4^+$-N (Marshack 1991). This value is substantially higher than the values shown for that column of Table 7. In addition, three other constituents common to nutrient pollution incoming at Goleta Valley Waste Water Treatment Plant (WWTP, Goleta, California) for sludge are shown at the bottom right of Table 7 (Goleta Valley Sanitary District 1992). These reference levels for nutrients demonstrate how low the nutrient values of the field samples were for both soil and water.

The results across the nutrient data summary in Table 7 indicate little to no current environmental impact in the canal waters or soils from rice paddy nutrients. It appears that no nutrient buildup from sorptivity exists in the canal soils and that the effluent waters were comparable to the waters entering the fields at the irrigation inlet canals. The residence time is short for the five nutrients studied in water and soil. A possible explanation for the soil results could be the large volume of water flowing in the canals, which, in effect, would wash the soils of any contaminants on a continuous basis. Agrochemicals might also be rapidly biodegraded in these warm tropical climates with high levels of solar irradiance. In addition, water moves relatively quickly down the drainage canals, making it difficult to catch any contaminant peaks in the surface effluents.

In summary, no consistent trend with position along the canals was found in any of the sampled basins. This could be due to high spatial and temporal variability of contaminant distributions not captured by the field sampling scheme or to insufficient number of replicates that could have hindered more detailed characterization of contaminant concentration at the selected sampling sites. An enlarged sampling scheme for nutrients and other agrochemicals might reveal contamination to downstream wetlands not discovered by our study. The cost of conducting such a study would be significant (perhaps nearing $0.5 million for a definitive spatial and temporal characterization of major agrochemicals), and
<table>
<thead>
<tr>
<th>Location</th>
<th>Yrs*</th>
<th>pH**</th>
<th>NO3-N Water</th>
<th>NH4-N Water</th>
<th>TKN Water</th>
<th>PO4-P Water</th>
<th>TP Water</th>
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<tr>
<td>Quebrada la Mula</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Control)</td>
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<tr>
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<td>1*</td>
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<td>12.1</td>
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<td>0.14</td>
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<td>2**</td>
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<td>23.6</td>
<td>0.3</td>
<td>0.05</td>
<td>0.07</td>
<td>0.7</td>
</tr>
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<td>3***</td>
<td>7.5</td>
<td>7.1</td>
<td>0.2</td>
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<td>12</td>
<td>ND</td>
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<td>ND</td>
</tr>
<tr>
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<td>9.3</td>
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<tr>
<td></td>
<td>1</td>
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<td>&lt;0.007</td>
<td>0.9</td>
</tr>
<tr>
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<td>ND</td>
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<tr>
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<td>0.8</td>
<td>0.07</td>
<td>&lt;0.007</td>
<td>1.6</td>
</tr>
</tbody>
</table>

All samples were paired and the average recorded above.

* Years cultivating rice.
** Water only, measured in the field with a Hanna Instruments pH meter.
*** Irrigation canal inlet waters (only).
**** Sample taken near rice field.
***** Sample taken half the distance between “1” and “3”.
****** Near the discharge point of the drainage canal.

TKN Total Kjeldahl nitrogen
NO3-N Nitrate nitrogen
NH4-N Ammonium nitrate
PO4-P Phosphate phosphorus
TP Total Phosphorus

Y EPA Drinking Water Standard:
    EPA Suggested Health advisories, SNARLS NO3-N: 10 mg/L or 714 \mu M
YY Nutrient levels for Goleta Valley WWTP, California
    NH4-N: 126 \mu M
    Sludge from treatment plant: NH4-N: 205 \mu mol/g
    TKN: 1964 \mu mol/g
    TP: 1571 \mu mol/g
ND No data.
\mu M Micro molar.

that level of investment appears unjustified based on our preliminary work. Our work suggests that effluent discharge into the streams of the lower La Quebrada La Mula draining into the ecological reserve of Palo Verde National Park might only have the effect of increasing the amount of water entering the lagoons and marshland environments, with no apparent impact on water quality.

Summary and Conclusions

The delta plains of the Tempisque and Bebedero Rivers in Costa Rica provide excellent agricultural opportunities for large-scale farming. The need to bring vast tracts of this area under cultivation does not come without its environmental price tag. Loss of pristine habitats and irreplaceable ecosystems calls for careful development planning to minimize ecological impacts and preserve sensitive and unique landscapes. The proposed agricultural development of the micro basin La Quebrada La Mula is a controversial issue due to the basin’s adjacency and hydrologic connection with the Palo Verde National Park. Approximately three-quarters of the basin of La Quebrada La Mula (5163 hectares) is charted for rice paddy development. The land will be divided into 10 hectare parcels and sold to low income farmers.

Studies of the basin hydrogeology found classic vertisol (typic pellustersts, fine mixed, and ishypothermic)
low hydraulic conductivity values of less than 0.12 m/d to a depth of 1.5 meters, low infiltration rates of 0.02 to 0.4 m/d wet to dry season, and a wide spatial extent of fine-grained, clay-rich soils (specifically, vertisols). With this in mind, a sampling strategy was developed to study the environmental impact from paddy effluent carrying agrochemicals. The research undertaken compared soil and water samples from the principal drainage canals of the three nearby cultivated basins, all with varying years of exclusive rice cultivation (Pelón de la Bajura, Bagatzi, Rancho Horizonte), to the relatively undisturbed La Quebrada La Mula Basin.

Two rounds of sampling were conducted, each following the sampling strategy and protocol. The results of the two rounds, the first looking at pesticides and the second at nutrients, suggest that rice paddy effluent does not carry significant amounts of contaminants to produce identifiable peaks in either water or soil analytical test results. Insofar as agrochemical concentrations are concerned, effluent waters from the three farms are similar to that of the streams of La Quebrada La Mula based on our sampling results. The proposed agricultural development of the micro basin appears to have little or no adverse effects, through the mechanism of nutrient and pesticide transport in surface and ground waters, on the preserved lands of the Palo Verde National Park.

The sampling strategy of this study adequately addressed the questions posed by the goals of the research project. However, the absence of more frequent sampling raises questions about the impact of rice paddy cultivation in the study area, since agrochemical applications in paddy rice are sporadic, and contaminant discharge off-site occurs in condensed peaks with substantial periods of clean water in between (Scarasci et al. 1987). For the rice fields of the Arenal/Tempsique Irrigation Project, it is the occasional field discharge that could bring pervasive concentrations of agrochemicals, whether they be nutrients from fertilizers or pesticides, to the downstream environments. More comprehensive and better supported conclusions could be drawn by either increasing the temporal frequency and/or the spatial coverage of field sampling. This would allow, in addition, the calibration of multicomponent transport models, with a resulting overall better characterization of the time/space distribution of agrochemicals in and around the study area.

Acknowledgments
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Biographical Sketches

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Overexploitation and Deterioration of Aquifers in Venezuela

by H. Jegat, J. Alvarado, and H.A. Loaiciga

Introduction

Following a pattern encountered at a worldwide scale (Zektser and Loaiciga 1993), approximately 50 percent of the municipal, industrial, and agricultural water used in Venezuela is ground water (Alvarado 1989a; 1990a). There are some 35,000 to 40,000 ground water wells in production throughout the national territory. Several Venezuelan aquifers are subject to overdraft, caused by a rate of ground water mining in excess of the natural recharge levels, and this is primarily reflected in steadily increasing drawdowns of piezometric surfaces and water tables. A second impact of overdraft conditions is induced sea water intrusion along coastal fresh water aquifers and vertical upwelling of deep, brackish ground water, which contaminates overlying fresh water aquifers (Alvarado 1990b). In this work, the authors have analyzed conditions in overexploited aquifers of Venezuela. Specifically, the focus of this work is on the Maracaibo and Coro plain coastal aquifers located in the states of Zulia and Falcon of northern Venezuela, the Valencia Lake Watershed, and the intermontane Carora and Quibor Valley Aquifers (see Figure 1). These aquifers are notorious for their degree of overdraft, adverse environmental impacts, and importance as municipal, industrial, or agricultural water sources.

The Coro Aquifer

The Coro Aquifer is situated in the northern coastal plain of the

Abstract

Approximately 50 percent of the potable, industrial, and agricultural water supply in Venezuela comes from ground water, mined through some 40,000 wells scattered around the country. The majority of the productive aquifers consist of quaternary deposits in mountain valleys and coastal lowlands, all of which are situated in areas with limited or low precipitation. Intensive exploitation of several of these aquifers for the last 30 years has resulted in overdraft conditions and ground water contamination, causing serious socio-economic consequences in various regions of Venezuela. This paper reviews the quality and quantity aspects of overdrafted aquifers in Venezuela, which can be classified into three major categories: (1) aquifers in the coastal lowlands in the states of Falcon and Zulia of northern Venezuela; (2) the intermontane Carora and Quibor Valley Aquifers; and (3) aquifers in the Lake Valencia Watershed. If current trends of aquifer overexploitation continue, further water deficits and irreversible environmental damage are predicted.
of past uncontrolled ground water mining. Soil salinity has risen accordingly, creating additional socio-economic difficulties. Soil-water salinity, measured as electrical conductivity, in some areas exceeds 4000 µhos/cm. Soil salinization has engendered shifts, not necessarily optimal from an economic perspective, in agricultural practices. One case in point is the demise of onion cropping in some areas in favor of more salt-resistant crops, such as watermelons. Unfortunately, watermelons have also succumbed as a commercial crop with the heightened salinity levels in some farms overlying the Coro Aquifer. The next step was to rotate to pastures, even higher up in the scale of salinity-resistant plants, but lower in profitability. At present, even grass grown commercially is not viable in these salinized lands. A sort of (chemical) desertification is appearing in otherwise productive lands of these tropical latitudes, with associated reductions in local food production.

Maracaibo Plain

Due southwest and west of the city of Maracaibo, in the northern state of Zulia (see Figure 1), extensive clastic deposits are present, belonging mainly to the El Milagro Formation of tertiary age. These deposits form the Maracaibo Plain Aquifers, which extend over approximately 2250 km². The most productive eastern aquifers of the Maracaibo Plain exhibit an aquifer thickness of about 200 m, and their estimated ground water storage is some 250 × 10⁶ m³ (Alvarado 1990b). During 1968-1969, it was estimated that the natural ground water recharge and ground water pumping were 19 × 10⁶ and 60 × 10⁶ m³/year, respectively. About 80 percent of the ground water production went to the city of Maracaibo alone (Alvarado 1989a; 1990b). Excessive over-pumping initiated cones of depression that ultimately led to salt water intrusion from the saline Maracaibo Lake, which bounds the Maracaibo Plain to the north. Measurements taken during 1968-1970 revealed piezometric levels in two major cones of depression between 10 m to 20 m below mean lake level. In these two areas, TDS in ground

state of Falcon (see Figure 1) and belongs to the regional Coastal Plain Hydrogeological Province (Alvarado 1989a; 1990a). The aquifer has an area of 150 km². The general hydrostratigraphy of the aquifer consists of interbedded recent alluvial sand-and-gravel and clay layers, with an average total thickness of about 200 m. Hydraulically, the Coro Aquifer is a mixture of unconfined, semi-confined (i.e., leaky), and confined aquifers with storage coefficient values ranging from 0.25 to 5 × 10⁻³, and transmissivities ranging from 280 to 3000 m²/day (hydraulic conductivities between 1.4 and 15 m/day, which are very high values). Water level measurements undertaken by INOS-Tahal (1970) indicate a division of the Coro Aquifer into a western region and an eastern region according to the status of cone of depression in each of them. In the western region, called El Patillal, the central portion of the cone of depression was found to be between 2 m to 3 m below mean sea level. The eastern region, El Oriental, exhibited cone-of-depression levels not exceeding 1 m below mean sea level at its center. (The Coro Oriental region is situation due east from the city of Coro).

Hydrogeologic mapping of piezometric surfaces as of 1984 showed that ground water levels in the El Patillal region of the Coro Aquifer had dropped as much as 2.6 m below mean sea level in certain areas. Likewise, the cone of depression in the eastern El Oriental region had reached about 2.5 m below mean sea level. As of this writing, water table and piezometric surfaces in the Coro Aquifer vary between 9 m to 86 m below mean sea level. One of the immediate impacts of these sharp water table and piezometric surface drawdowns is the likely encroachment of sea water along the northern boundary of the Coro Aquifer. To support this assertion, total dissolved solids (TDS) in ground water measured in 1984 varied between 500 and 3500 ppm, with the higher values found near the coastline. Chloride concentrations were measured in the range between 500 and 1500 ppm, with the higher concentration also toward the north, near the coastline. The high chloride concentrations near the Caribbean coast and the observed (declining) concentration gradient in a southerly direction are strong evidence of large-scale sea water encroachment landward. Further evidence of sea water encroachment into the Coro Aquifer was observed in the geographic variation of the Cl/HCO₃ ratio. Specifically, in the inland piedmont discharge areas, 1984 measurements of the Cl/HCO₃ ratio was less than one, which is typical of average fresh ground water aquifers. More recent measurements of the chloride/bicarbonate ratio (Alvarado 1990b) taken in the northern Coro Aquifer near the Caribbean coastline indicated values of that ratio to be higher than 15, again pointing to serious sea water intrusion.

The Falcon coastal lowland, where the Coro Aquifer resides, is one of the most important agricultural regions in that state, and ground water plays a significant economic role there. It has been established, as previously discussed, that long-term ground water overdraft and sea water intrusion is pervasive in this area as a result

Figure 1. Map of Venezuela with locations of the study areas and aquifers.
water exceeded 1000 ppm. Presently, north of the city of Maracaibo and in the coastal plains, the piezometric level is found to be 30 m to 40 m below the lake level. TDS in these regions are of the order of 15,000 ppm, palpable testimony of severe salt water encroachment, where ground water salinization has rendered it unsuitable for essentially any imaginable beneficial use.

Lake Valencia Watershed

The Lake Valencia watershed is located in north central Venezuela and extends over 3200 km² (see Figure 1). The watershed's plain is covered by alluvial deposits with an area of approximately 1200 km². This watershed is an intermontane, closed basin. Lake Valencia sits in its central region, the recipient of regional drainage. More than 85 percent of developed water resources in the Valencia watershed are ground water. Watershed runoff has been estimated to be between 1.2 and 6.9 m³/s (Alvarado and Seiler 1990), while ground water pumping was estimated at about 14 m³/s. This large volume of ground water extraction is believed to be responsible for concomitant changes in ground water circulation regimes and in ground water chemistry that have been identified in the Valencia watershed. In certain areas of the Maracay aquifers, located in the eastern part of the watershed, registered water levels for 1969-1983 showed a declining trend. The greatest decline was observed in the area east of Maracay City, where in 13 years water levels dropped 24 m, reaching a piezometric level of 10 m below lake level. Likewise, levels dropped 7 m to 14 m in the central part of the Valencia Aquifer to 10 m below lake level. The resulting cones of depression have induced vertical upwelling of brackish water from deep semiconfined aquifers and recharge of lake water into the underlying and cleaner ground water of the Valencia Aquifer.

In some areas of the Lake Valencia watershed, chemical ground water characteristics have been altered by a combination of lake water and contaminated surface water intrusion (from landfills, rivers, irrigation reservoirs) and upward vertical flow from deep aquifers high in sulfate content. The origin of various chemical contaminants has been established by isotopic methods reported in Alvarado and Seiler (1990). Figure 2 shows the results of $\text{H}_2$ and $\text{O}^{18}$ isotope determinations (in %o) measured in ground water samples west of Lake Valencia. The relative $\text{H}_2$ and $\text{O}^{18}$ compositions revealed the origin of the isotopes from sources such as the Taguáguay Lagoon, Lake Valencia, and irrigation waters. TDS levels increased from about 200 ppm along the bedrock aquifer boundary upland from the lake to 3800 ppm near Lake Valencia. This more saline water is not suitable for human consumption or for irrigation of salt-resistant crops in low-permeability soils not easily subject to drainage.

Carora Aquifers

Development of agriculture activities in adverse climatic conditions, as in semiarid regions, hinges on irrigation to meet the water consumption of crops. The Torres District of western Venezuela is a typical example of such a low rainfall farming area that depends on ground water to support agriculture. The Torres District is located in the state of Lara, in a region roughly located between 9° 44 feet and 10° 29 feet north latitude, and 63° 36 feet and 70° 43 feet west longitude (see Figure 1). It has a total area of about 6518 km². More than 50 percent of the surface area is barren, with few alternative possibilities to support agriculture, as rainfall is limited here. The present land use pattern consists predominantly of sugar cane cultivation and dairy farming. Precipitation falls irregularly during the wet season between April and December, with maxima reached usually in May and October. Annual total precipitation varies highly, a typical range being between 560 mm and 1100 mm.

The Carora Aquifer is composed of quaternary alluvial deposits from a complex drainage system and is situated within the Torres District. The aquifer has become a source of irrigation water in the area, mainly to support sugar cane plantations and pasture lands. More than 400 wells have been inventoried, with pumping rates ranging between 10 and 60 L/second, with a regional average of 35 L/second (CIDIA 1980; 1992). Typical well depths vary between 80 m and 120 m, and drawdowns range between 5 m and 30 m. Typical specific capacities of wells (i.e., the yield of a well per unit of drawdown) are between 7 L/second/m. Total water extraction in the Carora Aquifer is estimated to be $105 \times 10^6$ m³ annually, or an equivalent rate of 3.33 m³/s. The Carora Aquifer hydrostratigraphy is made up of generally confined interbedded medium and fine sands, coarse sand, gravel, and clay layers, with identifiable patterns of spatial variability throughout the aquifer. Estimates of transmissivity by pumping test are of the order of 150 to 1500 m³/day, with corresponding hydraulic conductivities between 5 and 150 m/day (CIDIA 1992). Ground water recharge is mainly by percolating rainfall in the piedmont areas surrounding the aquifer, where the confined permeable beds outcrop, or in direct hydraulic contact with the ground.
Taking this figure as representative of the order of magnitude of natural recharge to the Carora Aquifer, where the rate of ground water extraction was established as being close to 3.33 m³/s, it is evident that aquifer overdraft is occurring. Figures 3 and 4 show the piezometric contours for 1980 and 1990, respectively, in the Diquiva sector located in the western part of the Torres District. It is clear from Figures 3 and 4 that several pronounced cones of depression developed in this 10-year period with drops in piezometric surfaces reaching up to 20 m in the western part of the Diquiva sector. Sampling of ground water in the Diquiva sector for TDS analysis in 1980 and 1992 showed increases in ground water salinity.

Quibor Valley Aquifer

The Quibor Valley is located in the central section of the state of Lara (see Figure 1). It has an arid climate, and, oddly enough, it is mainly an agricultural region of about 240 km². Irrigation is mainly from ground water sources. The general hydrostratigraphy of the Quibor Aquifer consists of quaternary sand and gravel deposits with interbedded lacustrine clay deposits. Saturated thickness and average porosity are 90 m and 29 percent, respectively, in the northern sector of the Quibor Aquifer, while the same parameters are 100 m and 39 percent, respectively, in its southern sector (Alvarado 1989b).

The current ground water storage is estimated at about 125 × 10⁶ m³. The volume of ground water extracted in 1975-1987 was 22 × 10⁶ m³/yr, while natural annual recharge is approximately 17 × 10⁶ m³, pointing to an annual overdraft during that period of 5 × 10⁶ m³/yr. If this rate of overdraft is maintained into the future, the current estimated ground water reserves indicate that the remaining life of the resource is about 25 years. It is quite possible, however, that other environmental conditions might destroy the aquifer at an earlier time. For example, as the piezometric levels in the productive zone of the Quibor Aquifer dropped, vertical upward flow of deeper brackish ground water (high sulfate content) has occurred. Presently, the TDS levels in Quibor ground water range between 600 and 3000 ppm. In the northern sector of the Quibor Valley, sulfate and calcium concentrations are higher than current potable water quality standards (Alvarado 1989b). Again, the pattern of overdraft is associated with water quality degradation.

Conclusion

Overexploitation of aquifers in Venezuela is due to two clearly differentiated conditions: (1) very high water demand in heavily populated areas; and (2) intensive agriculture in areas with limited rainfall and low rates of natural aquifer recharge. The major immediate environmental problem associated with overdraft in several important aquifers has been the deterioration of ground water quality. This is caused by induced intrusion of sea water or other polluted surface waters, as well as by vertical upwelling of deep, brackish ground water into the productive fresh water aquifer.

In addition, soil salinization induced by ground water overdraft has lowered its productivity in several impacted areas and, in extreme cases, seems to be causing desert islands. Additionally, unquantified ecological effects include the consequence of decreased spring flow and the effects that lowered tables and piezometric levels have on effluent streams, stream ecology, and dependent flora and fauna. Coordinated strategies for wellhead protection areas are being developed by national authorities.

Acknowledgment

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A Systematic Approach to Designing a Multiphase Unsaturated Zone Monitoring Network

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Abstract

A systematic approach is presented for the design of a multiphase vadose zone monitoring system recognizing that, as in ground water monitoring system design, complete subsurface coverage is not practical. The approach includes identification and prioritization of vulnerable areas; selection of cost-effective indirect monitoring methods that will provide early warning of contaminant migration; selection of direct monitoring methods for diagnostic confirmation; identification of background monitoring locations; and identification of an appropriate temporal monitoring plan. An example of a monitoring system designed for a solid waste landfill is presented and utilized to illustrate the approach and provide details of system implementation. The example design described incorporates the use of neutron moisture probes deployed in both vertical and horizontal access tubes beneath the leachate recovery collection system of the landfill. Early warning of gaseous phase contaminant migration is monitored utilizing whole-air active soil gas sampling points deployed in gravel-filled trenches beneath the subgrade. Diagnostic confirmation of contaminant migration is provided utilizing pore-water samplers. Conservative tracers can be used to distinguish between chemical species released by a landfill from those attributable to other (e.g., off-site) sources or present naturally in the subsurface. A discussion of background monitoring point location is also presented.

Overview of Systematic Approach

While the subsurface environment varies widely at a regional and even local level, a systematic approach can be followed that will result in the design of the most appropriate and feasible monitoring network for unsaturated regions of the vadose zone at any given hazardous waste site. Everett et al. (1984) stated, “A vadose zone monitoring program for a waste disposal site includes premonitoring activities followed by an active monitoring program.” Other authors refer to premonitoring activities as site characterization (Sara 1991) and have identified characterization tasks that must be accomplished before selecting locations and depths of ground water monitoring wells. Everett et al. (1984) identified alternative techniques that can be used to characterize a site in preparation for development of a vadose zone monitoring program.

Essential elements required to develop a vadose zone monitoring strategy at a site include the following:

1. Establish the feasibility of monitoring unsaturated regions of the vadose zone
2. Identify the monitoring goals (e.g., release detection, performance assessment, etc.)
3. Interpret the chemical and physical characteristics of the contaminants of concern and the likely mode of transport
4. Interpret characterization data to:
   a. Construct a conceptual model of the subsurface
   b. Identify likely contaminant transport pathways in light of facility engineering design features
   c. Determine the likely effect of the unsaturated zone stratigraphy and lithology on retarding or attenuating contaminant migration
   d. Provide the basis for design of the unsaturated zone monitoring network.

Ground water monitoring networks often do not provide complete coverage for detection of contaminants. Similarly, currently available technologies will not provide complete coverage for unsaturated regions of the vadose zone in a cost-effective manner. For example, comprehensive suction-lysimeter network coverage cannot be reasonably achieved because it requires a large number of sampler installations, which is prohibitively expensive. Model simulations for a 1 ft² leak source in homogeneous medium-textured soil (Bumb et al. 1988) resulted in a lysimeter spacing of approximately 15 feet. Using this spacing, complete coverage of a 40-acre site would require 6000 to 35,000 samplers depending on soil physical properties. Lysimeters provide the best current means for collecting pore-liquid samples and confirming the chemical constituency of contaminant releases. Lysimetry can be effectively complemented by the use of other more economical indirect sampling methods to infer the status of pore-liquids, and consequently to detect contaminant movement. Monitoring programs using intelligently combined, selected techniques focused at vulnerable areas beneath waste disposal facilities can maximize the likelihood of leachate release detection at reasonable cost.

The conceptual design approach recommended herein will result in a reasonably comprehensive unsaturated zone monitoring system that balances the need to monitor areas most likely to transmit fugitive waste fluids (liquids or gases) and financial constraints. It is founded on a risk-based evaluation of the site and landfill design in which critical areas judged most vulnerable to leachate escape are prioritized and monitored.

**Designing the Unsaturated Zone Monitoring Network**

The process of designing an unsaturated zone monitoring network using a risk-based approach includes the following:

1. Identification and prioritization of critical areas most vulnerable to contaminant migration
2. Selection of indirect monitoring methods that provide reasonably comprehensive coverage and cost-effective, early warning of contaminant migration
3. Selection of direct monitoring methods that provide diagnostic confirmation of the presence and migration of contaminants
4. Identification of background monitoring points that will provide hydrogeologic monitoring data representative of preexisting site conditions
5. Identification of a cost-efficient, temporal monitoring plan that will provide early warning of contaminant migration in unsaturated regions of the vadose zone.

**Identification of Vulnerable Areas**

Designing a monitoring system for unsaturated regions of the vadose zone begins with an evaluation of the site hydrogeologic characterization data and the waste disposal facility engineering design to identify areas most vulnerable to contaminant migration. Figure 1 illustrates a schematic design of a landfill with a typical composite compacted soil/geomembrane liner and leachate collection and removal system (LCRS). Vulnerable areas should be identified and prioritized from most to least vulnerable.

Presented in order of decreasing vulnerability, critical areas at a hazardous waste landfill that should be identified include unsaturated regions of the vadose zone beneath unlined, uncapped portions of facilities; lined but uncapped portions of facilities; leachate sumps; leachate recovery collection lines; intermodule seams; and subsurface preferred flow pathways.

**Unlined, Uncapped Portions of Facilities**

Uncapped portions of landfills are unprotected from
infiltration from above. Infiltrating water from precipitation will generate leachate within the waste pile, which can escape the unlined bottom of the facility. The presence, extent, and nature of suspected contamination in this area must be investigated and monitoring positions established in potential vadose zone flow pathways. Generally, unlined and uncapped portions of facilities require the most intensive monitoring networks.

**Lined But Uncapped Portions of Facilities**

These portions of facilities are also unprotected from production of leachate due to precipitation that is not intercepted and diverted from the facility. The produced leachate will pond on top of the liner and be channeled into the leachate collection and recovery system (LCRS). When the landfill is properly designed and constructed, this may not represent a vulnerable location if it can be assured that there are no low spots in the LCRS where ponded leachate can develop a hydraulic head. Risk of a leak is greater because of the added leachate produced by infiltration. Increased infiltration through uncapped portions of an active site can result in greater hydraulic head developing at the liner, LCRS, and sumps.

**Leachate Collection Sumps**

Leachate collection sumps are considered high-risk areas in lined landfills because they are most likely to pond leachate, resulting in a hydraulic head that acts to drive contaminants through the underlying liner system. In some designs, leachate sumps may not be designed as double-lined liquid retaining storage areas, nor with flexible membrane liners. If there is no well-defined accommodation for removing leachate buildup in the sumps, an evaporation pond or other double-lined or flexible membrane-lined storage area for this liquid, the monitoring concerns are increased. The schematic diagram in Figure 1 shows the bottom and side walls of the leachate collection sump as containing a compacted, low-permeability soil base liner with an overlying flexible geomembrane liner. Compacting the sidewalls and ensuring leak-proof joints presents some logistical problems for compaction equipment operators. Any breeches or other perforations in the geomembrane and base liner system could allow immediate escape from the sumps.

**Leachate Recovery Collection Drains**

Leachate collection systems for landfills typically consist of granular (or geosynthetic) drainage layers that are graded to drain to one or more central trenches or troughs containing a leachate collection drain. These collection trenches/troughs are linear design elements more likely to leak than other areas of the lined landfill because they are areas of lower relative elevation where leachate flow is concentrated by design. Liquid is collected and available for saturated flow through breeches or imperfections in an underlying geomembrane and base liner layer. Leachate can also saturate and migrate through the compacted clay liner. In most designs, the liner is not overbuilt (thickened) along these designed drainages.

**Intermodule Seams**

In an effort to distribute the cost of construction over the life of a landfill, some designs provide for construction of the facility in cells or modules. In order to join the liners of adjacent cells, refuse from the old module must then be cut back to expose the liner edge to be tied into the new module liner under construction. The time lapse between construction of the module liners (typically measured in years), the variability of material available for construction at different times, and the fill practice all make module joints problematic and seams potential vertical pathways for release of contaminants through the liner.

Because refuse is filled over the ridge formed at the joint between module liners, seams will be exposed to leachate and are more likely to fail than are adjoining areas. The fact that they are at leachate drainage divides diminishes the probability of long continuous leaks. However, it does not eliminate the possibility for sudden flushing events such as might occur in response to high-intensity rainfall events. Furthermore, during the period of time before the newest module is placed into operation, the seams are often located at the bottom of fill slopes, which could generate a considerable concentration of runoff at times during the filling process. Landfill module construction designs and module seam designs, which prevent the accumulation and ponding of leachate and water as the result of precipitation and runoff, reduce the vulnerability of these seams to contaminant release.

**Subsurface Preferred Flow Pathways**

Constructed fill placed in topographic lows, unless compacted, will most likely be at lower dry bulk densities than naturally occurring geologic material. When these areas are also underlain by clay-rich deposits, they can become saturated flow pathways for leachate running along perching horizons. The source of that leachate can be from directly above or from any point topographically upgradient. Preexisting drainages, often identifiable from predevelopment topographic maps, are also candidates for this type of subsurface flow. Other potential preferred pathways might be coarse-textured layers overlying fine-textured layers identifiable on geologic cross sections constructed from borehole logs collected during the site characterization phase.

**Identifying Appropriate Monitoring Methods**

In order to illustrate the process of identifying appropriate monitoring methodologies, an example of an existing landfill that illustrates the techniques used to monitor vulnerable areas for contaminant release is presented. The example landfill is being constructed in modules. Part of the landfill was constructed during a period of time before liners were required as under current regulations. Module I, as shown in Figure 2, is not underlain by a liner system or overlain by a final cover system. Module II, as shown in Figure 2, is lined but has no completed cover system. Existing modules are being built to current landfill specifications, and
future adjoining modules are also planned. Figure 3 is a plan view and general site map of the example facility.

Existing landfilled modules can present unique monitoring problems in that portions (for example, Module I in Figure 2) are not underlain by a liner system or overlain by a compacted earthen cap; likewise, Module II (Figure 2) is not capped. As such, these modules are susceptible to penetration of precipitation water into the existing landfilled cells, which could result in landfill leachate and gases migrating from beneath the cells, particularly for unlined portions.

Areas of the vadose zone underlying previously constructed portions of landfills can be accessed by either drilling directly through the landfill or by utilizing directional (angle) drilling techniques. While posing potential health and safety concerns from the standpoint of methane and other landfill gas emissions, drilling through a landfill to install monitoring instruments is a viable option. Refuse in the landfill can usually be penetrated using the dual wall percussion hammer technique, the air rotary casing hammer method, and/or the auger technique. Encounters with steel materials can occasionally result in drilling refusal. Tires, bundled newspaper, and other materials can slow the progress of drilling or can cause sufficient bouncing of the drill stem to effectively lead to drilling refusal. However, drilling of the problem location with a high-torque auger rig can usually result in penetration.

Directional drilling methods are appropriate in cases where vertically drilling through the waste fill would result in unacceptable penetration of and damage to an underlying liner system. Hair (1993a), Hair (1993b), and O'Donnell (1993) summarize various aspects of directional drilling techniques.

Unsaturated zone monitoring installations can be installed in the area in and adjacent to existing unlined landfill (Modules I and II in Figure 2). When landfilled refuse (as in Cell I) has been placed on uncompacted material brought to grade, it is likely that migration of potential contaminants moving as a saturated or near-saturated wetting front in the subsurface would be in the direction of the topographic surface drainage that existed prior to grading and landfilling operations. When fill material is placed such that its depth is greatest in the topographic low-lying areas during grading operations, uncontrolled compaction by vehicular traffic at the time of grading will typically be least in these deeper areas. The lower density also tends to promote these relic drainage surfaces as soil gas migration pathways under dry subsurface conditions, particularly in the presence of advective or temperature gradients.

In the example shown, monitoring installation locations should be placed on the downslope (southwest) side of Cell I to identify the impact of the unlined portion of the facility on the monitoring program designed for the downslope, lined facility. Downslope installations (as shown in Figure 3, Module III) can be surveyed in using historical topographic data and constructed in the preexisting natural drainage ways. A background monitoring installation should also be installed to assess vadose zone conditions at a location that is unaffected by the landfill. Locations of appropriate unsaturated zone monitoring installations in the example are shown in Figure 2.

Soil water content and matric potential should be monitored during drilling operations for monitoring installations in order to identify horizons of sufficient water content and matric potential, which would readily facilitate pore-liquid sampling using suction lysimetry. Soil core sampling in the fill and sediments beneath the cell should be conducted at the time of borehole drilling to identify the extent and degree of any existing contamination. Field screening of duplicate samples using headspace analysis and portable gas chromatography (with a flame ionization detector and photoionization detector) can be used to identify the depth of penetration of volatile organic contaminants and reduce laboratory costs associated with “nondetects.” Samples that are suspected of being contaminated based on the field screening should be sent to a chemical laboratory under chain-of-custody for analysis.

Combination Monitoring Installations

To take advantage of the most favorable aspects of both vapor-phase (soil gas probes) and direct (lysimeters) and indirect (neutron probe) pore-liquid monitor-
Neutron Probe Logging

Relatively inexpensive vadose zone soil moisture data can be obtained by installing neutron probe access tubes (NPATs) and conducting neutron moderation logging in the installed NPATs. Neutron logging data can be used to substantiate the assumption of no leachate migration below the site, or if fluctuations in moisture levels occur, to identify potential preferred flow pathway strata for future monitoring. Additionally, neutron logging data can be used to approximate infiltration depths and rates within the waste pile or flow beneath or adjacent to it if remediation feasibility investigations are required.

Several investigators have shown the importance of small borehole size and limited grout material thickness to sensitivity of the neutron moisture logging technique. Teasdale and Johnson (1970) showed that the neutron probe is most sensitive in ungrouted NPATs with minimal distance between the tube and soils. Keller et al. (1990) showed that the greatest inhibiting factor for penetration of thermal neutrons into the soil formation was large-diameter NPAT casings. Amoozegar et al. (1989) demonstrated that slurry backfills surrounding NPATs yielded neutron count rates as high as NPATs that were in direct contact with soil materials at the borehole wall, but that decreased sensitivity resulted with increasing hole diameters. Kramer et al. (1990) showed that monitoring well casings having grout thicknesses less than about 3 inches provide the best neutron count sensitivity.

NPATs can be constructed of 2- to 2.5-inch I.D. aluminum, iron, stainless steel, or polyethylene casing. Slightly larger-diameter tubes may be needed when tight curves that cannot be negotiated by the logging tool are likely to occur.

Solitary, small-diameter boreholes can be drilled to provide for installation of NPATs. Neutron moderation monitoring in vertical monitoring installations can be constructed at minimal additional cost if these installations are installed during the same mobilization effort as the lysimeter/soil gas probe installations. NPATs can be installed immediately adjacent to combination lysimeter/soil gas probe installations to provide access for moisture logs to document the presence or absence of fluctuating moisture conditions in the soil zone above and below the depth of the adjacent lysimeters. When NPATs are installed alongside the lysimeter boreholes, no additional intensive (duplicative) soil sampling is typically required for the NPAT installations, saving time and analytical costs.

The goal of the combined installations is to place a lysimeter below the depth of any present contamination. When it is known that contamination is not present, the lysimeter should be placed at the first potential perching zone beneath the facility. The expected result is that if the lysimeter is able to obtain a soil pore-liquid sample, migration of particular contaminant compounds can be documented. Under dry subsurface conditions, the neutron probe can detect moisture level changes associated with liquid-phase migration. Such changes can also be documented along the entire extent of the access tube. Neutron logging provides an indirect means of obtaining ongoing quantitative vadose zone monitoring even when subsurface conditions are too dry to permit direct collection of soil pore-liquid samples using suction lysimeters. NPAT excavations/borings should be backfilled.
in a manner such that a vertical conduit for contaminant migration is not created.

**Direct Pore-Liquid Sampling Beneath Sumps**

As described before, leachate collection sumps represent an additional vulnerable area for contaminant release at landfills. Installation of suction lysimeters beneath these sumps is recommended to detect leachate migration that may occur.

The depth at which lysimeters should be installed will be determined by the physical properties of materials encountered at depth in each boring. An important criteria is that if a low-permeability silt or clay bed is encountered near the bottom of a boring, the lysimeter should be installed at that bed to intercept any leachate migrating along the bedding interface.

The lysimeters recommended for these types of installations to be installed are pressure/vacuum ceramic cup lysimeters. Numerous comparative studies indicate that these lysimeters deliver the best monitoring results and generally function better than other available lysimeters. The pressure/vacuum units can be used at depths down to approximately 50 feet (15.2 m). A schematic illustration of a typical completed installation of a pressure/vacuum lysimeter is shown in Figure 5.

Prior to initiating field work, the lysimeters should be decontaminated in order to remove any residual chemical contaminants that may have sorbed to the ceramic cups during manufacture. The decontamination procedure involves passing 1 N hydrochloric acid through each ceramic cup and then repeating the process twice using 500 mL of distilled water. The lysimeters should also be pressure and vacuum tested upon receipt to ensure that they are functioning properly. The instruments are fragile, and hairline cracks in the ceramic cups can prevent proper functioning.

Upon completion of borehole preparations, the lysimeters should be prepared for installation by again being vacuum tested and then fitted with centralizers. The centralizers can be constructed of PVC standoffs and stainless steel bands that, when adjusted, fit the borehole diameter. The two polyethylene lysimeter access tubes are threaded through 1½-inch-diameter PVC conduit in order to protect the tubes during and after installation and to provide a means to convey the lysimeters to the installation depth.

Each borehole should be accurately depth-sounded, and each lysimeter casing assembly measured, to ensure precise depth of placement. It is important to ensure that the ceramic cup end of the lysimeter not be crushed by the weight of the PVC casing upon accidental contact with the borehole bottom. After the lysimeters are lowered downhole to their installation depth, they should be suspended in the borehole center by a vice grip and landing plate apparatus at the surface.

After the lysimeters are installed to the appropriate depth, a slurry of 99 percent pure, 200 mesh silica sand should be prepared. Approximately 4 gallons of the slurry are required for each installation in an 8-inch borehole so that the entire cup of the lysimeter is surrounded by the silica slurry. The silica slurry can be tremied downhole using a PVC tremie pipe.

After the silica slurry is emplaced, further installation work should be terminated until the silica slurry “sets up” around the lysimeters. During this period, several lysimeter volumes (approximately 850 mL each) of water should be extracted from each unit in order to aid the “setting up” process.

After allowing the silica flour to set up, the annular space between the borehole wall and the PVC conduit should be backfilled with a layer of native material above the upper surface of the silica flour. The native soils used to backfill the boreholes should be clean drill cuttings from the boring. The soil backfill should be screened to remove coarse gravel-size material and foreign matter before insertion. A seal of prehydrated bentonite should be placed above the native soil. The balance of the borehole volume can be pumped with a grout (a mixture of bentonite, solids, and water). The uppermost portion of the boreholes should be fitted with 6-inch-diameter locking steel monuments held in place with concrete puddled into the borehole. Traffic guards and barrier signs should be put in place to prevent vehicular damage to installation monitoring access.

Prior to sampling the newly installed lysimeters, each unit should be purged periodically for a period of approximately two weeks, rendering approximately 4 liters of fluid. The procedure for retrieving a soil pore-liquid sample involves applying a suction (partial vacuum) to the lysimeter, leaving the suction on for a period of time to draw soil pore-liquid into the lysimeter, and then pumping the sample out of the lysimeter into a sample collection vessel. The lysimeters can be pumped out using commercially available mechanical, hand-operated pressure/vacuum pumps. If deeper (greater than about 120 feet) lysimeters are required, a greater pressure source is needed because of the increased hydraulic lift required for deeper depths. Special lysimeters are required for placements deeper than approximately 50 feet. Figure 6 shows the cross-sectional detail of a high-pressure/vacuum lysimeter. A regulated
Figure 6. Cross-sectional detail of a high pressure/vacuum lysimeter (courtesy of Soilmoisture Equipment Corp.).

pressure bottle filled with nitrogen gas (relatively chemically inert) can be used to develop the pressure required to force collected deep samples to the surface. Resultant samples should be handled and forwarded to the analytical laboratory under chain-of-custody in the usual and customary manner required for ground water samples.

Indirect Monitoring Using Tracers at Leachate Collection Sumps

One disadvantage with pore-liquid sampling is the high cost of repetitive analyses for a potential large number of chemicals of concern. Many parameters commonly monitored at landfills, such as chlorine, electrical conductivity, nitrates, and sulfates, are commonly found at high background concentrations in soils, particularly in arid regions. This can be compounded at some sites by the presence of nearby, off-site sources of contaminants. For example, one facility observed was bounded by a feedlot directly upslope and a liquid waste discharge area for a vineyard immediately downslope.

A specific indicator parameter diagnostic of leachate escape is desirable for two reasons. First, detection of such a parameter would provide conclusive proof of leachate escape without the interpretation and uncertainty required if commonly present background constituents are used. Second, the analytical costs for ongoing monitoring could be substantially reduced.

A commonly used conservative ground water tracer is bromide. Leap (1992) concluded that bromide may be a better tracer than tritium in a widely varying flow environment. Bromide has been used to prove hydraulic connection between landfill leachates and springs (Murray et al. 1981). An interesting aspect of bromide which enhances its early alert warning characteristics for vadose zone monitoring is anionic exclusion, which causes it to move ahead of the advective front in clay-rich materials. Bromide is nontoxic, rare in the natural environment, and relatively inexpensive to analyze (by ion chromatography or by specific ion electrode in the field). Leachate risers at landfill sumps are suitable locations for introduction of small, appropriate quantities of bromide solution. Bromide could also be codispersed in the landfill leachate as a broader approach to using tracers, as long as the tracer constituency in the waste is adequately known.

Neutron Probe Monitoring Beneath Leachate Collection Drains: An Indirect Technique

Monitoring by neutron probe in horizontal access tubes has several advantages discussed at length by Kramer et al. (1991, 1992); Franklin et al. (1992); Unruh (1990); and Brose and Shatz (1986). Its primary advantage is increased coverage at low cost, but it has the disadvantage of not discriminating between leachate and natural water flow or identifying steady-state flow. The natural false positive problem is addressed by placing access tubes as close to liners and sumps as possible, without placing the sensor such that its radius of influence intersects the potential leachate source(s) themselves. This minimizes the natural transport pathways to the detection system. The steady-state issue is addressed by collecting background information before the landfill accepts wastes. Steady-state flow from a slow, continuous leachate leak would become apparent at its outset when compared to background. Direct sampling with lysimeters can be used to indicate steady-state leaks when present.

Alternative designs for access tube layouts beneath facilities of modular design have been considered. One involves one or more access tubes installed diagonally across the site, cross-cutting beneath several future modules at an oblique angle. This has been considered in an attempt to simultaneously provide coverage and minimize installation expense. Disadvantages of this design approach are that it:

- Does not conform to the modular design of the landfill
- Locks the owner/operator into this technology for the life of the facility
- Requires redundant construction of terminal monitoring stations as the access tube is extended for each new module
- Creates construction complexities concerning the access tube installation trench depth and grading as it passes beneath the leachate drainage crests between modules
Waste

Drainage layer

Main leachate collection drain

Flexible membrane liner (FML)

Compacted low permeability soil

Grout

Lysimeter installed approximately 12-15' below grade

Bentonite Seal

200 mesh Silica Sand

Figure 7. Landfill liner and monitoring cross section (end view) (Cullen and Kramer 1992).

Figure 8. Detail of neutron probe access trench with lysimeter/soil-gas conduit (Cullen and Kramer 1992).

- Can require extremely long access tube runs
- Does not provide full monitoring coverage beneath the leachate collection drain trenches, which have been identified as vulnerable areas.

The recommended neutron probe monitoring alternative is horizontal neutron access tubes beneath leachate collection lines emplaced approximately 2 feet below the base liner in shallow trenches dug prior to liner construction. This design completely covers the third high-risk area of concern: the leachate collection pipeline along the axis of each module. Figure 7 shows a landfill liner cross section with typical trench design to facilitate installation of a neutron access probe, lysimeter access tubes, and soil gas sampling lines. Figure 8 illustrates cross-sectional detail of a NPAT trench with the emplacement of pressure/vacuum lysimeters beneath. Figures 9 and 10 illustrate cross-sectional details of a neutron probe access tube termination and lysimeter/soil gas monitoring tubes at the landfill margin.

Figure 9. Cross section through typical landfill module showing neutron probe access tube position (courtesy of John H. Kramer 1992).

Figure 10. Termination of neutron probe access tube, lysimeter access tubes, and soil-gas sampling lines at landfill margin (courtesy of John H. Kramer 1992).

Indirect Monitoring with Electrical Resistance Blocks

Intermodule seams, the seams in a liner that occur at the joints between modules, represent potential contaminant migration pathways and leachate leak points. The engineering design and operational practices can and should be designed to minimize or eliminate this possibility.

In the example landfill described here, five gypsum blocks, equally spaced along the upslope (northeast) margin of Module III, are installed to monitor for pore-liquids emanating from the landfill at this vulnerable point. Five additional gypsum blocks are also similarly installed at the downslope margin of Module III. The approximate location of the gypsum block installations are shown on Figure 2. When module seam joints are designed such that module liner seams are eliminated as vulnerable leak points, gypsum blocks are not needed beneath liner seams.

Gypsum Blocks

Gypsum blocks are one design of what are more generically known as electrical resistance blocks. Electrical resistance blocks measure the electrical potential, using an AC half bridge, between two wires spaced a known distance apart. This distance is typically on the order of centimeters. Some designs utilize concentric stainless steel coils, which are carefully spaced using a plastic frame to secure the coils in place during manufacture. In any case, they represent a point measurement in which the wires or coils are imbedded in a porous matrix that soil pore-liquids can freely enter and leave. As the soil/sediment water potential changes, the water in the porous matrix of the block achieves an equilibrium with the surrounding soil. When soils (and thus
Native and landfill-originated salts can affect the electrolytic concentration of pore water and consequently the electrical resistance of the pore-liquid solution. To avoid this problem, the most effective electrical resistance blocks are constructed of gypsum (calcium sulfate), one of the most soluble of naturally occurring soil salts. Because of its high solubility, the gypsum in gypsum blocks is continuously dissolving into soil solution, creating a background condition of electrolytes, which buffers the effect of native or landfill-generated soil salts on the measurement.

The same feature that makes soil water potential measurements possible also limits the life and accuracy of gypsum blocks. While no information is available in the literature on the life of gypsum blocks in an arid environment beneath a well-sealed landfill, experience in irrigation management (where water is typically applied on a regular, weekly basis) shows that gypsum blocks have a life span of about three years. This life span would be increased in an arid subsurface environment. However, the service life under these conditions is not clearly known.

The accuracy of gypsum blocks is generally considered to be approximately ± 15 percent. They should not be considered a highly accurate method for the measurement of soil suction. However, they are quite acceptable as a means of detecting the arrival of a wetting front in an otherwise dry soil. Experience in agricultural applications indicates that they are most effectively used in fine-textured soils (silt loams) in relatively arid environments. Gypsum blocks provide a straightforward, inexpensive means of detecting wetting front movement in arid soil/sediment environments over limited time periods.

Gypsum blocks are recommended only as part of a short-term unsaturated zone monitoring program. They can be effectively used to provide an inexpensive means of obtaining quality assurance information. In the example case landfill, they are used to ensure the integrity of the compacted earthen liner joint between modules.

The approximate resistance of typical double-stranded wire leads used on gypsum blocks is 52 ohms per 1000 feet. Under dry conditions, typical readings are on the order of $10^4$ ohms. The line resistance is therefore insignificant relative to the soil water electrical resistance under the soil water conditions of interest. Long electrical leads for monitoring installations are workable.

When monitoring beneath intermodule seam joints, lysimeters are also recommended for installation at the seam between modules to enable collection of pore-liquid samples for chemical analysis in the event of a wetting front detection by the gypsum blocks. These kinds of installations can be used as a dual function monitoring point to detect vertical migration of leachate from the module seam joint and to monitor lateral leachate migration from beneath upgradient modules. In the example, one lysimeter is located southeast of the northwestern boundary of the landfill along the intermodule seam. The second lysimeter is located along the historical surface drainage, which leads to the existing ponds. The final depth for lysimeter placement should be determined in the field based on the presence of a coarse-textured, permeable layer overlying a less permeable, fine-textured layer. Lysimeter access tubes can be run in the same conduit used for electrical leads from the gypsum blocks. Approximate location of the lysimeter installations shown in the example are depicted in Figure 2.

**Direct Monitoring of Soil Gases Beneath Landfills**

Soil gas migration, particularly under advective, temperature, and density-driven gradients and/or low soil water potential gradients, can precede pore-liquid migration in unsaturated regions of the vadose zone. When the soil is dry beneath a facility, unsaturated hydraulic conductivities typically are very small (on the order of $10^{-7}$ cm/sec and smaller). In addition, air-filled pore space increases under dry conditions, and the conditions conducive to vapor transport by advection or diffusion are maximized.

A soil gas monitoring component is recommended for the purpose of detecting volatile organic compound (VOC) contaminant migration in the vapor phase under dry soil conditions. A soil gas monitoring design is presented for the example waste landfill.

Seven soil gas sampling installations per module (future, longer modules will require more sampling points to maintain an equivalent spatial distribution) are suggested for the example landfill. In this example, soil gas sampling points consist of shallow trenches that are dug concurrently and perpendicular to the trench to be used for the neutron probe access. The trenches are spaced along opposite sides of, and perpendicular to, the module centerline approximately 125 feet apart, as shown in Figure 2. Each trench is excavated 6 inches wide, 6 inches deep below grade and backfilled with drain rock. Each trench is approximately 50 feet in length perpendicular to the neutron access tube trench, as shown in Figure 7.

In the example, four of the sample lines are run to the northwest margin of the landfill module IV and three run to the southeast margin of the landfill module. One main conduit, 1000 feet in total length (1-inch I.D. Schedule 80 PVC), is buried below the uppermost lift (6 feet deep) in the backfill of the neutron probe access tube trench. At each soil gas trench, a reducing tee is connected to a smaller conduit (.5-inch PVC, Schedule 80, for example) consisting of five flush-threaded 10-foot sections. Three alternate 10-foot sections are screened (.020 inch). Going away from the tee, the conduit can be described as 10 feet screened, 10 feet unscreened, 10 feet screened, 10 feet unscreened, 10 feet screened for a total of 50 feet in length. A fitting is installed on the inside of the reducing tee to connect to ¼-inch polyethylene tubing, which is threaded inside the 1-inch

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conduit for protection and run back to the margin c
t he landfill for sampling access.

Subsequent modules in the example should have an
equivalent soil gas sampling system installed. The result
will be a brickwork-shaped monitoring network that
will provide spatially distributed access to soil gas sam-
ple s from beneath the landfill.

Analysis of soil gas samples can be made cost effec-
tively in the field using field-portable gas chromatog-
raphs or organic vapor totalizers. The method is similar
to the method recommended for soil sample headspace
analysis. If VOCs are detected and confirmed using
portable soil gas analysis instrumentation, a follow-up
sampling event should be immediately scheduled with
a whole air sample taken for laboratory analysis and
speciation to provide final confirmation of the contami-
ant.

Direct Monitoring of Subsurface Preferred Flow
Pathways

In the case of a leak caused by a breach in the landfill
liner, saturated pore-liquid migration is a likely result.
Subsurface liquids released from the landfill could
preferentially flow along preexisting topographic drain-
ageways that existed prior to initiation of landfilling
activities.

In order to intercept and detect these migration
events, suction lysimeters are recommended. Depend-
ing on the final location and elevation of the modules
as the result of grading activities, lysimeters can be
located along the length of and into the bottom of the
trench used to install the neutron probe access tube.
The approximate installation points for the example
are designated in Figure 2. The number of lysimeters to be
installed will be determined by the presence of preferred
flow pathways as interpreted from the conceptual hydro-
geologic model of the site developed during the site
characterization phase. The lysimeters should be
installed in zones where permeable layers overlay finer-
textured, less permeable material. Final depth of place-
ment should be determined when the actual installation
boring is conducted. Cross-sectional detail of the installa-
tion of a lysimeter in the bottom of the neutron probe
access tube trench is shown in Figure 8. In the example
case landfill, one lysimeter is installed beneath each
module approximately 50 feet southeast of the north-
west margin of the landfill to detect potential off-site
leachate migration. A lysimeter is also installed, in the
example, along the historic surface drainage that bisects
the length of the landfill modules. Prior careful survey
work will reduce the effort required to find old topo-
graphic surfaces.

Lysimeter installations should be prepared, installed,
and sampled using the standard protocols for lysimeters.
For economy, the polyethylene sample lines from the
lysimeters and the sample lines from the soil gas moni-
toring trenches can be threaded and run through the
same conduit to a monitoring station at the margin of
the landfill.

Because of the long runs of lysimeter sample lines,
combined with the depth of placement below the even-
tual sampling elevation after the landfilling is com-
pleted, high-pressure/vacuum lysimeters should be con-
sidered for installations beneath the middle of landfill
modules. Because it contains two one-way check valves,
damage to the ceramic cup is prevented when pressuriz-
ing the lysimeter in order to retrieve pore-liquid sam-
ple s. High-pressure/vacuum lysimeters should not be
acid-washed without first removing the stainless check
valves. Acid will etch the seating surface of stainless
steel check valves and render them inoperative.

Background Instrumentation

Careful consideration should be given to the loca-
tions of background monitoring points. Monitoring data
collected at these points will be compared to data col-
lected from the “active” areas later. The resulting com-
parison and statistical analysis will form the basis of
decision-making regarding a suspected release from a
facility.

In ground water monitoring system design, back-
ground sampling points are typically selected in an
upslope or upgradient position with respect to ground
water flow. In any case, the goal is to place background
instrumentation in locations where samples are
representative of the nonactive area of the site. The
direction of water flow in unsaturated regions of the
vadose zone, however, does not necessarily coincide
with the direction of saturated ground water flow, and
procedures for locating background ground water moni-
toring wells are not applicable to unsaturated zone
applications.

Problems in locating appropriate background moni-
toring points are not uncommon. Based on the concep-
tual model developed during site characterization,
uncontaminated areas of the site should be identified
that are as similar as possible to the active site with
respect to site stratigraphy, lithology, and geomorphic
position. Heterogeneity in field situations is typically
the rule rather than the exception. Background data
should be collected following protocols that mimic those
used in the active area beneath the active site. Borehole
logs and monitoring installation completion diagrams
should be recorded to verify the similarity between the
active and background areas.

Since background sampling points are often near
property boundaries, background data can be
influenced by off-site conditions. In the example,
the site was bounded by two feedlots that were located
upslope, and a vineyard applying reclaimed waste water
was located just downslope. All three of the nearby
enterprises represent potential sources of contaminants
that could compromise the goal of background sampling
at the subject site. Background sampling points should
be located away from areas toward which natural surface
and subsurface drainage patterns will channel water dur-
ding precipitation events. Areas toward which the engi-
neered design of the facility will channel leachate should
also be avoided.

Whenever possible, sampling should be conducted
in the active area prior to initiation of activities at a
waste disposal site in order to provide a baseline comparison of the active versus background areas. Adequate background consists of data collected from all phases (i.e., soil cores, pore-liquid, and soil gases) monitored in the active portions of the facility. Background data should be collected for the indirect as well as direct sampling techniques.

Conclusion

As with ground water monitoring systems, complete coverage is often not a realistic goal for monitoring the vadose zone underlying landfill facilities. Early warning of contaminant migration can be reliably accomplished by implementing a design approach that addresses waste disposal site locations most vulnerable to contaminant release and migration. Because contaminants may occur in waste disposal sites, which can migrate in the liquid or gaseous phase, an effective monitoring system must have the capability of detecting multiphase migration.

A realistic monitoring system should minimize the cost of installation and periodic monitoring. A monitoring system that combines indirect monitoring techniques (such as the neutron moisture probe, conservative tracer sampling, and electrical resistance blocks) and direct sampling techniques (such as pore-liquid sampling and soil gas sampling) can provide early warning of contaminant migration as well as diagnostic confirmation of contaminant species without the expense typically attendant to periodic direct sampling and laboratory analysis of the saturated zone. While vadose zone monitoring can provide early detection of contaminant migration for the purpose of preventing ground water contamination, it should not be considered a replacement for ground water monitoring. The status of water quality in an aquifer can only be determined by direct ground water sampling.

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Biographical Sketches

Stephen J. Cullen, M.S., is a principal scientist at Geraghty and Miller (5425 Hollister, Ste. 100, Santa Barbara, CA 93111) and a hydrologic specialist at the Institute for Crustal Studies at the University of California at Santa Barbara, where he specializes in subsurface hydrology, soil science, and the development of vadose zone characterization and monitoring techniques. He directs a wide range of vadose zone characterization, monitoring, and remediation projects in both a research and applied field environment. In addition to directing investigations and providing litigation support on subsurface DNAPL contaminant characterization and remediation, landfill monitoring system design, contaminant source-tracking, natural remediation, laboratory column studies, and computer-aided contaminant flow and transport analysis, he has published numerous technical papers on the subject and holds several patents. He is a principal editor and author of the Handbook of Vadose Zone Monitoring and Characterization.

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Abstract

The vadose zone is the portion of the geologic profile above a perennial aquifer. Inclusion of mandatory vadose zone monitoring techniques as an approach to aquifer protection was first proposed under the Resource Conservation and Recovery Act in the United States in 1978 and has since received increasing acceptance at federal and state levels. The goals of a vadose zone characterization and monitoring effort are to establish background conditions, identify contaminant transport pathways, identify the extent and degree of existing contamination, establish the basis for monitoring network design, measure the parameters needed in a risk assessment, and provide detection of contaminant migration toward ground water resources. The benefits of vadose zone monitoring include early warning of contaminant migration, potential reduction of ground water monitoring efforts, reduction of contaminant spreading and volume, and reduced time and cost of remediation once a contaminant release occurs. Vadose zone characterization and monitoring techniques should be considered as critical hydrologic tools in the prevention of ground water resource degradation.

Regulatory Background

As early as 1978, the United States Environmental Protection Agency (EPA) formally proposed requiring vadose zone monitoring for all Resource Conservation and Recovery Act (RCRA) hazardous waste landfills, surface impoundments, and land treatment facilities. These early proposals were based on the concept that a vadose zone monitoring strategy offered an approach that would provide an early warning system for a release of potential contaminants and facilitate corrective action before extensive ground water contamination occurred. As a result, regulations applicable to interim status facilities were published on May 19, 1980 (EPA 1980), and regulations applicable to permitted facilities were published on July 26, 1982 (EPA 1982; 40 CFR [Code of Federal Regulations], Part 264, Section 264.278).

EPA did not require vadose zone monitoring at landfills and surface impoundments in the final 1980 and 1982 regulations. This decision was based, in part, on the technical difficulties associated with retroactively installing vadose zone monitoring instrumentation and equipment at landfills and surface impoundments and on a need for further research and testing of vadose zone monitoring technology. While vadose zone monitoring was not fully incorporated into the rule-making at the time, the preamble to the 1980 regulation specifically notes that the EPA will continue to evaluate the appropriateness of requiring vadose zone monitoring at new landfills and
surface impoundments. At the time, however, EPA felt it impractical to require vadose zone monitoring at landfills and surface impoundments because monitoring equipment could not be installed down through the unit without removing the waste, redesigning the facility, or disturbing the integrity of any liner systems present.

EPA instead focused on land treatment facilities in the original regulations. Soil core and soil pore-liquid monitoring have been required at RCRA land treatment facilities since the regulations were promulgated. The purpose of vadose zone monitoring at these "open-ended" types of facilities is to provide feedback on the success of treatment and to document that contaminants have not migrated below the allowable treatment zone. Monitoring data in these situations can be used to adjust facility operating parameters in order to maximize degradation, transformation, and immobilization of hazardous constituents in the treatment zone.

When promulgating these regulations, EPA emphasized that vadose zone monitoring at land treatment facilities is not a substitute for saturated zone monitoring. While vadose zone monitoring can serve as an early warning for contaminant migration, it is not an efficient or practical means of documenting the status of water quality in aquifers. Figure 1 illustrates the relationship between the vadose zone, with its component unsaturated regions, and the underlying aquifer saturated zone.

The 1982 regulations require that a land treatment facility monitoring program include soil core and soil pore-liquid monitoring. Soil core monitoring provides a means of monitoring less mobile constituents, such as heavy metals, which tend to accumulate in the near-surface soils. Pore-liquid monitoring, on the other hand, is very useful for sampling and monitoring the more mobile soluble constituents. Monitoring for hazardous constituents must be performed on a background plot (until background levels are established) and immediately below the treatment zone (active portion). The number, location, and depth of soil core and soil pore-liquid samples taken must allow an accurate indication of the quality of soil pore-liquid and soil below the treatment zone and in the background area. The land treatment vadose zone monitoring regulations require that background values for soil pore-liquid be based on at least quarterly sampling for one year on the background plot, whereas background soil core sampling values may be based on one-time sampling. The frequency and timing of soil core and soil pore-liquid sampling on the active portions must be based on the frequency, time, and rate of waste application; proximity of the treatment zone to ground water; soil permeability; and amount of precipitation. The regional administrator has the authority to specify in the facility permit the sampling and analytical procedures to be used. The owner or operator must also determine if statistically significant increases in hazardous constituents have occurred below the treatment zone. The 1982 regulations for land treatment units also provide the option of monitoring for selected indicator hazardous constituents, referred to as principal hazardous constituents (PHCs), in lieu of all hazardous constituents.

The Goals of Unsaturated Zone Characterization and Monitoring

To pursue the larger purpose of protecting ground water resources, characterization and monitoring of the vadose zone is required in order to understand the media through which contaminants travel and subsequently degrade soils, sediments, and ground water. Everett (1980) suggested different goals for ground water monitoring including ambient, source, case preparation, and research monitoring. Similarly, short-term goals for implementing an unsaturated zone characterization and/or monitoring effort can be categorized as the following: establishment of the background condition; identification of contaminant transport pathways; identification of the extent and degree of contamination; establishment of the basis for design of a monitoring network for unsaturated regions of the vadose zone; and measurement of parameters needed in a risk assessment.

Establishment of the Background Condition

Establishing the background condition of unsaturated regions of the vadose zone at a treatment, storage, or disposal facility (TSDF) primarily serves to document the preexisting quantity and quality of the pore-liquids and any associated sorbed and dissolved contaminant levels that existed prior to commencement of activities at a TSDF. Contaminants from off-site sources should be observed and documented. An example of this situation is a TSDF located in or adjacent to oil fields. Petroleum hydrocarbons are common in these situations, and detection of their presence in the subsurface after installation and operation of a TSDF would not necessarily represent diagnostic evidence of the occurrence or source of a release.

Background characterization is the first step in monitoring unsaturated regions of the vadose zone and documents the chemical and physical nature of the subsurface at time zero with respect to TSDF operations. Collecting data regarding the level of unsaturated zone contamination existing prior to arrival of hazardous materials at a TSDF is critical. Data should be collected to document the preexisting condition and provide the basis for interpreting future monitoring data.

Identification of Contaminant Transport Pathways

Identification of contaminant transport pathways is critical to developing an understanding of mechanisms
by which the subsurface environment may be impacted, in the event of a release from a TSDF. This process involves developing an understanding of the geologic medium through which liquid and gaseous contaminants migrate, including the potential for rapid and far-reaching flow through preferential transport pathways. The result of achieving this goal may include development of a fresh appreciation for the kind of data input that will be required as part of risk assessment. Many times, this goal can also be accomplished simultaneously with the goal of identifying the extent and degree of contamination. Knowledge of contaminant transport pathways is vital to the development of a vadose zone monitoring network that maximizes the probability of intercepting and detecting contaminant movement to ground water.

Identification of the Extent and Degree of Contamination

Once subsurface contamination is identified above an aquifer, knowledge of the vertical and lateral extent of contamination is needed in order to estimate the volume of contaminated vadose zone and the risk to public health and the environment. Vadose zone monitoring conducted to identify the extent and degree of contamination is mostly based on field and laboratory chemical procedures.

Establishment of the Basis for Design of a Monitoring Network in Unsaturated Regions of the Vadose Zone

Design of the monitoring system for unsaturated regions of the vadose zone is the ultimate outcome of meeting the three previous goals. Together with information on the chemical and physical characteristics of the contaminant of interest, knowledge of the contaminant transport pathways and extent and degree of contamination (if present) can be used to optimize a monitoring network that efficiently maximizes the probability of detecting a contaminant release from a TSDF or detecting further migration outside a known contaminated volume of the vadose zone.

Measurement of the Parameters Needed in a Risk Assessment

When contamination is detected and verified in the subsurface beneath a TSDF, the next question is what immediate risk does the contaminated vadose zone pose to public health and the environment. Eventually, the long-term effects of the contamination must also be addressed. When the unsaturated zone is contaminated, a risk assessment will require input of vadose zone chemical and physical parameters. Measurement of risk assessment parameters can be accomplished in combination with efforts directed toward meeting other goals of vadose zone monitoring, such as site characterization and monitoring efforts.

Benefits of Monitoring Unsaturated Regions of the Vadose Zone

The vadose zone is an important buffer zone that stands between surface contamination sources and underlying aquifers. Beyond the pure logic of detecting contamination before it reaches aquifer water supplies, sole reliance on ground water monitoring and remediation as a strategy to protect ground water resources is fraught with expense and technical difficulties. While recognizing that there is relatively little known about the vadose zone, Ballestero et al. (1991) refer to it as the most important portion of the geologic profile with respect to human impact on ground water and other subsurface resources. Recent attention has focused on the importance of monitoring unsaturated regions of the vadose zone with respect to protecting ground water in aquifers (DiGiano et al. 1988). From a legislative standpoint, Sections 3004(u) and 3005(l) of RCRA and 264.100 and 264.101 currently authorize EPA to require corrective action for all releases of hazardous waste or constituents from any waste management unit at a TSDF. This authority encompasses releases to all media, including ground water and soils (50 CFR 28702, 28713, July 15, 1985). From a technical point of view, there are a number of advantages to monitoring the unsaturated regions of the vadose zone.

Early Warning of Contaminant Migration

Monitoring of contaminant migration in the unsaturated regions of the vadose zone provides the possibility for detecting a contaminant release to the subsurface at the earliest possible time. Combined with an appropriate premonitoring site characterization program documenting the background condition, unsaturated zone monitoring provides the possibility for tracking a contaminant plume before significant volumes of detrimental contaminants are released to the subsurface environment. During the incipient phases of a leak from a facility, much of the migrating contaminated liquids (either free product or aqueous solution) can be attenuated and immobilized within the unsaturated pore spaces by partitioning reactions and capillary forces. In some situations, the rate of a leak can be high enough to cause saturated flow in localized areas. In the presence of barriers restricting saturated vertical flow (such as strata of low permeability), the potential for lateral migration and contamination of significant volumes of soil and sediments is increased. Early detection in the vadose zone facilitates the opportunity to carefully evaluate monitoring data before serious subsurface contamination occurs and provides a rational approach to protecting underlying ground water resources.

Reduction of Ground Water Monitoring Efforts

Monitoring unsaturated regions of the vadose zone at a TSDF is intended by RCRA 263.97(k) to supplement rather than replace ground water monitoring well systems. It is recognized, however, that there may be circumstances wherein the number, location, and depth of ground water monitoring wells in the uppermost aquifer can be modified because of the presence of an effective unsaturated zone monitoring system.

Similar to EPA's approach to the placement of ground water monitoring wells for detection monitoring (EPA 1986), it must be emphasized that the design and
placement of instrumentation in a vadose zone monitoring network can only be reliably accomplished when based on the results of a thorough site characterization.

Consideration of proposals to reduce the ground water monitoring requirements because of the presence of a supplementary vadose zone monitoring system must be based on site-specific hydrogeologic and engineering information that will vary widely depending on location and specific operations of the TSDF. Generally, reduction of ground water monitoring requirements should be considered when the site characterization is complete enough to reasonably ensure a thorough understanding of the likely contaminant transport pathways through the vadose zone, and when it can be demonstrated that the vadose zone monitoring network has a high probability of intercepting and detecting contaminants migrating beneath the TSDF.

**Reduction of Contaminant Volume and Spreading**

The sooner a detection system can identify a release of contaminants to the subsurface, the more successful (i.e., efficient) will be the effort to limit and subsequently clean up the contamination. The early warning approach of vadose monitoring offers the best opportunity to achieve this aim. In parts of the United States, particularly in the arid and semiarid areas of the Southwest, the depth to the uppermost aquifer can be 10s to 100s of meters. The subsurface in these environments could be seriously impacted by the time contaminants migrate to and are detected by a ground water monitoring network.

This situation is often exaggerated by increased pumping and reduced recharge that can lower the water table and thus rapidly increase the depth of the overlying vadose zone, especially during drought periods. Immiscible hydrocarbons located within the capillary fringe and top of the ground water table can become immobilized in the unsaturated zone in the newly created intergranular pore spaces and throat necks as the water level drops. The expanded unsaturated zone can be contaminated with both immiscible and dissolved contaminants during low water years. Return of the water table to the level of previous years can cause mobilization of the contaminants previously trapped in occluded and deadend pore spaces and create a dramatic increase in contaminants observed in ground water samples obtained from the saturated zone (Eccles and Bradford 1977). These kinds of subsurface contamination problems can be anticipated by monitoring unsaturated regions of the vadose zone.

Monitoring systems placed in the unsaturated zone near the source can be used for early detection of contaminant migration. Detecting contaminant migration near the source is a benefit to both the regulators and the regulated, especially when the detection results in minimizing the spread of a potentially costly contaminant plume and reduced volume of contaminated subsurface.

**Reduced Time and Cost of Remediation**

The most obvious benefit to vadose zone monitoring is that contaminant migration detected in the unsaturated zone can be remediated without impacting aquifers. In addition, the volume of contaminated subsurface is often reduced, and the total mass of contaminant is less than it might otherwise be if a contaminant plume had remained undetected until impacting ground water. The net result of early detection is that the overall efficiency (i.e., the efficiency of monitoring plus remediation) of protecting aquifers is improved. The early warning provided by this supplementary monitoring approach translates directly into cost benefits for both owner/operators and society.

Since the unsaturated zone is generally characterized by intergranular pores that are partially air-filled and in communication with the atmosphere, oxygen levels are typically higher in the vadose zone (measured in percentages) than below the water table (measured in parts per million). Though not true of all compounds, many subsurface biotransformations and abiotic transformations that require oxygen typically proceed most rapidly under aerobic conditions (Johnson et al. 1989). Thus, both passive and active remediation strategies that require oxygen management are often easier, more rapid, and less costly to conduct in the vadose zone.

**Applicability of Mathematical Flow and Transport Modeling to Unsaturated Zone Monitoring**

**Predicting Contaminant Distribution and Flow**

Mathematical models are available in both the proprietary and public domains, which predict water flow and contaminant transport in the unsaturated zone (Kramer and Cullen 1995). In a literature review conducted to determine the capability of mathematical models to predict contaminant transport in the vadose zone, Nielsen et al. (1990) conclude that “the reliability of vadose zone models has not been established even for site-specific conditions.” Further, they conclude that “because of the uncertainty of modeling, monitoring of contaminants in the vadose zone remains a necessity into the foreseeable future.” Flow and contaminant transport in the vadose zone is extremely complex and characterized by a three-dimensional heterogeneity in which flow occurs under conditions of uncontrolled and variable positive (in perched zones) and negative (in unsaturated zones) hydraulic head conditions.

Nielsen et al. (1986) points out a number of simplifying assumptions and problems commonly encountered in models that, when taken together with the heterogeneity issue, account for a portion of the unreliability associated with predicting contaminant transport in the unsaturated zone. These include the assumption of instantaneous adsorption by dissolved contaminants, the assumption of steady-state flow, the assumption of no hysteresis, nonconsideration of heterogeneous hydraulic conductivity, anisotropy, and indiscriminate use of adsorption isotherms without consideration of other chemical reactions that affect the amount of a given contaminant occurring in the adsorbed phase.

Exclusive use of mathematical models to predict contaminant distribution above a water table in the event
of release at a TSDF is an unreliable approach to preventing ground water contamination. Field validations of vadose zone models are lacking, and their predictive capabilities remain largely untested in field-scale settings (Stein and McTigue 1989) and problematic even on a laboratory scale (Glass et al. 1989). Therefore, it is not reasonable to expect accurate and reliable predictions of contaminant travel times to any given depth, including that of the water table, in the absence of site-specific characterization and monitoring data.

Using Vadose Zone Models for Risk Assessment

Risk assessment is carried out once contaminant leakage has been detected in the early warning system. The goal of a risk assessment with respect to subsurface contamination is to evaluate the present and the potential for future subsurface degradation as the result of a contaminant release from TSDF. Major elements of a risk assessment include risk identification, evaluation, and reduction (Miller 1986). Risk identification at a TSDF in the subsurface is usually straightforward. It is the threat to chemical degradation of the subsurface and public ground water supplies. Risk reduction includes eliminating the source of the contaminant release (such as liner repair and operations shutdown), release containment (subsurface flow barriers), and remediation (for example, soil vapor extraction, excavation, bioremediation, and others). Vadose zone modeling is a useful tool for the second step: risk evaluation.

EPA (1986) details the steps in a risk assessment effort required under RCRA as part of the ground water monitoring effort. A similar approach can be appropriately applied to a risk assessment associated with an unsaturated zone monitoring effort. Mathematical modeling can aid in refining conceptualizations of the flow and transport regimes and pathways of the unsaturated zone, yield rough approximations of the travel time of contaminants to an underlying aquifer, identify key parameters that influence vadose zone contaminant transport, and assist in the development of unsaturated zone remediation alternatives.

While modeling is the only means of predicting future contaminant fate and transport, the results of modeling efforts should not be regarded as absolutes. All assumptions and boundary conditions should be clearly understood. Modeling results should not be overemphasized to the exclusion of actual measurements in terms of locating unsaturated zone monitoring points or in the selection of remedial alternatives.

Use of Vadose Zone Models in Designing an Unsaturated Zone Monitoring Network

Just as the general equations of flow and transport in the vadose zone can be used to describe the migration of vadose zone fluids, they can also be used to determine the zone of effectiveness of various unsaturated zone monitoring techniques (Bumb et al. 1988). Computer-aided mathematical modeling can enhance and facilitate development of a conceptual model for potential contaminant release migration at a TSDF and assist in the calculation of the appropriate spacing and placement for direct and indirect sampling devices and in the calculation of the frequency of monitoring required. Kramer and Cullen (1995) review available vadose zone models and their appropriate application.

Because of the heterogeneity of the vadose zone, accuracy and calibration of a model to even a specific site requires large volumes of high-quality data. Once the premonitoring site characterization and monitoring network design is complete, subsequent data can be used to further refine the input parameters of the model and improve calibration of the model with respect to subsurface conditions beneath a specific TSDF. If a release is detected beneath a TSDF, confirmation sampling, in addition to verifying the occurrence of a release, will begin the process of monitoring the plume propagation. The data can be evaluated in terms of the model. This iterative process improves understanding of specific site conditions, validates use of a model at a specific site, can be suggestive of additionally needed or unnecessary monitoring points (both in the saturated and unsaturated zone), and provides a means of quality control for both the model and the monitoring system.

Use of Site Characterization and Monitoring Data in a Vadose Zone Modeling Effort

The use of models for risk assessment and as tools for monitoring network design should incorporate and be based on measured, site-specific, hydrologic parameters of the vadose zone. While certain analyses can only be conducted in a laboratory, these parameters should be measured in situ, where possible, in order to minimize errors attributable to sampling sizes and techniques. The measured parameters required for a given model will vary somewhat depending on the application, simulation approach, and contaminant composition. In general, however, parameters that are usually required for flow models include bulk density, porosity, water content or soil water tension, field capacity water content or tension, residual saturation water content, infiltration capacity, saturated hydraulic conductivity, soil water characteristic curve, and the conductivity-pressure head relationship. Dealing with the problem of contaminant transport generally requires additional information regarding specific surface area, cation exchange capacity, adsorption coefficient, diffusion coefficient (gaseous and liquid), organic carbon content, and partitioning coefficients. Table 1 lists typical input parameters required for use in vadose zone models.

Criteria for Determining the Feasibility of Monitoring Unsaturated Regions of the Vadose Zone

Monitoring unsaturated regions of the vadose zone is appropriate unless it can be shown that it is not feasible or that there are no monitoring devices that will function under the specific site hydrogeologic conditions. Factors affecting the feasibility or appropriateness include the
Typical Input Parameters Required for Use in Vadose Zone Flow and Transport Models (Cullen and Everett 1993)

<table>
<thead>
<tr>
<th>Input Parameters Typically Required for Vadose Zone Flow Models</th>
<th>Additional Parameters Needed for Vadose Zone Transport Models</th>
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<tbody>
<tr>
<td>Bulk density</td>
<td>Specific surface area</td>
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<tr>
<td>Particle density</td>
<td>Cation exchange capacity</td>
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<tr>
<td>Porosity</td>
<td>Adsorption coefficient</td>
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<tr>
<td>Soil water tension</td>
<td>Diffusion coefficient (liquid and vapor)</td>
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<tr>
<td>Field capacity water content</td>
<td>Organic carbon content</td>
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<tr>
<td>Field capacity soil water tension</td>
<td>Partitioning coefficients</td>
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<tr>
<td>Residual saturation water content</td>
<td>Constituent chemical and physical properties</td>
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<tr>
<td>Infiltration capacity</td>
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<td>Saturated hydraulic conductivity</td>
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<td>Soil water characteristic curve</td>
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<td>Conductivity/pressure head relationship</td>
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<tr>
<td>Local vertical recharge rate</td>
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</table>

Evaluating the Efficiency of Ground Water Monitoring Networks

Networks designed or evaluated using simplistic formulas, such as one upgradient and three downgradient wells, are insufficient to address the complex three-dimensional flow regimes in ground water systems. Unfortunately these complexities are often unappreciated. The capability of the ground water monitoring network to provide early detection of contaminant escape can be evaluated with qualitative or computerized ground water flow models that simulate plumes passing through the network. Hypothetical contaminant release events for chemicals of concern can be used to simulate contaminant plumes with 3-D shape and duration. Plume cross sections at any travel distance are related to site-specific geology and transport processes. The potential performance of the network can be expressed as the probability of missing a target release event by either insufficient sampling density or sampling frequency. Unfortunately, these simulations must rely on uncertain input parameters (i.e., flow direction and dispersion) and cannot be validated. As pointed out by Cherry (1990), evaluating the potential performance of ground water monitoring networks is problematic because of uncertainties in the determination of heterogeneous geologic conditions and weak transverse dispersion of contaminant plumes. Even sophisticated evaluations of ground water monitoring networks that use complicated statistically treated computerized simulations can do no better than to indicate how to minimize failure probabilities (Massmann et al. 1991).

Potential problems (Figure 2) related to the ability of ground water monitoring systems to detect contaminant migration include the following:

- Regional recharge flow lines may cause contaminants to dive beneath well screens undetected
- Overestimated dispersion coefficients allow contaminants to escape between wells
- Flow lines follow facies changes oblique to ground water table gradient. As pointed out by Loaiciga et al. (1992), “in strongly anisotropic aquifer systems the hydraulic head or potentiometric head map will not indicate true ground water flow directions except in areas where the hydraulic gradient happens to be collinear with one of the principal axes of hydraulic conductivity”
- Fracture flow in preferred pathways evades well screens.

In situations where technological or financial resources to adequately characterize and monitor ground water systems are not available, means to minimize vulnerability should be employed. With the notable exception of facilities sited in ground water discharge areas (Heath 1984), parameter uncertainties decrease with proximity to the source. Therefore, monitoring networks should be as compact in space and time as resources permit, with sampling points located as close to the source as possible and sampled with a frequency designed to intercept short-lived releases. Monitoring unsaturated regions of the vadose zone provides these advantages and should be considered an important enhancement in monitoring network capabilities.

Evaluating the Efficacy of Monitoring Unsaturated Regions of the Vadose Zone

An unsaturated zone monitoring network is feasible if it meets either or both of the first two following criteria and the third.

Criteria 1: Provide early warning
Criteria 2: Enhance monitoring capabilities
Criteria 3: Be affordable

Discussion of these criteria follows.
Criteria 1: Provide Early Warning

A monitoring network for unsaturated regions of the vadose zone must be capable of detecting a release before contaminants can reach the ground water monitoring system. Monitoring schedules must be designed to intercept rapid and short-lived release events where appropriate. Contaminant travel time through the vadose zone depends on:

1. Type of contaminant (i.e., chemical and physical properties, degradation rates)
2. Thickness of the vadose zone
3. Properties of hydrogeologically significant units including percolation rates, sorptive capacity, soil water characteristics, unsaturated hydraulic conductivity-pressure head relations, and saturation percentage, as well as structural features in the vadose zone that may control preferred pathway flow
4. Local vertical recharge rate.

In areas of shallow water tables, high moisture contents, and/or rapid flow pathways, this criteria may not be met. Even when this criteria is not met, it may still be feasible to monitor the vadose zone if monitoring will yield important spatial data that reveals the location of contaminant leak sources as discussed next.

Criteria 2: Enhance Monitoring Capabilities

Unsaturated zone monitoring must enhance spatial monitoring capabilities. Enhancements may occur in two forms.

First, unsaturated zone monitoring must provide a better definition of the location of leak sources. For example, flexible membrane liner seams are more likely to fail than other areas (Brown et al. 1987). Effective unsaturated zone monitoring below seams could pinpoint a leak. With this information, an area can be repaired and the leak source eliminated when access permits. When a leak source is inaccessible, the unit could be managed to minimize leachate production.

Second, by detecting leaks that would otherwise escape the ground water monitoring network, monitoring capabilities are improved. For example, spatial monitoring coverage can be improved by monitoring in unsaturated regions of the vadose zone near areas with higher leak probabilities, such as beneath sumps, in spatially extensive areas near the source, or in known contaminant transport pathways. This is especially true in hydrogeologically complex regimes.

Criteria 3: Be affordable

A variety of cost-efficient unsaturated zone monitoring techniques are available to enhance monitoring networks, particularly real time geophysical methods that require minimal analytical costs. The advantages of monitoring unsaturated regions of the vadose zone in terms of the risks/costs differ for each site, contaminant, and time. Although it is difficult to value the benefits of different components of an unsaturated zone monitoring network, estimates of potential savings can be made using an approach outlined in Freeze et al. (1990). The approach is a risk-based philosophy of monitoring design that couples three separate models, including a...
decision model incorporating a risk-cost-benefit objective function, a simulation model for flow and transport, and an uncertainty model that encompasses both geological uncertainty and parameter uncertainty. Similar approaches can be applied to the vadose zone.

**Conclusion**

Vadose zone characterization and monitoring techniques should be considered as critical hydrologic tools in the prevention of ground water resource degradation. Experience in the United States has shown that the benefits of vadose zone monitoring include early warning of contaminant migration, potential reduction of ground water monitoring efforts, reduction of contaminant spreading and volume, and reduced time and cost of remediation once a contaminant release occurs. Vadose zone modeling alone cannot presently be considered a reliable method of predicting contaminant flow and transport above a water table in the subsurface. Vadose zone characterization and monitoring approaches should be implemented unless it can be shown that it is not feasible for the specific hydrogeologic conditions that exist at a site.

**References**


**Biographical Sketch**

Stephen J. Cullen, M.S., is a principal scientist at Geraghty and Miller (5425 Hollister, Ste. 100, Santa Barbara, CA 93111) and a hydrologic specialist at the Institute for Crustal Studies at the University of California at Santa Barbara, where he specializes in subsurface hydrology, soil science, and the development of vadose zone characterization and monitoring techniques. He directs a wide range of vadose zone characterization, monitoring, and remediation projects in both a research and applied field environment. In addition to directing investigations and providing litigation support on subsurface DNAPL contaminant characterization and remediation, landfill monitoring system design, contaminant source-tracking, natural remediation, laboratory column studies, and computer-aided contaminant flow and transport analysis, he has published numerous technical papers on the subject and holds several patents. He is a principal editor and author of the Handbook of Vadose Zone Monitoring and Characterization.
Planning Urban Growth in Ground Water Recharge Areas: Central Valley, Costa Rica

by Hugo Rodriguez-Estrada

Abstract

Nitrate levels in the ground water of the Central Valley of Costa Rica have increased in relation to the past. Previous studies determined that the unsewered sanitation systems in the recharge areas are the main source of nitrogen. Calculations are made in this study to estimate the maximum population density allowable without improved sewage systems in order to keep the nitrogen levels in ground water below the World Health Organization (WHO) criteria. Results were achieved employing a mass balance that involved the concentration and rate of domestic effluents and the flow rate in the aquifer, as well as an estimation of the effects caused by the agricultural activity. It was concluded that, in general terms, the population density must not exceed 45 inhabitants per hectare. Otherwise, sewage systems and treatment plants are necessary. These conclusions provide a basis for urban growth planning, which will protect ground water quality. The method used in this case should apply to similar situations.

Introduction

Nearly 50 percent of the water supply for the Costa Rican metropolitan area is satisfied with water from the Colima aquifers, either from wells or springs. Approximately 2300 liters per second (L/sec) are withdrawn from those two aquifers for domestic, industrial, irrigation, and other uses. A project has been considered to drill 28 new wells and obtain 2000 L/sec additional supply for the metropolitan area up to the year 2015. The recharge area to these aquifers is located at the north and northeast parts of the Virilla River watershed, precisely where significant urban growth is taking place. This growth is expected to produce an impact on the aquifer system in both quality and quantity. This study deals only with the quality aspect as it relates to ground water pollution.

Study Area

Figure 1 shows the area involved in this study, including those areas contributing to the Norte Wellfield (about to be developed), the La Valencia Wellfield (operational at present), and the Sur Wellfield (about to be developed). The contributing zones were delineated based on the expected equipotential lines for the Colima Superior Aquifer (which includes the Norte and Valencia Wellfields) and for the Colima Inferior Aquifer (Sur Wellfield) for the year 2015, according to a simulation model (TAHAL 1990).
Methodology

Aquifer pollution from urban sources has been subject to intensive studies worldwide. The major source of nitrogen in urban areas is unsewered sanitation systems, mainly septic tanks whose drainage trenches infiltrate sewage into the ground. Figures 2 and 3 show the variation in nitrogen content in the ground water of the aquifers of the area. These nitrogen concentration values were determined during a water quality monitoring program carried out by the Department of Water Resources of the Costa Rican Institute of Water Supply and Sewage (AyA). The figures show that water from the shallowest aquifers (Belen, Libertad, Ojo de Agua) exhibited the highest nitrogen concentrations, pointing to their greater vulnerability. Also, it is clear that water located far from humans (e.g., Fuente Perez) showed the lowest nitrogen concentrations of all sampled points, which supports the premise of urban impact on ground water quality in unsewered areas. It is important to note the increasing trend during the monitoring period shown in Figures 2 and 3.

The methodology of this investigation calculates a population density such that the nitrogen concentration in the aquifer would be lower than a specified limit under proposed future conditions of demographic density. Explicitly, the method assumes that: (1) ground water flows under the study area with a rate equal to Q1 with a natural nitrogen concentration (equal to background concentrations plus agricultural inputs) of C1; (2) infiltration of polluted water originating from the urban areas occurs at a rate equal to Q2, and its nitrogen concentration is C2; and (3) within the aquifer, the resulting mixture will flow with a rate Q1 + Q2, the sum of which is Q3. The final nitrogen concentration in ground water would be expected to be a combination of C1 and C2, referred to as C3, which is equal to the concentration in the flow rate Q3 (i.e., Q1 · C1 + Q2 · C2 = Q3 · C3). The concentration C3 is the basis for determining the allowable population density. Figure 4a shows the analog mixture model involving the water types mentioned in the previous paragraph, and Figure 4b indicates what may be expected to occur in the natural environment. In order to find the concentration C3 and its relationship to the number of inhabitants in the wellhead area, their water consumption, and the volume of infiltration water, the following mass balance relationship was used:

$$C_3 = \frac{Q_1 \cdot C_1 + Q_2 \cdot C_2}{Q_1 + Q_2}$$

in which all terms have been defined. The natural ground water flow rate Q1 is mainly horizontal flow...
within the aquifer in the area located upstream of the urban growth area, or in the northeast section of Figure 1. Equation 1 can be rewritten to solve for any of the other intervening concentrations or flow rates, provided that the values for the other four variables are specified. For example, if $Q_1, C_1, C_2$, and $C_3$ are known, then the flow $Q_2$ is equal to

$$Q_2 = \frac{Q_1 (C_3 - C_1)}{C_2 - C_3}$$

(2)

which must be positive.

**Determination of $Q_1$ and $C_1$**

$Q_1$ was calculated from the Darcian relationship $Q = Ti/b$, where $Q =$ flow rate; $i =$ hydraulic gradient as calculated from the equipotential lines expected for the year 2015 (i.e., 0.05 for Colima Superior and 0.044 for Colima Inferior); $b =$ width of aquifer cross section (i.e., perpendicular to streamlines); and $T =$ aquifer transmissivity, or 500 m$^2$/d for both Colima Superior and Colima Inferior (SENARA/British Geological Survey 1988). Based on these data, the resulting ground water flow rates were calculated to be 175,000 m$^3$/d and 154,000 m$^3$/d for the Colima Superior and Colima Inferior Aquifers, respectively. The natural concentration $C_1$ (in flow rate $Q_1$) was based on water chemical analysis from springs located distant from human impacts. It was concluded that $C_1 = 1$ mg/L. It is important to note that in some places the concentration was lower than this value, but 1 mg/L was assumed to incorporate a safety factor and avoid erring on the low side of the potential ground water pollution threat. This value of $C_1$ is preliminary; it must be modified to account for a nitrogen input from water recharging into the water table from percolation of precipitation. This recharge water leaches nitrogen in the soil, the result of agricultural applications into the aquifer.

In addition to the natural nitrogen concentrations, agricultural chemicals (i.e., fertilizers) contribute an additional amount of nitrogen to ground water in the study region. In order to quantify this latter nitrogen input, both the mean annual recharge rate (1,500 mm/yr; SENARA/British Geological Survey 1988) and the annual fertilizer application rate (300 kg N/ha/yr; Reynolds 1991) were taken into account. It was assumed that 75 percent of the annual nitrogen application was taken up by plants, adsorbed by the soil or rock matrix, gasified, or otherwise biotransformed or removed so that only 25 percent of the amount applied reached the aquifer. This is an approximation that needs to be validated in the future by further field investigations. With the data just presented, the nitrogen concentration in the recharge water was calculated as illustrated in Table 1.

The recharge water (628,767 m$^3$/day) at a concentration of 2.5 mg/L mixes with the ground water flow (175,000 + 154,000 = 329,000 m$^3$/day) with a concentration of 1 mg/L so that the concentration of the resulting mixture of waters (flow rate is 628,767 + 329,000 m$^3$/day) is given by $C_1 = [628,767 \cdot 2.5 + 329,000 \cdot 1]/[628,000 + 329,000] = 2$ mg/L. This value of $C_1$, which accounts for the fertilizer effect, is adopted herein for further calculations.

**Determination of $Q_2$, $C_2$ and $C_3$**

The flow rate $Q_2$ is the volume of waste water from human use plus leakage from water pipes that could infiltrate into the ground and percolate to the water table. TAHAL (1990) estimates that on a per capita basis, $Q_2$, also known by the name “return flow,” equals 60 percent of the per capita water demand. Assuming that the per capita water demand is 300 liters per day per person (L/dp), the return flow $Q_2$ would then be 180 L/dp. The total return flow in a given area depends on the population of that area, and will be determined below.

According to CEPIS (1991), the mass of nitrogen produced by a person is approximately 4 kg/yr. Walker et al. (1973) and Thompson and Foster (1986) suggest that only 50 percent of this human load may be expected to be leached to the aquifers with the return flow. Using the per capita return flow figure of 180 L/dp, it follows then that the concentration of the return flow, $C_2$, is 30.44 mg N/L ($= 2 \times 10^4 / 180 \times 365$).

Finally, the N standard in drinking water by the World Health Organization is 10 mg/L. This value was chosen as the maximum allowable nitrogen concentration in the total aquifer flow. Thus, $C_3$ is set equal to 10 mg/L.

| Table 1
Calculation Table for Nitrogen (N) in Recharge Water |
<table>
<thead>
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</thead>
<tbody>
<tr>
<td>Amount used/yr</td>
</tr>
<tr>
<td>Amount leached (25% /yr)</td>
</tr>
<tr>
<td>Area of application</td>
</tr>
<tr>
<td>Amount of N in recharge water</td>
</tr>
<tr>
<td>Recharge rate</td>
</tr>
<tr>
<td>N concentration in recharge water</td>
</tr>
</tbody>
</table>
The Norte and Valencia Wellfields Area

For this area the data are: area = 8200 ha; natural aquifer flow $Q_1 = 175,000 \, m^3/d$; concentration in $Q_1$, $C_1 = 2 \, mg/L$; concentration of the return flow $Q_2$, $C_2 = 30.44 \, mg/L$; and concentration of the total ground water flow $Q_3 = (Q_1 + Q_2)$, $C_3 = 10 \, mg/L$. Using these data in Equation 2 yields that the total return flow $Q_2 = 68,493 \, m^3/d$. Since the per capita return flow is $180 \, L/day$, then the population needed to produce the estimated total return flow is simply $68,493/0.18 = 380,517$ people, for a demographic density of $380,517/8200 = 46.4 \, people/ha$ or $4640 \, people/km^2$.

Potrerillos Wellfield Area

The data in this case are: area = 7100 ha; natural ground water flow $Q_1 = 154,000 \, m^3/d$; $C_1 = 2 \, mg/L$; $C_2 = 30.44 \, mg/L$; and $C_3 = 10 \, mg/L$. With these data, the total return flow is, according to Equation 2, $Q_2 = 60,274 \, m^3/d$. Since the per capita return flow is $0.18 \, m^3/d$ ($= 180 \, mg/L$), then the population needed to produce the total return flow is $60,274/0.18 = 334,885$ people. The corresponding demographic density is $334,885/7100 = 47.2 \, people/ha = 4720 \, people/km^2$.

Land Use Planning

Based on water quality preservation criteria, it seems prudent to recommend a population density not in excess of 45 people/ha in urbanized, unsewered areas. Population densities in excess of this recommended threshold require the installation of adequate sewage systems. Otherwise, unacceptable ground water quality would be experienced at or in areas downstream from the newly urbanized areas. It is important to bear in mind that this study deals only with domestic sewage discharge. Industrial waste water must be treated separately because it involves other types of chemical constituents.

Summary and Conclusions

A method has been proposed to plan unsewered urban growth over aquifer recharge areas. Assumptions were made about basic input parameters due to limited field data. Other assumptions on water quality processes were also unavoidable, and these suggest a need for further investigations on the subject matter. In summary, it was assumed that a homogeneous mixture of ground water and nitrogen is achieved. This is not necessarily true, as there could be layers with different water qualities within the aquifer.

The estimated leached amounts of pollutant inputs were adopted from specialized studies. Wide ranges exist in the available data, and considerable uncertainties pervade the actual influence of nitrogen on the quality of the resultant water.

The diluting effect on nitrogen by percolating rain water was calculated from the average annual amount of precipitation that percolates to the water table. This precipitation recharge was assumed to be uniformly distributed throughout the year. In truth, precipitation recharge is seasonal, concentrated during the May through November wet months. The seasonal pattern of applied nitrogen dilution in the soil could produce fluctuations in the chemical and physical characteristics of ground water not taken into account in this study. These fluctuations may be revealed by improved monitoring programs.

The actual distribution of nitrogen fertilizer application in the recharge area must be better delineated by canvassing the sources of fertilizer applications.

The identification of ground water protection guidelines in the Costa Rican Central Valley is a complex task involving multiple parameters that must be better quantified and considered. This is due to the highly complex ground water regime, which involves several aquifers, a heterogeneous land use pattern, a seasonal nitrogen input, a variable hydraulic system, and specific pollutant characteristics. Therefore, this study represents an initial attempt to quantify the effects urban growth may exert on ground water quality. The land use guidelines emerging from this study are not definitive. Rather, they are a baseline for policy making, which is subject to revision as better data and water quality process modeling become available.

Acknowledgments

The author would like to thank Dr. Stephen Foster (British Geological Survey) for his collaboration in planning the methodology of this study; Engr. Federico Arellano Artig (AyA, Wells Department) for his suggestions and recommendations about water-pollutant relationships; and Dr. Jenny Reynolds (Universidad Nacional, School of Biology) for her help in relation to agricultural land use and the behavior of fertilizers. Thanks also go to Engr. Oscar Jimenez for his corrections to the manuscript and to Ana C. Hernandez for typing the text in its original form. Special thanks to Engr. Arturo Rodriguez (AyA, Pipelines Department) for reading and analyzing this report and suggesting essential corrections. This study was made at the Water Resources Department of the Costa Rican Institute of Water Supply and Sewage.

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**Biographical Sketches**

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Experimental and Numerical Study of the Transport of Acid Solutions and Copper in Tailings Impoundments

by José Francisco Muñoz and Pablo Rengifo

Introduction

The migration of chemical substances in soils is a complex phenomenon to which a great deal of importance is currently attributed. The study of such migration may be performed through the application of mathematical models that must take into account the characteristics of the soil or porous medium and the various chemical, physical, and biological processes involved in each case. However, each situation involving the migration of chemical substances through a porous medium constitutes a unique case since some or all of the following phenomena may intervene to a greater or lesser degree: advection, dispersion, adsorption, solubilization, removal, and decay.

In situ acid leaching in tailings impoundments (i.e., the waste material resulting from conventional ore dressing processes impounded behind dams) is being considered as an alternative by the Chilean mining industry for the extraction of copper metal. This process consists of the recovery of metals from minerals in the tailings by dissolution with an acid solution forced through the ore body (the tailings deposit), a naturally permeable medium, without causing any apparent changes in the physical properties of the tailings deposit.

Any leaching process of this type involves a superposition of various physical and/or chemical phenomena, such as the transport of the

Abstract

A two-dimensional mathematical model for acid leaching of copper from mine tailings using injection and pumping wells is presented. The model considers the transport mechanisms of convection and dispersion with reactions that govern the fates of copper and acid. Reactions considered are acid neutralization, copper solubilization, and copper adsorption. The results of acid leaching experiments in laboratory columns (one-dimensional) and in the field at a tailings impoundment are presented. The proposed model was validated for a one-dimensional experiment, and the model parameter fitting was found to be adequate in terms of the field experiment.
leaching agent, the chemical interaction between the lixiviant and the ore, and the transport of the resulting leachate. This process may be described conceptually and mathematically as consisting of the simultaneous transport of two solutes through a given porous medium, but with differing physical and/or chemical interactions occurring during the migration of each through the medium. A model of this type necessarily involves hydrodispersive and physicochemical parameters. The parameters must be determined by means of an adequate experimental design to enable the parameters to be estimated independently.

Given the horizontal stratigraphy typically present in tailings impoundments, it is possible to force the leaching solution (sulfuric acid) through the impoundment using a system of injection wells and to subsequently recover the pregnant leaching solution containing copper sulfate by means of pumping wells. Optimization of this copper recovery system requires the adequate determination of the locations for the wells, the injection and pumping flows, and the definition of the initial acidity of the leaching solution.

The purpose of this study is to develop a mathematical model to adequately represent the phenomenon of leaching while having the capability to simulate the copper extraction process under a variety of design and operating conditions, such as changes in the number of wells and their pattern of arrangement in the tailings impoundment basin, operational flows, and the initial acidity of the leach solution. The model also must be capable of enabling economic evaluations for projects of this type, along with the assessments of potential environmental impacts that may be caused on downstream aquifers due to the use of sulfuric acid.

**Modeling**

**Overview**

When the leaching solution migrates through the tailings, the acid in the injected solution reacts with solid copper mineral particles within the soil constituting the tailings deposit. The dissolution of solid copper with sulfuric acid results in soluble copper sulfate that migrates with the bulk flow through the tailings. Thus, two solutes (acid and copper) are present simultaneously in the flowing solution. These solutes additionally interact between themselves, thus giving rise to the following two well-defined phenomena: (1) the movement of the solution (a mixture of water, acid, and copper) flowing through the tailings material, represented by the flow equation for a fluid moving through a porous medium; and (2) the movement of solutes (acid and copper) within the solution, represented by the solute transport equation for porous media, in which the mechanisms of convection, mechanical dispersion, and molecular diffusion are taken into account, along with the phenomena of sorption and decay that may affect each solute.

**Flow Equation**

The equation describing the movement of the solution through an anisotropic porous medium as a function of position and time (two dimensions) for a homogeneous, compressible fluid may be stated as follows (Pinder and Bredehoeft 1968):

\[
\frac{\partial}{\partial x} \left( T_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left( T_y \frac{\partial h}{\partial y} \right) = S \frac{\partial h}{\partial t} - Q_{ext}
\]

where \( h \) is the hydraulic head [L]; \( T_x \) and \( T_y \) are the transmissivity in the \( x \) and \( y \) directions respectively [L\(^2\)/T]; \( S \) is the storage of the medium [L\(^3\)/L\(^2\)]; and \( Q_{ext} \) is the flow added or removed from the medium externally per unit of area [L\(^3\)/L\(^2\)/T].

**Solute Transport Equation**

The solute transport equation for solutes in a porous medium, assuming a two-dimensional case and considering the effects of convection and hydrodynamic dispersion, sources, or sinks, and the chemical reactions involved, and ignoring the effects of molecular diffusion, may be stated as follows (Bear and Bachmat 1990):

\[
\rho \frac{\partial S_i}{\partial t} + n_x \frac{\partial C_i}{\partial x} = \frac{\partial}{\partial x} \left( n_x D_{xx} \frac{\partial C_i}{\partial x} \right) + \frac{\partial}{\partial y} \left( n_y D_{xy} \frac{\partial C_i}{\partial y} \right)
\]

\[
- \frac{\partial}{\partial x} \left( n_x V_x C_i \right) - \frac{\partial}{\partial y} \left( n_y V_y C_i \right) + W_i(S_i, C_i, t) + A(x,y,t)
\]

where \( C_i \) is the concentration of solute \( i \) in solution [M/L\(^3\)]; \( S_i \) is the concentration of solute associated with the solid phase [M/M]; \( V_x \) and \( V_y \) are the seepage velocities in the \( x \) and \( y \) directions, respectively [L/T]; \( D_{ij} \) is the hydrodynamic dispersion coefficient [L\(^2\)/T]; \( n_e \) is the effective porosity of the medium [L\(^3\)/L\(^2\)]; \( W_i(S_i, C_i, t) \) is the component resulting from internal changes (for example, chemical reactions) [M/L\(^3\)/T]; \( A(x,y,t) \) is the component resulting from external influences [M/L\(^3\)/T]; \( \rho \) is the density of the material [M/L\(^3\)].

**Application of the Transport Equation to the Migration of Acid**

The sulfuric acid (a solute) becomes neutralized during migration through the porous medium, i.e., it is consumed as a result of interactions with a number of minerals found in the medium, particularly copper. All of these reactions can be grouped in one term, \( W_i(S_i, C_i, t) \), assumed to be a first order decay process that is a function of the concentration of H\(_2\)SO\(_4\) (Montero et al. 1994). The equation representing this consumption may be stated as follows:

51
W_{H_2SO_4} = -n_e \mu C_{H_2SO_4}

(3)

where \( W_{H_2SO_4} \) is the change (loss) in the acid concentration in the liquid phase per unit of solution volume and per unit of time [M/L^3T], \( \mu \) is a consumption coefficient of first order [T^-1]; and \( C_{H_2SO_4} \) is the acid strength in the solution [M/L].

By substituting Equation 3 in Equation 2, the following equation is obtained for acid transport:

\[
\frac{\partial C_{H_2SO_4}}{\partial t} = 
\left( \frac{\partial}{\partial x} \left( D_{xx} \frac{\partial C_{H_2SO_4}}{\partial x} \right) \right) + 
\left( \frac{\partial}{\partial y} \left( D_{xy} \frac{\partial C_{H_2SO_4}}{\partial y} \right) \right)
\]

\[
+ \left( \frac{\partial}{\partial t} \left( D_{xt} \frac{\partial C_{H_2SO_4}}{\partial t} \right) \right) + \left( \frac{\partial}{\partial y} \left( D_{yt} \frac{\partial C_{H_2SO_4}}{\partial y} \right) \right)
\]

\[
- \frac{\partial}{\partial x} (V_x C_{H_2SO_4}) - \frac{\partial}{\partial y} (V_y C_{H_2SO_4}) - \mu C_{H_2SO_4} + \frac{A}{n_e} (x,y,t)
\]

Application of the Transport Equation to the Migration of Copper

The mobility of copper particles in the mass of tailings material is governed by two well-defined phenomena. The first phenomenon is a chemical reaction occurring between the leaching agent (H_2SO_4) and copper particles, whereby the copper present in the grains of tailings material is dissolved as copper sulfate, thus passing from the solid state to the liquid state (i.e., extraction). The second phenomenon is the adsorption of soluble copper onto the solid phase (i.e., removal). The change in copper concentration in the solid phase may thus be expressed as the combined effect of these two mechanisms: extraction and adsorption.

The leach kinetics (extraction) can be expressed by the following equation (Braun et al. 1974):

\[
W_{Cu}(S_{Cu}, C_{H_2SO_4}) = n_e k_s C_{H_2SO_4} S_{Cu}
\]

(5)

where \( W_{Cu}(S_{Cu}, C_{H_2SO_4}) \) is the change (gain) in the copper concentration in the liquid phase per unit of solution volume and per unit of time [M/L^3T]; \( k_s \) is a kinetic constant of the first order [T^-1]; and \( C_{H_2SO_4} \) is the copper concentration in the solid phase [M/M].

The copper adsorption (removal) phenomenon can be modeled through the use of a linear isotherm:

\[
S_{Cu} = k_d C_{Cu}
\]

(6)

where \( k_d \) is a dimensionless distribution constant.

By substituting Equations 5 and 6 in Equation 2, the following equation is obtained for the transport of copper:

\[
R_{Cu} \frac{\partial C_{Cu}}{\partial t} = 
\left( \frac{\partial}{\partial x} \left( D_{xx} \frac{\partial C_{Cu}}{\partial x} \right) \right) + 
\left( \frac{\partial}{\partial y} \left( D_{xy} \frac{\partial C_{Cu}}{\partial y} \right) \right)
\]

\[
+ \left( \frac{\partial}{\partial t} \left( D_{xt} \frac{\partial C_{Cu}}{\partial t} \right) \right) + 
\left( \frac{\partial}{\partial y} \left( D_{yt} \frac{\partial C_{Cu}}{\partial y} \right) \right)
\]

\[
- \frac{\partial}{\partial x} (V_x C_{Cu}) - \frac{\partial}{\partial y} (V_y C_{Cu}) + k_d C_{Cu} S_{Cu} + \frac{A}{n_e} (x,y,t)
\]

where \( R_{Cu} = 1 - \frac{n_e}{n_e} k_d \) is the retardation factor.

Therefore, the total change in copper concentration in the solid phase is the sum of Equations 5 and 6, viz.:

\[
\frac{\partial S_{Cu}}{\partial t} = k_d \frac{\partial C_{Cu}}{\partial t} - \frac{n_e}{n_e} k_s S_{Cu} C_{H_2SO_4}
\]

(8)

The initial concentration of Cu in the solid phase is defined by the ore grade and is denoted by \( G \) [M/M]. Laboratory tests (Montero et al. 1994) demonstrate that only a part of this concentration (\( \lambda \)) can be leached. Hence, the initial condition for the copper concentration in the solid phase is expressed by:

\[
S_{Cu} = \lambda \frac{G}{100}
\]

(9)

where \( \lambda \) is determined experimentally.

General Model Functional Characteristics

The equations for flow (1), acid transport (4), copper transport (7), and the extraction and removal of copper (8), together with the boundary and initial conditions, define the mathematical model. This set of interrelated differential equations requires the use of several parameters, most of which must be determined by experimental means.

The major hypotheses and assumptions made in the development of the proposed model are as follows:

1. Flow is constrained in a horizontal plane (two-dimensional flow).
2. Darcy’s Law is valid, and the hydraulic head gradients are the only mechanisms responsible for establishing flow.
3. Porosity and hydraulic conductivity are uniform in space and constant in time.
4. The density, viscosity, and temperature gradients of the flow do not affect the distribution of velocities.
5. Values of head and concentration are vertically uniform.
6. The porous medium is incompressible and completely saturated and is homogeneous and isotropic with respect to the transverse and longitudinal dispersion coefficients.
7. Molecular diffusion effects are to be ignored.
8. The consumption of acid is modeled proportional to its strength.
9. The extraction of copper is by means of kinetics of the first order.
10. The removal of dissolved copper is modeled by instantaneous, reversible linear sorption.

In order for the model to function suitably, the various equations used to define problems must be clearly related. The model works by substituting the solution for the flow equation into the transport equation in order to obtain a solution representing the acid strength (\( C_{H_2SO_4} \)). This stage of modeling requires that we know the value of the parameters \( \mu \). Thereafter, the solutions from the flow and
acid equations are substituted into the copper transport equation, thus obtaining a solution representing the distribution of copper concentration in space and time in both the leaching solution \( (C_{Cu}) \) and the solid phase \( (S_{Cu}) \). This stage of modeling requires knowledge of the values of the parameters \( R_{Cu} \), \( k_5 \), and \( \lambda \).

**Column Leaching Tests**

Leaching tests were carried out in three laboratory columns for the purpose of validating the proposed model.

The experimental setup for test columns is illustrated in Figure 1, with further details provided in Table 1. The major properties of the tailings are shown in Table 2.

![Experimental setup](image)

**Table 1**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of material, ( L (\text{cm}) )</td>
<td>41.00</td>
<td>41.60</td>
<td>42.10</td>
</tr>
<tr>
<td>Section, ( A (\text{cm}^2) )</td>
<td>38.02</td>
<td>38.61</td>
<td>38.31</td>
</tr>
<tr>
<td>Moisture content (( \text{cm}^3/\text{cm}^3 ))</td>
<td>0.341</td>
<td>0.341</td>
<td>0.359</td>
</tr>
<tr>
<td>Bulk density (gr/cm(^3))</td>
<td>1.630</td>
<td>1.590</td>
<td>1.590</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific weight of solids</td>
<td>2.70</td>
<td>2.70</td>
</tr>
<tr>
<td>Copper contents (%)</td>
<td>0.19</td>
<td>0.27</td>
</tr>
<tr>
<td>( d_{10} (\text{cm}) )</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>( d_{50} (\text{cm}) )</td>
<td>0.012</td>
<td>0.015</td>
</tr>
<tr>
<td>( d_{90} (\text{cm}) )</td>
<td>0.03</td>
<td>0.035</td>
</tr>
</tbody>
</table>

At the onset of experimental work, a tracer test was performed with sodium chloride (NaCl) in each column to determine the hydraulic dispersion and pore velocity parameters independently from the parameters governing the overall leaching phenomenon from the results of the chloride (\( Cl^- \)) breakthrough curve. Thereafter, an acid solution was run through the three columns in order to study the leach process on a macroscopic basis and to estimate the physicochemical parameters governing this process.

![Distribution curves for Cl concentration at the outlet of Column 1](image)

**Figure 2. Distribution curves for Cl concentration at the outlet of Column 1.**

The results of the tracer test conducted with sodium chloride are shown in Table 3. The \( Cl^- \) concentration of each sample was determined by titration using standard A\(_5\)NO\(_3\) solution with potassium chromate as an indicator. Figure 2 gives the fit obtained by the model at the outlet of each column. Pore velocity was determined by direct measurement through obtaining flow samples at the column outlet. Water contents (\( q \)) were estimated directly by measuring the weight of dry and wet material for a like sample volume contained in the column. Finally, hydrodynamic dispersion was obtained through the use of a parameter fitting process (Montero et al. 1994) by using an analytical solution (van Genuchten and Alves 1982).

A retardation factor slightly greater than unity was determined for chloride \( (R_{Cl}) \), see Table 3. Aside from experimental error, there are other possible reasons for this value of \( R_{Cl} \), such as anion adsorption (Shackelford and Redmond 1995).

**Table 3**

<table>
<thead>
<tr>
<th>Property</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T^* (\text{°C}) )</td>
<td>15.7 ± 0.5</td>
<td>15.7 ± 0.5</td>
<td>15.7 ± 0.5</td>
</tr>
<tr>
<td>( V_X (\text{cm/sec}) )</td>
<td>3.275 ± 0.154 \times 10^{-4}</td>
<td>2.697 ± 0.057 \times 10^{-4}</td>
<td>2.233 ± 0.042 \times 10^{-4}</td>
</tr>
<tr>
<td>( D_X (\text{cm}^2/\text{sec}) )</td>
<td>3.275 ± 0.154 \times 10^{-4}</td>
<td>4.167 ± 0.645 \times 10^{-4}</td>
<td>1.586 ± 0.073 \times 10^{-4}</td>
</tr>
<tr>
<td>( R_{Cl} )</td>
<td>1.168 ± 0.0050</td>
<td>1.210 ± 0.0188</td>
<td>1.175 ± 0.0035</td>
</tr>
<tr>
<td>( \rho )</td>
<td>0.9994</td>
<td>0.9987</td>
<td>0.996</td>
</tr>
</tbody>
</table>
The equations representing the acid leaching phenomenon for the one-dimensional case may be stated as follows:

1. Analytical transport model for the acid. The governing equation is:

\[
\frac{\partial C_{\text{H}_2\text{SO}_4}}{\partial t} = \frac{\partial}{\partial x} \left( D_x \frac{\partial C_{\text{H}_2\text{SO}_4}}{\partial x} \right) - \frac{\partial}{\partial x} (V_x C_{\text{H}_2\text{SO}_4}) - \mu C_{\text{H}_2\text{SO}_4} \tag{10}
\]

The boundary and initial conditions for a steady-state water flow, assuming that a solute solution of known \( H_2SO_4 \) concentration \( (C_{\text{H}_2\text{SO}_4})_0 \) is applied at the soil column surface for given duration, \( T \), are expressed as:

\[
\begin{align*}
C_{\text{H}_2\text{SO}_4} &= 0 \quad x \geq 0, \quad t = 0 \\
\frac{\partial C_{\text{H}_2\text{SO}_4}}{\partial x} &= 0 \quad x = \infty, \quad t \geq 0 \\
V_x (C_{\text{H}_2\text{SO}_4})_0 &= -D_x \frac{\partial C_{\text{H}_2\text{SO}_4}}{\partial x} + V_x C_{\text{H}_2\text{SO}_4} \quad x = 0, \quad 0 \leq t \leq T
\end{align*}
\]

The analytical solution given by van Genuchten and Alves (1982) is:

\[
C_{\text{H}_2\text{SO}_4}(x = L,t) = (C_{\text{H}_2\text{SO}_4})_0 A(x,t) + (C_{\text{H}_2\text{SO}_4})_0 B(x,t) \tag{12}
\]

where:

\[
A(x,t) = \exp(-\mu t) \left[ 1 - \frac{1}{2} \text{erfc} \left( \frac{x - V_x t}{2 \sqrt{D_x t}} \right) \right] - \sqrt{\frac{V_x^2 t}{\pi D_x}} \text{exp} \left( \frac{-x^2 - V_x t^2}{4D_x t} \right) + \frac{1}{2} \left( 1 + \frac{V_x x}{D_x} \right) \text{exp} \left( \frac{V_x x}{D_x} \right) \text{erfc} \left( \frac{x + V_x t}{2 \sqrt{D_x t}} \right)
\]

\[
B(x,t) = \frac{V_x}{V_x + W} \text{exp} \left( \frac{V_x W x}{2D_x} \right) \text{erfc} \left( \frac{x - W t}{2 \sqrt{D_x t}} \right) + \frac{V_x}{V_x - W} \text{exp} \left( \frac{V_x + W x}{2D_x} \right) \text{erfc} \left( \frac{x + W t}{2 \sqrt{D_x t}} \right) + \frac{V_x^2}{2 \mu D_x} \exp \left( \frac{V_x^2}{D_x} - \mu t \right) \text{erfc} \left( \frac{x + V_x t}{2 \sqrt{D_x t}} \right)
\]

and \( W = \sqrt{V_x^2 + 4 \mu D_x} \)

2. Numerical transport model for the copper. The governing equation is:

\[
R_{\text{Cu}} \frac{\partial C_{\text{Cu}}}{\partial t} = \frac{\partial}{\partial x} \left( D_x \frac{\partial C_{\text{Cu}}}{\partial x} \right) - \frac{\partial}{\partial x} (V_x C_{\text{Cu}}) + k_C C_{\text{H}_2\text{SO}_4} S_{\text{Cu}} \tag{13}
\]

The boundary and initial conditions are given by:

\[
\begin{align*}
C_{\text{Cu}} &= 0 \quad x \geq 0, \quad t = 0 \\
\frac{\partial C_{\text{Cu}}}{\partial x} &= 0 \quad x = \infty, \quad t \geq 0 \\
0 &= -D_x \frac{\partial C_{\text{Cu}}}{\partial x} + V_x C_{\text{Cu}} \quad x = 0, \quad t \geq 0
\end{align*}
\]

The Cu transport equation was solved through an implicit finite difference scheme (Vauclin et al. 1979).

3. Copper extraction and sorption equation. The representative equation is given by:

\[
\frac{\partial S_{\text{Cu}}}{\partial t} = k_d \frac{\partial C_{\text{Cu}}}{\partial t} - \frac{\partial}{\partial x} \left( \frac{\rho}{k_S} S_{\text{Cu}} C_{\text{H}_2\text{SO}_4} \right) \tag{15}
\]

The operational conditions under which the column leach tests were performed are listed in Table 4. The initial concentrations of acid and copper in the medium are denoted by \( C_i \). The concentrations of acid and copper in the inflow are denoted by \( C_0 \).

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Operational Conditions for Leach Test in Each Column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg/L)</td>
<td>Column 1</td>
</tr>
<tr>
<td>( C_i (H_2SO_4) )</td>
<td>0.00</td>
</tr>
<tr>
<td>( C_i (H_2SO_4) )</td>
<td>9287</td>
</tr>
<tr>
<td>( C_i (Cu) )</td>
<td>0.17</td>
</tr>
<tr>
<td>( C_i (Ca) )</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The model parameters were estimated independently through the performance of the following three processes: (1) obtaining the hydraulic and dispersive parameters \( (D_x \) and \( V_x ) \) according to the analysis of the results obtained in the NaCl test run; (2) obtaining a value for \( \mu \) through fitting the experimental values obtained for \( H_2SO_4 \) concentrations at the outlet of the column with the values given by the model; and (3) obtaining the parameters \( k_d \), \( k_S \), and \( \lambda \) on the basis of fitting the copper concentration at the outlet of the column with the values given by the model.

Table 5 shows the result of the estimates of parameters, and Figure 3 shows the fitting obtained with the model for the evolution of the copper concentration measured at the outlet of Column 1. The model fit the data well.
<table>
<thead>
<tr>
<th>Property</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>14.2 ± 3.6</td>
<td>14.2 ± 3.6</td>
<td>14.2 ± 3.6</td>
</tr>
<tr>
<td>$V_x$ (cm/sec)</td>
<td>$2.686 ± 0.035 \times 10^{-4}$</td>
<td>$3.422 ± 0.045 \times 10^{-4}$</td>
<td>$2.456 ± 0.036 \times 10^{-4}$</td>
</tr>
<tr>
<td>$D_x$ (cm²/h)</td>
<td>$3.792 \times 10^{-4}$</td>
<td>$5.011 \times 10^{-4}$</td>
<td>$3.228 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\mu$ (L/sec)</td>
<td>$1.264 \times 10^{-4}$</td>
<td>$1.550 \times 10^{-4}$</td>
<td>$1.153 \times 10^{-4}$</td>
</tr>
<tr>
<td>$k_x$ (L/g/sec)</td>
<td>$4.944 \times 10^{-6}$</td>
<td>$6.783 \times 10^{-6}$</td>
<td>$4.042 \times 10^{-6}$</td>
</tr>
<tr>
<td>$R_{Cu}$</td>
<td>1.805</td>
<td>1.895</td>
<td>1.449</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.627</td>
<td>0.587</td>
<td>0.689</td>
</tr>
<tr>
<td>$C_{Cu}$ max (g/L)</td>
<td>1.68</td>
<td>1.850</td>
<td>3.14</td>
</tr>
<tr>
<td>$S_{Cu}$ start (g/g)</td>
<td>0.272</td>
<td>0.272</td>
<td>0.272</td>
</tr>
</tbody>
</table>

Figure 3. Distribution curves for copper concentration at the outlet of Column 1.

**Two-Dimensional Leaching Study**

Two-dimensional experiments were performed in the laboratory and in the field in order to study the technique of extracting copper from minerals contained in tailings impoundments by acid leaching with the use of injection and pumping wells.

**Laboratory Testwork**

The experimental facilities used were two parallelepiped-shaped vats of 0.5-m³ capacity (1 m by 1 m at the base by 0.5 m high), which were filled with tailings materials and set up with an arrangement of injection and pumping wells such as to enable two different types of flow to be achieved.

The feed solution was provided under a constant head placed on the injection wells, which was achieved through the use of an overflow system. Extraction of the pregnant leach solution was performed through pumping wells that were simulated by maintaining levels of the water table in the desired position.

The tailings used were selected such as to achieve a homogeneous, isotropic material. The filling of each vat was performed by placing previously liquified tailings in layers and allowing the material to drain at the bottom.

The injection and pumping wells installed were made out of pieces of PVC tubing 50 cm long and 20 cm in diameter, which were grooved along a 30-cm length at the middle. Additionally, each well was wrapped in plastic mesh material of 1-mm mesh opening and surrounded by a sand filter 2 cm thick, designed on the basis of the finest grain size fraction present in the tailings material. Each tank was also provided with observation wells equipped for obtaining 5-mL samples and piezometers to indicate the water level inside the tailings.

![Figure 4. Schematic arrangements of laboratory-scale leaching experiments.](image-url)
One experiment was conducted for each of the two geometric configurations of injection and pumping wells. The wells were arranged to provide the following two types of flow: (1) a one-way flow arrangement (Experiment 1), set up between two parallel rows of wells of constant height (see Figure 4a); and (2) a converging flow arrangement, made with four injection wells located at each of the corners of a square surface and a pumping well located in the center of the square (see Figure 4b).

The hydraulic and metallurgical characteristics and operating conditions of both of these experiments are shown in Table 6.

<table>
<thead>
<tr>
<th>Characteristics of Laboratory-Scale Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristics</td>
</tr>
<tr>
<td>Copper grade (%)</td>
</tr>
<tr>
<td>Specific weight (g/cm³)</td>
</tr>
<tr>
<td>Permeability (cm/sec)</td>
</tr>
<tr>
<td>Tailings volume (cm³)</td>
</tr>
<tr>
<td>Flow (L/sec)</td>
</tr>
<tr>
<td>Initial acidity (g/L)</td>
</tr>
<tr>
<td>Duration (days)</td>
</tr>
<tr>
<td>pH at outlet</td>
</tr>
</tbody>
</table>

Figure 5 shows the evolution of copper concentration measured at the outlet of both experimental configurations. A distinguishable difference was found in the effluent copper curves plotted for these two experiments. Major experimental results confirm that in the one-way flow experiment (Experiment 1), the peak in the leaching rate was almost two times greater than in the converging flow experiment. The time elapsed before achieving the peak leaching rate was longer in the one-way flow experiment (86 hours) than in the converging flow experiment (46 hours).

Also, the tailing of the elution curve after reaching the peak leaching rate (4.14 g/L for the one way flow and 2.13 g/L for the converging flow) was steeper in the one-way flow experiment than in the converging flow experiment. Finally, the final copper recoveries obtained from these two experiments after 50 days in operation, based on the total volume of tailings material placed in each vat for leaching, were 1100 g for Experiment 1 and 830 g for Experiment 2.

**Field Trials**

A leaching experiment was conducted at a tailings pond through the use of a battery of four injection wells (IW) and one pumping well (PW) arranged in a geometrical configuration similar to that used in Experiment 2 of the laboratory stage of testing, but based on the use of a square measuring 15 m on each side. Also, three observation wells (OW) were set up to provide a check on the hydraulic and metallurgical performance of each trial, as shown in Figure 6.

![Figure 6. Well locations.](image)

Table 7 shows the characteristics of the tailings material obtained by sampling with Shelby tubes and the pumping tests performed at the time the wells were drilled. It was evident that the tailings material at this site is made up primarily of sands, silt, and slimes, which are emplaced with a pronounced horizontal stratification.

<table>
<thead>
<tr>
<th>Material Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
</tr>
<tr>
<td>0 – 24</td>
</tr>
<tr>
<td>24 – 28</td>
</tr>
<tr>
<td>28 – 32</td>
</tr>
</tbody>
</table>

The dispersion characteristics of the aquifer were obtained on the basis of a tracer test without recirculation between a pumping well and an injection well. The test consisted of injecting a pulse of a tracer (NaCl) during a 1.67-day period and measurement of the concentration of Cl⁻ in the pumping well during a 14-day period. A porosity of 55 percent and a longitudinal dispersivity of 1.6 m were estimated on this basis.

The leaching trials consisted of the continuous injection of 2 L/s of an acid solution into the four injection wells and subsequent pumping out of the pregnant leaching solution through the pumping well. The duration of this experiment was 120 days, and the acidity of the solution injected into the tailings deposit was vari-
able at between 10 and 40 g/L. The variable employed for control of acidity was the pH of the solution pumped from the pumping well, which ranged between 2.5 and 3. The behavior of the phreatic level during the performance of these trials was not as expected due to the heterogeneous nature of the ground and due to the presence of impermeable areas that caused problems along with the formation of cracks and obstructions in the vicinity of the pumping well.

The copper extracted through the pumping well amounted to approximately 7000 Kg. This would indicate a recovery of 31 percent, assuming an average depth of tailings of 20 meters on a base measuring 15 m by 15 m.

Conclusions

In situ leaching of tailings by methods such as those proposed herein is feasible. The mathematical modeling of these phenomena satisfactorily predicted trends in the evolution of copper and acid in the laboratory columns. In effect, the vat leaching test gave clearly satisfactory results from the standpoint of copper recovery and hydraulic operational characteristics. However, work still remains to be performed in order to validate the two-dimensional model on the basis of information obtained from the two-dimensional laboratory vat leaching tests. Also, certain operational problems were encountered during the trials conducted in a natural setting in the field, such as obstructions in the pumping well and the development of piping in the tailings material. Such problems will be studied in greater detail. The proposed model also offers a tool for use in performing economic evaluations of large-scale copper recovery schemes and assessments of the potential environmental impacts that may arise from the use of acid and the solubilization of metals.

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Biographical Sketches

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