An Evaluation of Factors Affecting the Transport of Pharmaceutical Compounds and Pathogens in Selected Hawaii Soils for Land Application of Wastewater

Problem and Research Objectives

Mobility of viruses, bacteria, and other wastewater contaminants (including hormones) in subsurface media and their arrival in groundwater can have public health as well as aesthetic concerns. The sources of human and animal pathogens that may impact groundwater quality include land-applied sludge, manure, and wastewater; storage sites for manure; cesspools and septic tanks; leaky sewers; lagoons for the storage of human and animal wastes; barnyards; and feral animals. Wastewater and manure are also typical sources of hormones and other pharmaceutical compounds. Potential exists for pathogens and hormones/pharmaceuticals and other wastewater contaminants to leach through the soils and to finally reach the drinking water aquifers.

Generally, it is believed that the physical and chemical characteristics of the soil and to some extent the characteristics of the pathogens (as well as hormones) affect transport in subsurface media. If a soil is aggregated, it provides preferential pathways for pathogen- or hormone/pharmaceutical-containing water to pass through the topsoil. Fractures and cracks in subsoil accelerate the movement of this water. The clay and organic matter content of the soil affect the sorption of pathogens, hormones, and pharmaceuticals, while soil pH and the isoelectric point of the pathogens affect their attachment. Also, it is believed that the mineral oxides provide positively charged sites to retain these pathogens in the soil. The degree of saturation of the subsoil media may have some effect on the mobility of pathogens. If the water content is reduced, it is hypothesized that the travel path will be longer and the water film thickness with be smaller. A smaller thickness of the water film around the particles allows greater attachment potential of the pathogens to the particles.

An initial evaluation of a local soil (a tropical Oxisol) showed that it has high potential for retaining a large number of bacteria and viruses in the top three inches of packed soil columns. Oxisols contain a large percentage of clay-size particles and contain significant amounts of the oxides of iron, aluminum, and manganese. For this soil, batch-equilibration sorption experiments conducted for bacteriophage showed a high sorption distribution coefficient. As for bacterial sorption, although methodological problems caused some difficulties in quantitation, the initial results showed higher retention. Although this result has aroused widespread interest locally on the reuse of effluent on land directly overlying potable water aquifers, we strongly believe that additional laboratory and field evaluations are essential prior to undertaking large-scale land application efforts. More remains to be done in characterizing various soils in terms of their physical and chemical properties where land application of wastewater is being or is planned to be practiced. Most soils in temperate climates have fixed charges, whereas many soils in the tropics exhibit variable charges. In addition, quantification of attachment and detachment of the bacteria and viruses through batch-equilibration sorption tests or through flow-through column experiments needs to be evaluated.

The initial goal of this research was to evaluate the transport of pathogens and pharmaceutical compounds as influenced by soil properties, especially under Hawaii conditions. The planned study was proposed to be carried out over a two-year funding cycle. Since funding was provided for just one year, only the transport of selected wastewater contaminants and hormones was considered. Thus the objectives were modified to address the following:

1. How would the wastewater contaminants and hormones move through Hawaii soils?
2. Can the soil properties be manipulated by amendments to affect contaminant transport?
3. Can the existing models be used to quantify contaminant transport in the subsurface?

Methodology

In order to answer the above-outlined questions, the following tasks are being undertaken.

Task 1. How would the wastewater contaminants and hormones move through Hawaii soils?

In a related wastewater reuse project, secondary treated wastewater from the Honouliuli treatment plant on Oahu was characterized (W.M. Muirhead, E.M. Kawata, and R.W. Crites, 2003, “Assessment of recycled water irrigation in central Oahu,” presented at the 2003 WEFTEC Conference, Water Environment Federation, Alexandria, Va.). Table 1 provides a comparison of concentrations of seven chemicals found in groundwater with that found in secondary treated, filtered, and chlorinated effluent (called R1 effluent).

Table 1. Comparison of Concentrations of Trace Organics in Wastewater Prepared for Reuse With That in Central Oahu Groundwater

Constituent	R1 Effluent (ng/l)	Control Groundwater (ng/l)
Atrazine	210–400	<44
17β-estradiol	4.13	0.27
Estrone	224	0.94–3.99
Lindane	16–67	<8
N-nitrosodimethylamine (NDMA)	8.2	0.75
Nonylphenol	12,300	130–216
Octylphenol	15,800–29,600	150–190

Source: W.M. Muirhead, E.M. Kawata, and R.W. Crites, 2003, "Assessment of recycled water irrigation in central Oahu," presented at the 2003 WEFTEC Conference, Water Environment Federation, Alexandria, Va.

The predominant soils in the planned reuse areas of Oahu are the Oxisols. The Wahiawa Oxisol is the most prominent soil in these areas. This soil was retrieved from the Poamoho Experiment Station of the University of Hawaii at two depth ranges: (1) 30 to 60 cm depth, to avoid the influence of surficial organics (referred to as TOP here) and (2) 370 to 390 cm, from the saprolites (referred to as SAP here) where the soil is poorly developed. Table 2 provides the pH measured in water and in KCl, selected ions, and the organic matter of the soil at various depth ranges.

Table 2. Selected Physico-chemical Parameters for the Poamoho Soil of Central Oahu

Sample Depth Range (cm)	Soil Reaction		Ions				Organic Carbon (%)
	H_2O pH	KCl pH	P (mg/g)	K (mg/g)	Ca (mg/g)	Mg (mg/g)	
0 to 15	6.3	6.0	343.0	680.0	1,450.5	382	1.556
15 to 30	6.0	5.5	243.0	358.5	1,326.5	400.5	1.397
30 to 60	6.3	5.8	39.5	92.5	1,023	322	1.064
60 to 90	6.3	5.9	7.8	45.0	879	205	0.475
183 to 213	—	—	—	—	—	—	0.302

Air-dried and sieved (2.33 mm) soils were packed in stainless-steel columns with an internal diameter of 4.75 cm and a length of 7.60 cm to a bulk density of around 1.1 g/cm^3 (typical of that found in the field). Each column had a tensiometer in the mid-section to monitor the pressure. The bottom of the column was exposed to a pressure of around –5 cm . The column was saturated with a background solution from the bottom to expel the air out. The background solution was prepared from deionized water and 0.0005 M $CaCl_2$, resulting in a concentration of Cl^- equal to 36 mg/l. Such a level of Cl^- was found previously in leachate from the TOP soil column leached with deionized water. Using this composition of influent water, an attempt was made to minimize leaching of the Cl^- from the soil to prevent the breakdown of structure. After infiltration of one pore volume of background solution, the leaching solution was switched either to a tracer (bromide at 10 mg/l from KBr, referred to as pilot run here) or to a contaminant solution (in bromide tracer at 5 mg/l with the background leaching solution, known as artificial groundwater [AGW] and the R1 water). The concentrations of the spiked chemicals are presented in Table 3.

Table 3. Concentration of the Compounds in the Influent Water

Experiment	Compound							
	NDMA (mg/l)	Lindane (mg/l)	Nonylphenol (mg/l)	Octylphenol (mg/l)	Atrazine (mg/l)	17β-estradiol (mg/l)	Estrone (mg/l)	Bromide (mg/l)
Pilot run	—	0.4	0.1	0.2	0.008	0.004	0.002	10
AGW	2.5	0.002	0.2	0.4	0.008	5	5	5
R1 water	1	0.002	0.6	0.6	0.008	1	1	5

Note: For the R1 water experiment, the values are for the spiked concentration; actual concentration values can be higher due to background concentration.

After infiltrating the solute pulse at a steady flow rate, the inlet concentration was switched to that of the background solution. Then the experiment was continued to acquire the desorption phase of the breakthrough curve (BTC). Effluent was collected and analyzed regularly to develop the BTC. A schematic of the column setup is shown in Figure 1. The flow rate, column pressure, ambient and the solution temperatures, and the weights of individual columns were recorded electronically.

Figure 1. Schematic of experimental setup for conducting BTC experiment (left) and details of the soil-column assembly (right)

Several flow interruptions were made in the column experiments in which the inflow to the column was stopped for various time intervals to examine the degradation of the contaminants in the column. Breakthrough concentrations were prepared by sampling the effluent in a fraction collector and analyzing those using a combination of gas chromatography, high performance liquid chromatography (HPLC) either with a diode array detector or with a mass-selective (MS) detector. Lindane and the two phenols were first extracted with hexane. The hexane extract was directly injected into a gas chromatograph with an electron capture detector for the analysis of lindane. The extract was further evaporated with a stream of nitrogen, redissolved with a mixture of 50:50 acetonitrile and water, and analyzed by HPLC-MS. For estrone and estradiol, 50-ml water samples were lyophilized (freeze-dried) to dryness. The residue was transferred to autosampler vials after multiple rinses with acetone. The acetone solution was then evaporated to dryness under a stream of nitrogen. The residue was redissolved with 0.5 ml of 50:50 acetonitrile and water and analyzed by HPLC-MS. For the analysis of atrazine and NDMA, filtered effluent water samples were directly injected to the HPLC.

Task 2. Can the physical and chemical parameters be manipulated by amendments or by the physical setting of the site to affect contaminant transport?

Soil amendments such as gypsum and lime affect the pH of the soil. This could also shift the zero-point charge on clay surfaces. Addition of manure and other organic waste material can affect the transport behavior of chemicals. For this purpose, we will limit our experiments to the addition of a surfactant and natural organic matter to the soils. Planned experiments are similar to that conducted in the preliminary study (T.P. Wong and C. Ray, 2001, "Effect of polymer and surfactant on bacteria and phage rransport in subsurface," presented at the World Water and Environmental Conference, Orlando, Florida, May 20–24, 2001, American Society of Civil Engineers, Reston, Va.). Sorption and transport experiments are planned to examine the impact of these additives on contaminant and hormone mobility. At the end, lime and gypsum can be added to two columns as a pH modifier.

Task 3. Can the existing models be used to quantify contaminant transport in the subsurface?

Data from batch and column experiments can be used to estimate sorption parameters for modeling. Estimation of sorption parameters from batch equilibration tests for predicting transport in column experiments has limited use. Apparent equilibration is normally assumed in batch studies, whereas kinetic sorption behavior is needed to describe transport in columns. However, one difficulty arises if no breakthrough of hormones from the column is obtained in a reasonable amount of time. Breakthrough data for wastewater contaminants from soil columns can provide needed transport parameters for simulation.

Principal Findings and Significance

Task 1 is nearly done. However, due to analytical difficulties with some of the compounds, a number of experiments will be repeated. A no-cost extension has been received until February 2006. Tasks 2 and 3 will be undertaken in the remaining period of this project. Below are the principal findings.

As shown in Figure 2, bromide behaved like an ideal tracer with 50% of the feed concentration appearing in the leachate after the passage of one pore volume of leaching solution. Lindane, atrazine, and NDMA were the three other compounds that appeared in the breakthroughs of the TOP and SAP columns. NDMA behaves like a tracer. The BTCs for lindane and atrazine showed certain amounts of retardation in the TOP columns. However, there was negligible retardation of the BTC in the SAP columns. No breakthroughs of estrone and 17β-estradiol were found. The BTCs of octylphenol and nonylphenol showed significant variations. It was later discovered that the standards had significant impurities. A new set of experiments will be conducted for these phenols.

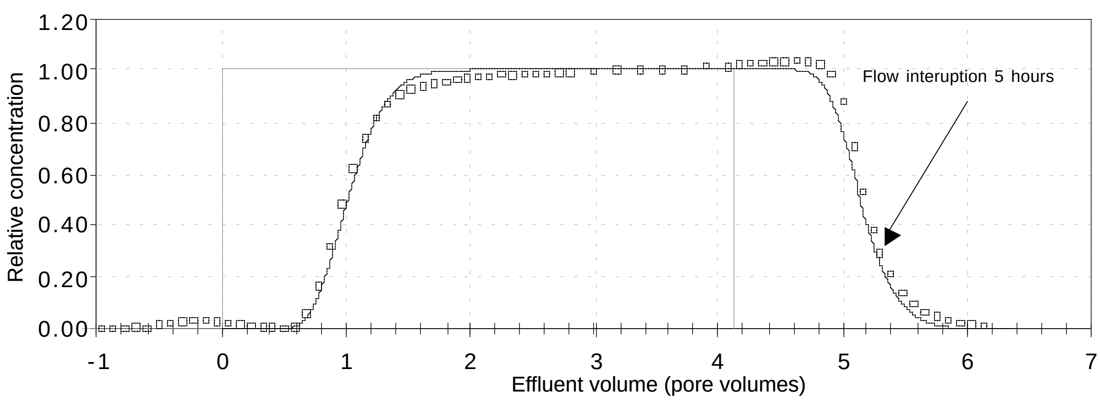

Figure 2. Bromide breakthrough curve from the pilot experiment

Currently, we are conducting inverse numerical modeling to obtain the parameters for the fate and transport of the studied contaminants in the TOP soil columns. Simulations are being conducted using HYDRUS 1D (J. Simunek, M. Sejna, and M.T. van Genuchten, 1998, The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media, version 2.0, IGWMC, Colorado School of Mines, Golden, Colo.). One presentation on the above work was made at the European Geosciences Union conference this year. The poster, entitled "Transport of selected wastewater contaminants in a tropical soil," by S. Mohanty, M. Snehota, C. Ray, J. Chen, and J. Lichwa, was presented to the European Geophysical Union General Assembly, April 24–29, 2005, Vienna, Austria.