Column Study of the Transport of Selected Contaminants in a Hawaii Soil Treated With Recycled Water

Michal Snehota
Jingyu (Joey) Chen
Sanjay Mohanty
Joseph Lichwa
Chittaranjan Ray

PREPARED FOR

Brown and Caldwell
119 Merchant Street, Suite 200
Honolulu, Hawaii 96813

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Principal Investigator: Chittaranjan Ray
WATER RESOURCES RESEARCH CENTER
University of Hawaii at Manoa
2540 Dole Street
Honolulu, HI 96822

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Executive Summary

The use of recycled water for landscape irrigation is considered by the Honolulu Board of Water Supply (BWS) as a means to reduce pumpage of fresh groundwater. In Hawaii, the most commonly used/produced recycled water is R-1 water, which has gone through secondary treatment followed by filtration and disinfection. Several wastewater treatment plants on Oahu either produce or have the potential to produce R-1 water. The central Oahu region is suited for the use of R-1 water because of the presence of agricultural land, golf courses, large parks, and highways. However, some of the most prolific aquifers of the island are also in central Oahu. Brown and Caldwell, Inc., in consultation with the BWS, conducted a field study to evaluate the leaching of common wastewater contaminants present in recycled water through the underlying soils. One component of the project was to estimate the concentrations of specific contaminants in the deep vadose zone and the ground water through mathematical modeling.

Estimation of the transport of wastewater contaminants in the vadose zone requires fluid flow and solute transport parameters that can only be determined from laboratory experiments. The Water Resources Research Center of the University of Hawaii was subcontracted with Brown and Caldwell, Inc. to conduct laboratory column experiments to obtain transport parameters for modeling.

The purpose of column experiments is to deliberately produce a breakthrough of the contaminants in recycled water at the bottom of short soil columns packed with a soil from central Oahu. Because many of the wastewater contaminants are present in very low concentrations, getting a breakthrough in laboratory columns may not be feasible in reasonable amounts of time. In addition to selecting small columns, it may be necessary to spike the effluent with high concentrations of the target compounds to make them appear at the bottom of the columns. Once a breakthrough curve (BTC) is developed for the effluent, from the shape and the peak values of the BTC, the transport parameters can be obtained by the inverse solutions of mathematical models that are used to predict the concentrations at the bottom of the soil columns. Thus we like to point out that the concentrations used for the breakthrough experiments were often thousands of times higher than that of actual recycled water, and the sole purpose of this experiment was to obtain the transport parameters for model studies in unsaturated surficial soils.

Methodology

The most predominant soils in central Oahu are the Oxisols. One soil, the Wahiawa Oxisol, was used for this study. This soil's reddish color is due to the presence of large amounts of iron oxides. The soil was collected from the Poamoho Agricultural Experiment Station of the University of Hawaii. The soils were collected from two depths for this study: the B horizon (30 to 60 cm depth zone) and the saprolite (370 cm to 390cm). The B horizon has less amounts of organic matter compared to the A (top) horizon and is less disturbed from plowing. The saprolite is basalt in its early stages of weathering. Normally, it is found at much greater depths and may contain chunks of basalt. The organic matter content of the saprolite is generally low.

Brown and Caldwell, Inc. reported the presence of seven organic contaminants in the wastewater. They are the pesticides atrazine and lindane, chlorination by-product nitrosodimethylamine (NDMA), the estrogen hormones estradiol and estrone, and octylphenol and nonylphenol. The Honouliuli treatment plant, that produced the R-1 water, is located in the Ewa peninsula of Oahu. The Oahu Sugar Company planted this area with sugarcane until it ceased operation in early 1990's. The ground water in this area contains pesticides such as atrazine and lindane. The sewer lines receive ground-water inflow through joint, which contributes to the presence atrazine and lindane in the wastewater. Estrogen hormone such as 17-β estradiol is present in wastewater and estrone is its breakdown product. The octyl- and nonyl-phenols are present in industrial cleaning compounds. The wash waters find their way to the sewers. All seven compounds have significant mammalian and aquatic toxicity.

Initially, a pilot study was conducted to estimate the hydraulic parameters of the soil column and the concentrations required for getting a breakthrough in a reasonable amount of time. Subsequently, two full-scale column-leaching experiments were conducted with (1) an artificial ground water (deionized water with small concentrations of calcium chloride) and (2) the R-1 water. The concentrations of most of the contaminants were increased in the full-scale experiments and the column dimensions were reduced to get a faster breakthrough. The soils from the B horizon, referred to as TOP and the saprolite referred to as SAP were packed in the columns to achieve a bulk density similar to that found in the field. In each case, the seven contaminants were spiked to the feed solution for certain amounts of time. The flow to the columns was interrupted in each experiment to obtain degradation parameters. In each experiment, bromide (from potassium bromide) was used as a reference chemical.

The column effluent and the eluates from the soil were analyzed for the seven contaminants as well as bromide using a combination of high performance liquid chromatography (HPLC) either with a mass selective (MS) detector or an UV-visible diode array detector, gas chromatography with an electron-capture detector, and ion chromatography. Sample concentrations and the analytical methods for this column study were somewhat different from that for the field study. Since the column study produced a limited amount of effluent at the bottom of the column, we had to deal with small volumes of samples often at concentrations higher than that of actual recycled water. Appropriate quality assurance measures were taken during the analyses.

Results

Bromide initially behaved like a conservative chemical (a tracer) during the pilot trial in the TOP, but it showed some sorption in the SAP. NDMA behaved like a tracer in the TOP and in the SAP, often moving faster than bromide. Atrazine and lindane showed moderate leaching potential. Estradiol and estrone did not move appreciably in the two soils. Estradiol appeared to be less stable than estrone. Generally, estrone is formed during the degradation of estradiol. In some column runs we noticed that the estrone concentrations increased toward the end of the experiment. Although estrone moved somewhat faster in the SAP than in the TOP, still the effluent concentrations were a mere fraction of a percent of the applied estrone. The concentrations were at or below detection limit for TOP. Most experiments with estradiol and estrone were conducted at or near their solubility limits to get a breakthrough within a few weeks. It was not possible to produce a breakthrough at lower concentrations. As a result, we had situations where estradiol or estrone precipitated in the solution. Temperature also affected the solubility. The lower temperature of the feed solution stored in a cooler to prevent degradation helped in precipitating the chemicals from the solution. Further, it was difficult to control bacterial degradation of the solution during the course of the experiment. As a result, the concentration of the feed solution fluctuated during the experiment.

Analytical difficulties with octylphenol and nonylphenol led to a breakthrough that seems questionable. Although a standard containing a given amount of the chemicals was used to make the feed solution, the concentrations of the feed stream samples were much lower than the amount in the standard. It was speculated that much of the loss occurred during fraction collection (over a period of days), sample concentration, and analysis. Further, the degradation of these chemicals in the soil column cannot be ruled out. Using a gas chromatograph – mass spectrometer (GC-MS) and its internal library, the standard was found to contain multiple peaks representing multiple compounds. Although the standard was available from a commercial source, its purity is questionable. The HPLC-

MS method did not involve the verification of the purity of the standard. As a result, this problem was not revealed early in the experiment and remained unresolved.

The volatility of lindane also posed some problems in the calculation of breakthrough concentrations. We speculate there might have been losses during fraction collection and sample analysis; however, the data were still reasonable to obtain the transport parameters from the leaching experiments. Differential temperatures for the feed solute and its exposure to air may have caused these discrepancies. Atrazine and NDMA produced the best results.

The adsorption parameter for NDMA was the lowest. The estrogens and phenols showed higher sorption to soil. Atrazine and lindane showed moderate sorption, with lindane sorbing more than atrazine.

The dispersion coefficient for the columns is on the order of 1 cm. The distribution coefficients ranged from 4.4×10^{-3} mL/g for NDMA to 1.8×10^{2} mL/g for estradiaol as well as estrone.

Conclusions
- Production of breakthrough of the estrogenic (estradiol and estrone) and phenolic (octylphenol and nonylphenol) compounds in small (3-inch-long) soil columns was difficult even when the feed solution contained these chemicals near their solubility limit.
- Breakthrough in TOP was more difficult than in SAP for all compounds except NDMA.
- NDMA moved like a tracer. Bromide in some instances showed slight adsorption to the column.
- Both atrazine and lindane showed moderate sorption behavior.
- Estradiol and estrone did not move appreciably in TOP to produce a breakthrough. Although traces of these compounds were found in the column effluent, the measured concentrations were low and often erratic in SAP.
- The concentrations of octylphenol and nonylphenol in the effluent were also low. However, the feed solution concentration varied erratically, possibly due to losses during sample collection and analysis and the impurities present in the standards.
- Residues of estradiol, estrone, and the phenols were found predominantly in the upper one-third of the columns of TOP after the experiments were finished. Very low amounts of residues present in rest of the column suggest their low mobility in TOP.

- Flow interruption during the leaching experiment enabled us to estimate the degradation parameters for some chemicals, such as atrazine.
- The column experiments did not account for microbial activity normally encountered in the organic-rich topsoil (A horizon). Thus the conditions for producing breakthroughs were extreme. Such conditions are not expected to occur in the field where R-1 water is applied to the topsoil of the A horizon at agronomic rates.

Recommendations

- It is recommended that the soil's physical and chemical properties be properly characterized prior to the development of recycled water projects.
- Volatilization losses should be minimized during the experiment. One way to reduce this is to limit the exposure time of vials to air in the fraction collector.
- In order to reduce the differential degradation, the sample reservoir and the fraction collector should be placed in a controlled low-temperature environment. The contaminants should be divided into two groups according to their mobility and the optimized experimental setup conducted separately for each group.
- The columns should be short and narrow to produce a quicker breakthrough in a short span of time. The minimum cross-sectional area of the column should be considered in order to get an adequate volume of water for chemical analysis.
- The contaminants should be divided into two groups according to their mobility, and the optimized experimental setup conducted separately for each group.

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1. Introduction

Ground water is the primary source of drinking water for all the islands of Hawaii. According to the U.S. Census Bureau[1], the estimated population for Oahu (which covers the City and County of Honolulu, CCH) was 902,704. On a given day, there could be one million residents and visitors combined, relying on ground water for drinking. With increasing population, there is also a gradual rise in water demand. The CCH currently disposes a major part of the wastewater that receives primary and secondary treatment into the ocean through outfalls. The U.S. Environmental Protection Agency (USEPA) is requiring CCH and many other coastal communities to consider alternatives for ocean disposal from the point of view of environmental pollution and impacts to biota. On Oahu, the traditional reuse areas overlie brackish water aquifers. These are also the areas designated for underground injection control. Oahu has a goal to reuse 20% of its wastewater in the near future. However, its coastal land area is too small to use all of this water. Consequently, there is a push to reuse treated effluent in the interior parts of the island for landscape and crop irrigation. The reuse of wastewater would also reduce pumpage of fresh ground water that is currently used for landscape irrigation. Thus, wastewater reuse has multiple benefits of (a) meeting regulatory requirements, (b) reducing the use of fresh ground water for irrigation, and (c) decreasing overdraft on aquifers due to population increases.

The interior parts of the respective islands lie over extensive basal aquifers which are the primary sources of water for each island. For example, the Pearl Harbor aquifer supplies 45 to 50% of all water consumed on Oahu. The depth to water table varies from less than 100 m to more than 300 m in targeted reuse areas. Despite this large depth to water table, the public is concerned about the use of effluent (even if treated, filtered, and disinfected) directly over the potable water aquifers. On Oahu, pesticides such as dibromochloropropane (DBCP) and ethylene dibromide (EDB) and pesticide impurities such as trichloropropane (TCP) have been found in drinking water wells located in central Oahu. Chemicals that travel past the root zones of crops could eventually appear in the basal aquifer. For example, DBCP, which was first used in 1959, took over 15 years to appear in drinking water wells (around mid 1970s). EDB, which was used between 1978 and 1985, has recently appeared in some wells at low concentration. TCP is a contaminant in the nematicides dichloropropane and dichloropropene (DD). It is found at the same or even higher concentration levels as DBCP. Treated wastewaters have been used in western states such as California and Arizona for ground water

[1] http://quickfacts.census.gov/qfd/states/15/15003.html

recharge. In these areas, the recharge wells or basins are located some distance away from the pumping wells. The travel times in these locations can be longer than on Oahu.

Typical contaminants in wastewater include dissolved solids, nutrients (nitrate and phosphate), organic chemicals such as pesticides, and dissolved organic carbon. It is also possible to find fecal bacteria and viruses in the effluent, depending on the degree of treatment. Other contaminants of concern are pharmaceuticals and personal care products and their metabolites, antibiotics, and hormones. Some of these compounds are not fully removed through traditional wastewater treatment processes. If wastewater is persistently used in one area, it can potentially migrate to aquifers and finally to public water supply wells.

Because many of these compounds are present in low concentrations nanograms to low micrograms per liter range, it is almost impossible to estimate their transport parameters in field settings in a reasonable amount of time. For example, many of these compounds initially will be adsorbed to soil organic carbon or degraded by microbes. However, their transport through the unsaturated zone aquifers can be more effectively addressed by conducting laboratory column experiments at elevated concentrations. Their possible appearance in ground water can be predicted through mathematical modeling.

Column studies are generally performed to characterize transport under well-defined initial and boundary conditions. Recent literature shows the importance of sorption kinetics and its impact on the leaching process. For example, (Fortin et al. 1997) performed flow experiments with a conservative tracer and the herbicide simazine on a packed column of loamy sand. They showed that the shape of the breakthrough curve was influenced by rate-limited and nonequilibrium sorption. Miscible-displacement studies on undisturbed and homogeneous soil columns were also conducted to study the influence of local-scale physical heterogeneity on the transport of trichloroethene (Johnson et al. 2003). These miscible-displacement studies were conducted under conditions of full saturation. Solute transport under unsaturated conditions is affected by lower water content, which may cause earlier breakthrough and longer tailing of the breakthrough curve (BTC) for conservative tracers due to the decreasing number of flow paths and the increased velocity variation (Padilla et al. 1999). (Kamra et al. 2001) conducted bromide and pesticide (atrazine and isoproturon) leaching experiments under unsaturated steady flow condition using 24 undisturbed columns. From these experiments, they estimated the transport parameters for the non-equilibrium model, based on the theory of mobile and immobile water. Only a few studies examined the

transport of hormones in soil. (Casey et al. 2003) performed soil column experiments using radioactively labeled hormones and fitted the breakthrough data using the HYDRUS 1D transport model. (Das et al. 2004) conducted batch sorption experiments as well as miscible-displacement experiments in columns packed with sand uniformly mixed with silty clay loam or in columns in which thin layers of silty clay loam was present in sand. The results of the forward modeling of the transport in column revealed that the Freundlich isotherm model is adequate for the description of hormone equilibrium sorption, but the first-order mass transfer in commonly used bicontinuum modeling was an approximation and therefore not accurate (Šimůnek et al. 1998).

The objective of this study was to determine the transport behavior of selected contaminants present in treated wastewater for a representative soil on the island of Oahu. The goals were achieved by conducting transport experiments in short laboratory columns, first using pure compounds (like those found in wastewater) in water solution, and later adding those pure compounds to treated wastewater.

2. Materials and Methods

2.1. Soil

The soil used in this study is an Oxisol (Rhodic Eutrustox, Wahiawa series). The soil was collected from the Poamoho Agricultural Experiment Station of the University of Hawaii. A detailed description of the soil at the Poamoho site is given in (Gavenda et al. 1996). The soil is formed in three layers from the parent material. The A horizon is developed from Asian aerosolic dust, the B horizon from volcanic ash, and the B2 horizon from basaltic residuum. The soil contains primarily kaolinite, with clays forming water-stable silt and sand-sized aggregates.

The typical particle density of soil is 2.93 g/cm^3. The bulk density in the A horizon ranges from 0.96 to 1.11 g/cm^3 and the typical bulk density of the B horizon is 1.33 g/cm^3 (Gavenda et al. 1996). Soils of the Wahiawa series have high residual water content due to the high proportion of micropores. Based on water retention measurements done on samples taken in central Oahu, (Miller et al. 1988) found the residual water content to range from 0.26 to 0.54 at 15,000 mm of suction. The organic carbon content reported by (Sanda et al. 2004) was 1.34% for the A horizon and 0.85% for the B horizon. The soil has net negative charge in both surface and subsurface horizons (Gavenda et al. 1996). Some of the physico-chemical properties of this soil are presented in Table1. Also, particle size data for this soil are presented in Appendix A.1.

Table 1. Selected Physico-chemical Parameters for the Poamoho Soil of Central Oahu

Sample Depth Range (cm)	Soil reaction			Cations				Organic carbon
	H$_2$0 pH	KCl pH	Δ pH	P (mg/g)	K (mg/g)	Ca (mg/g)	Mg (mg/g)	(%)
0 - 15	6.3	6.0	0.4	343.0	680.0	1450.5	382	1.556
15 - 30	6.0	5.5	0.6	243.0	358.5	1326.5	400.5	1.397
30 - 60	6.3	5.8	0.5	39.5	92.5	1023	322	1.064
60 - 90	6.3	5.9	0.4	7.8	45.0	879	205	0.475
183 - 213	-	-	-	-	-	-	-	0.302

Wastewater

The wastewater for this study was obtained from the City of Honolulu's Honouliuli Treatment Plant. The plant uses an activated sludge (secondary) treatment process. The treated wastewater is filtered and disinfected with ultraviolet (UV) light prior to reuse. Table 2 shows the concentrations of the organic constituents of interest in the two water sources used for field irrigation. First five are mean concentrations of measurements taken over the duration of the study (Brown and Caldwell 2005). The last two from early parts of the same study (Muirhead et al. 2003). We did not make any independent investigation on the content of these chemicals either in the R-1 water or in the control ground water used for the field study.

Table 2. Mean Concentrations of Trace Organics in R-1 Water Versus Control Ground Water

Constituent	R1 recycled water (ng/L)	Control ground water (ng/L)
Atrazine	47	48
17β-Estradiol	1.0	0.15
Estrone	7.2	0.2
Lindane	5.6	4.4
NDMA	11	2.9
Nonylphenol	12,300	130-216
Octylphenol	15,800-29,600	150-190

Sources: Data for atrazine, 17β-estradiol, estrone, lindane, and NDMA are from Brown and Caldwell (2005); data for nonylphenol and octylphenol from Muirhead et al. (2003).

In certain areas of Oahu, pesticides such as atrazine and lindane are present in soil and ground water. Sugarcane was grown in the Ewa plains where the sewer lines traverse before reaching the Honouliuli treatment plant. Atrazine was a major herbicide used by the plantations. Lindane was used as an insecticide in agriculture, for wood treatment, and in shampoo for lice control. We suspect that inflow and infiltration processes carry these chemicals from soils and ground water into the sewer system. As shown in Table 2, all of these compounds were present in various concentrations in control ground water. While atrazine and lindane were present in control ground water nearly at the same level

as R-1 water, the two estrogen hormones were present at low levels. Selected physical and chemical properties of these compounds are given in Table 3.

2.2. Soil column packing

Packed soil columns were prepared for the leaching study. Soil taken from the 30 to 60 cm depth zone represents the B horizon of the soil profile. Samples taken from this zone are denoted as TOP. Due to its lower organic carbon content, the B horizon soil was likely to allow faster breakthrough than the A horizon soil. Disturbed soil samples were taken using a hand auger. Samples of saprolite (SAP) were taken from the same boreholes. Extension tubes were attached to the auger to access deeper horizons. As the borehole drilling continued, the first traces of weathered rock appeared at a depth of 270 cm. Disturbed samples of SAP were taken from the 370 to 390 cm depth interval. Collected soil samples were kept in plastic bags and refrigerated until repacking. Replicate samples were taken from each of the two depth intervals. A total of seven columns (five TOP and two SAP) were used for the study.

Initially, one soil column was packed for a pilot experiment. The purpose of this pilot experiment was to evaluate the feasibility of attaining steady flow, suitability of automated tensiometers for pressure monitoring, ease of adjusting the rates of fraction collection at the outlet end of the column, and the methods to get other hydraulic and transport parameters. The soil column for the pilot experiment is referred to as TOP0. The soils were packed into a plexiglas cylinder (internal diameter of 7.6 cm × height of 6.0 cm). The rest of the soil columns were packed into stainless-steel cylinders (internal diameter 4.75 of cm × height of 7.60 cm) for the transport experiments. Narrower soil columns are more suitable for one-dimensional interpretation of the experiment results. The packing procedure was similar to that presented by (Fortin et al. 1997) and (Ni et al. 2004); but the pre-packing treatment was different. To simulate the field condition during the solute transport experiment, the bulk density of the soil column was kept close to that of the field samples found at the same depth in the place of excavation (~ 1.13 g.cm^{-3}). The soil was dried at 35°C to achieve a gravimetric water content of 20% and then sieved using U.S. sieve no. 8 (2.36 mm). The column was packed by gently compacting the soil in 0.5-cm layers, with uniform distribution of impacts achieved using a glazed ceramic rod. The bulk density was tested repeatedly after compaction of each layer to obtain a homogeneous distribution.

Table 3. Selected Physical and Chemical Properties of the Seven Constituents used in the Study

Constituent	Name	Physical Properties	Chemical Properties	Uses	Appearance
Lindane	1,2,3,4,5,6 hexaclorocyclo-hexane. $C_6H_6Cl_6$	Molecular weight (M.W.): 290.85. Solubility(g/100 g at 20°C): Acetone 43.5, ether 20.8, ethanol 6.4; almost insoluble in water		Insecticides	Crystal
Atrazine	6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine. $C_8H_{14}ClN_5$	M. W.: 215.68. Crystal, soluble at 25°C in water 70 mg/L; ether 12,000 mg/L; methanol 18000 mg/L.	Hydrolyzed to inactive hydroxyl derivative by alkali or mineral acids	Herbicides	Crystal
Octylphenol	(1,1,3,3-tetramethylbutyl)phenol	M. W.: 206.324			White crystal or powder
Nonylphenol	$C_{15}H_{24}O$	M. W.: 215. Soluble in benzene, chlorinated solvents, aliphatic alcohols, ethylene glycol and almost insoluble in water.	Slightly characteristic of phenolic odor	Uses in preparation of lubricating oil additives, resins, plasticizer, surface active agent	Pale yellow liquid
Estrone	3-Hydroxyestra-1,3,5(10)-trien-17-one. $C_{18}H_{22}O_2$	M. W.: 270.36. Solubility: 30 mg/L in water at 25°C. 20g/L at 150°C in acetone.		Use in preparation of commercial 19-non steroids.	Crystal form in acetone
17β-estadiol	Estra-1,3,5(10)-triene-3,17-diol	M. W.: 272.37	Stable in air, precipitate by digtonin	Hormones, a mixture of estradiol with merdoxy-progesterone 17- acetate are marketed as Provest	
NDMA	N-Methyl-N-nitroso-methanamine	M. W.: 74.08. Highly soluble in water, alcohol.		Formed during chlorination by-product of wastewater; additive for lubricants	Yellow liquid

Source: The Merck Index (2001)

Three soil columns of the same diameter but lower height (internal diameter 4.75 of cm ×
height of 3.80 cm) were prepared from each soil using identical packing methods. To
develop retention curves, a combination of tension table and pressure plate extractor
methods was used (Klute 1986). Parameters of the van Genuchten mathematical
expression (VG) were obtained for each retention curve by fitting the VG function to
measured values. Mean values of the parameters were then calculated for TOP and SAP
soil. Retention curves are shown in Figure 1 and the mean parameters are given in Table
4. Data for specific cores are presented in Appendix A.2. Flow rate through the column is
showed in Appendix A.3.

One micro-tensiometer was inserted into the soil column at the mid-point of column to
measure the suction pressure head during the transport experiment. The field values for
saprolite were not measured; therefore, an attempt was made to achieve the the same bulk
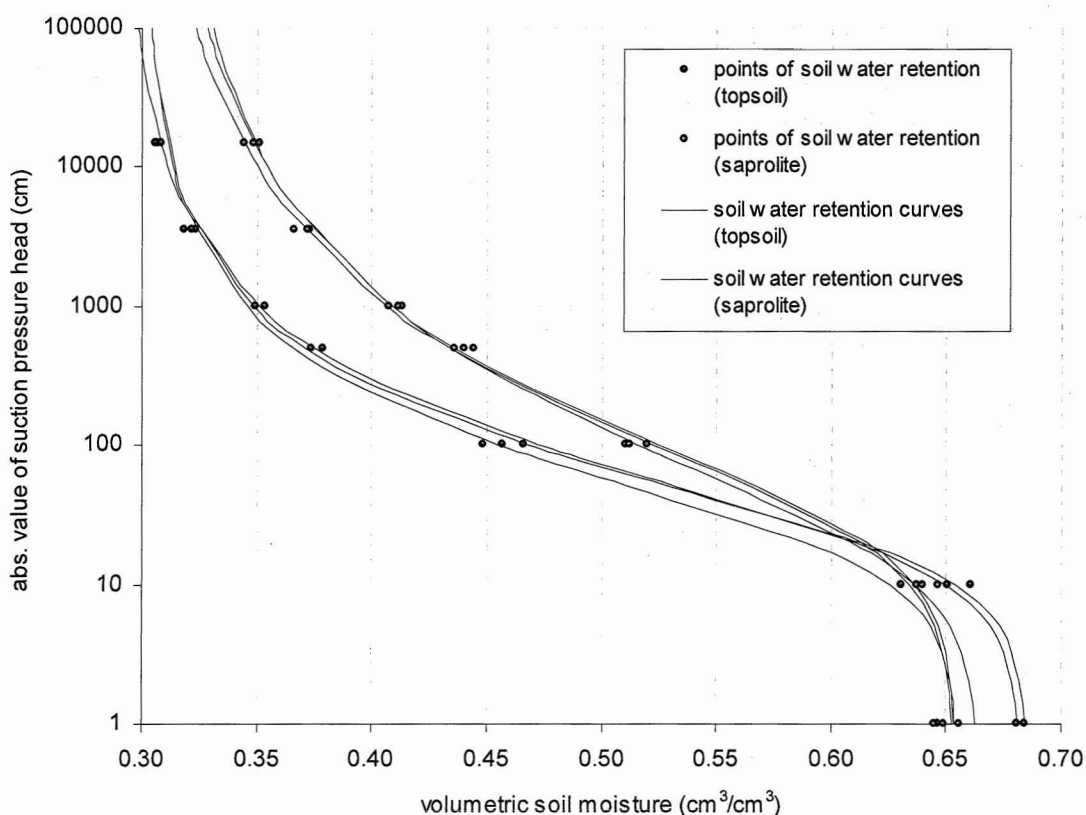densities in the SAP as in the TOP.

**Figure 1. Retention curves for TOP (blue) and SAP (red) soil. Measured values (points) were fitted
using the van Genuchten expression for retention curves (lines).**

2.3. Transport experiments

The pilot study of miscible displacement experiments was conducted on TOP0 to obtain BTC for a conservative tracer and the mixtures of the contaminants in Table 2, with the exception of NDMA. The principle of the experiment is similar to one presented by (Kamra et al. 2001). The packed soil column was positioned vertically. The column was saturated with a background solution from the bottom. 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 supplied with deionized water. Using this composition of influent water we tried to minimize leaching of the Cl^- from the soil structure. A small constant suction (-5 cm water pressure head) was applied at the bottom of the column to maintain an unsaturated or near-saturated condition. A constant flow of background solution was steadily supplied to top of the column, which remained at atmospheric pressure. The flow rate was adjusted in order to achieve steady-state flow with unit gradient of potential of driving forces, which results in uniform distribution of water content. 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) or contaminant solution (with bromide tracer 5 mg/L). After infiltrating the solute pulse at the steady-state flow rate, the inlet concentration was switched to that of the background solution. Then the experiment was continued to acquire the desorption phase of BTC. Effluent was collected and analyzed regularly to develop the BTC.

The column setup consisted of the following:
- the column assembly,
- a fraction collector for collecting column effluent samples in glass vials,
- an HPLC pump for uniform/accurate application of tracer/contaminant solution, and
- brown glass bottles for the storage of deionized water and the chemical solution.

The soil core was equipped with a tensiometer and a pressure transducer (PC236 Honeywell Microswitch). Pressure data were stored in a datalogger (21X Campbell Scientific, Inc.) at 10- to 60-second intervals, depending on the experimental run. Air temperatures of the room, as well as the temperature of the leachate collection chamber, were monitored at the same frequency as the soil-water suction. The experimental setup had a power backup system to cover power failures for up to 20 minute durations.

A fine wire mesh (TWP thread count 325 × 325, wire diameter 0.0014, air entry value ~18 cm water tension) was attached to the bottom of the soil column. The wire mesh was encased in a custom-made infiltration head and attached to the bottom of the soil column.

A Teflon FEP tubing connected the infiltration head to the fraction collector. The soil column assembly was elevated above the dripper of the fraction collector in order to gravitationally maintain a small water tension (~10 cm of water tension) in reference to the bottom of the column. The top of the soil column was covered by a thin layer of non-woven glass wool to distribute the water or tracer/contaminant solution from the drip source over the entire soil surface. The fraction collector and the bottles containing background solution, and the contaminant solution were placed in a large cooler. Low temperature was maintained by regular replacement of icepacks, to slow down the degradation of chemicals in the influent and the effluent. The temperature of the cooler's chamber was controlled between $6°C$ and $12°C$. A schematic as well as a picture of the flow cell is presented in Figure 2. The pumping system and the data-logging system are shown in Figure 3.

Table 4. Retention Parameters for Packed TOP and SAP Soil Samples

Soil	Depth (cm)	Retention curve parameters (van Genuchten expression)			
		θr	θs	α	n
Poamoho TOP	30–60	0.298	0.674	0.0434	1.530
Poamoho SAP	370–390	0.339	0.584	0.1690	1.343

The main miscible-transport experiments were conducted on the basis of the findings from the pilot study. Two experiments were conducted where three soil columns (two TOP and one SAP) were examined simultaneously. Deionized water with 0.0005 M $CaCl_2$ artificial ground water (AGW) spiked with the seven contaminants was used for the first set of experiments. The experiment was initiated by infiltrating 2 pore volumes of AGW through soil columns TOP1, TOP2, and SAP1. Then the input was switched to AGW containing the seven contaminants. After creating a long concentration pulse the input was switched back to AGW to maintain the desorption part of the experiment. The second experiment was conducted on a set of another three columns (TOP3, TOP4, and SAP2). R-1 water spiked with a pure form of the seven contaminants was used as the input. This second experiment with R-1 water did not include a desorption phase. Sampling of the effluent from three columns and from the influent for control purposes was carried out regularly using the fraction collector shown in the schematic in Figure 2. Samples of effluent water were collected in the fraction collector. According to method of the samples pre-concentration the effluent was stored in four different vial volumes according to sampling scheme and method of pre-concentration. Effluent samples for direct injection and microextraction were refrigerated until analysis.
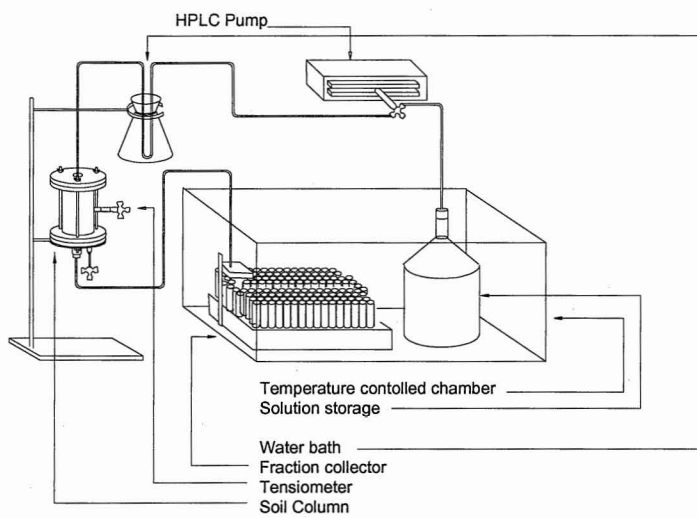
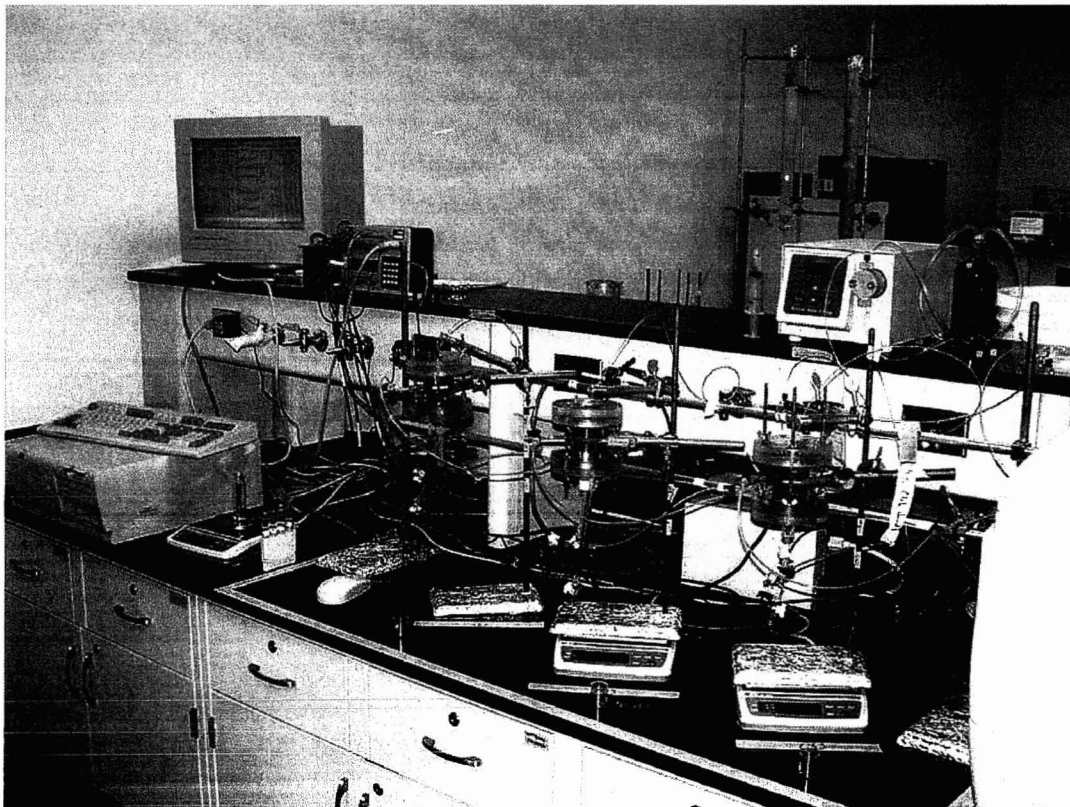**Figure 2. Schematic of experimental setup for conducting BTC experiment (left). Details of soil column assembly (right).**

Labels on schematic:
HPLC Pump

Temperature contolled chamber
Solution storage
Water bath
Fraction collector
Tensiometer
Soil Column

Figure 3. The pumping and the data logging system for the experimental setup

2.4. Column loading

The influent concentrations for the chemicals in the column experiments were set higher than those present in the wastewater because (1) to have a concentration that is higher than the detection limit of the instrument used for analysis because the sample volumes were small and (3) to produce a breakthrough in a reasonable amount of time which otherwise could take months or years for very-low-concentration samples.

Concentrations in the influent during the pilot experiment and experiments with AGW and R-1 water are given in Table 5. Based on the pilot study experience, the concentration was adjusted for the AGW and R-1 water experiments. Mainly, the concentrations were set higher for some compounds in the main transport experiment. The influent solutions were sampled periodically during the experiment to observe any changes in analyte concentration possibly caused by degradation in the storage bottle. To check the actual concentration of compounds in influent water pumped into the soil column, the inflow was sampled regularly.

Table 5. The Concentrations of the Compounds in the Influent Water.

Experiment	Compound							
	NDMA	Lindane	Nonylphenol	Octyphenol	Atrazine	17β-estradiol	Estrone	Bromide
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Pilot	N/A	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
R-1 water	1	0.002	0.6	0.6	0.008	1	1	5

Note that for R-1 water experiments, the concentration is the spiked concentration, while actual concentration can be higher due to background concentration.

2.5. Analysis of residual concentrations of compounds in soil

After the BTC experiment, each column was cut into three equal-sized pieces of 1-inch depth and stored in the freezer until further analysis of residues that sorbed to the soil during the transport experiment. The residues were then extracted from soil using acetone. To 40-mL glass vials (I-Chem, USA), 30 mL of acetone and 10 gm of soil were added and mixed overnight in a rotary mixer (Roto-Torque, Model-7637, Cole Parmer, USA) at a moderate speed (40 rpm) to prevent breakage of the aggregates. After proper mixing, samples were centrifuged (2,500 rpm) for 10 minutes, and 20 mL of clean solution was extracted to a beaker of 50-mL capacity and left to evaporate overnight. Then the residue was washed with 1 mL of acetone, divided into two equal volumes (0.5 mL each), and transferred into two HPLC vials of 1.5-mL capacity. Acetone was evaporated, and the residue was dissolved in 1 mL of 50:50 acetonitrile and hexane for analysis in HPLC-MS and GC, respectively. Solution (100% of the compounds) without soil was also processed similarly to find any loss due to degradation or method recovery errors. Partition coefficients of all the compounds in soil and acetone media were

determined by conducting batch sorption experiment at different concentrations (0%, 50%, and 100%) of all these compounds. Using the partition coefficient of these compounds in acetone, actual concentrations extracted from the soil were calculated. This method might not be suitable for volatile compounds such as lindane; however, less volatile compounds are expected to give less erroneous results.

2.6. Effluent sample preparation

For lindane and the two phenols, a microextraction technique based on method 6231B in *Standard Methods for the Examination of Water and Waste*water (APHA-AWWA-WEF 1998) was used. Approximately 6 g of NaCl and 3.0 mL of hexane were added to a 30-mL water sample in a 50-mL screw-cap test tube. The test tube was then tightly capped and shaken vigorously for 2 min. After the water and hexane layers separated, 1.5 mL of the hexane was removed with a Pasteur pipette and passed through anhydrous Na_2SO_4 in a second Pasteur pipette that was held in an autosampler vial.

This hexane extract was then first analyzed for lindane using a gas chromatograph with an electron capture detector (GC-ECD). It was then evaporated to dryness with nitrogen and the residue redissolved in 0.75 mL of 50:50 acetonitrile:water for analysis of octylphenol and nonylphenol using a HPLC-MS (Baronti et al. 2000; Corcia et al. 2000; Croley et al. 2000; Petrovic et al. 2001)

For estrone and 17β-estradiol, 50-mL water samples were lyophilized (freeze-dried) to dryness. The residue was transferred to autosampler vials using multiple rinses of 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:water and analyzed by HPLC-MS.

For the analyses of atrazine and NDMA, filtered effluent water samples were directly injected to the HPLC.

2.7. Sample analysis

GC-ECD. A Hewlett Packard 5890 Series II gas chromatograph (GC) equipped with an electron capture detector (ECD) using a J&W Scientific DB-XLB capillary column (30 m × 0.53 mm internal diameter × 1.5 μm film) at a helium carrier gas flow rate of 5mL/min was used for the analysis of lindane. The GC oven temperature program was started at 110°C and held for 1 min, ramped to 140°C at 20°/min, then to 280°C at 11°C/min, held for 1.75 min. The total run time was 17 min, and the injector and detector were operated at 250°C and 300°C, respectively. Exactly 2 μL of the hexane extracts were injected for analysis.

HPLC-MS. Atrazine, estrone, 17β-estradiol, octylphenol and nonylphenol were analyzed on a Thermo Finnigan Surveyor LC/MS (LCQ) system. Analytes were separated using a Waters XTerra MS C18 column [2.0 mm (internal diameter) × 150 mm (length), 5 μm (particle size)]. Mobile-phase solvents A and B were 10-mM ammonium bicarbonate and acetonitrile, respectively. For atrazine, an isocratic mobile phase (50:50 A:B) was used, with a run time of 8 min. For the other four compounds, the gradient began at 10:90 A:B, held for 5 min. A:B increased to 0:100 over 35 min, held for 3 min. The system was reequilibrated to 10:90 A:B for 10 min before the next sample injection. The flow rate was 0.3 mL/min, and the injection volume was 20 μL. The Thermo Finnigan LCQ is an ion trap mass spectrometer equipped with an ESI source. The capillary temperature was 250°C, and the flow rates of sheath gas and auxiliary gas were 70 and 15 (arbitrary units), respectively. The spray voltage was 4.5 kv. Atrazine was analyzed in positive-ion mode. The other four compounds were analyzed in negative-ion mode. The SIM (selected ion monitoring) mode was used for estrone and 17β-estradiol, and the SRM (selected reaction mode) was used for atrazine, octylphenol, and nonylphenol.

HPLC-UV. NDMA was analyzed on a Thermo Finnigan surveyor HPLC/UV system equipped with a Varian Polaris C18-A column [2.0 mm (internal diameter) × 150 mm (length), 3 μm (particle size)]. Solvents A and B were 10-mM ammonium formate and acetonitrile. An isocratic mobile phase (98:2 A:B) was used with a run time of 7 min. The flow rate was 0.2 mL/min; the injection volume, 25 μL; and the detection wavelength, 230 nm.

Methods summary: Spiked sample recovery experiments were performed to determine the precision, accuracy, and detection limits of the methods. Table 6 provides a summary of recoveries and detection limits.

Table 6. Mean Recoveries, Standard Deviations (in parentheses) and Detection Limits of the Seven Compounds Studied

Analytes	% Recovery (SD)[a]	DL (ug/L)[b]	Sample Preparation	Instrument Method
Lindane		0.02	Microextraction[c]	GC-ECD
NDMA		50	Direct injection	HPLC-UV
Atrazine		0.4	Direct injection	HPLC-MS
17β- estradiol	79 (3.06)	0.05	Lyophilization	HPLC-MS
Estrone	77 (5.5)	0.1	Lyophilization	HPLC-MS
Octylphenol	95 (1.8)	5	Microextraction	HPLC-MS
Nonylphenol	107 (0.78)	2.5	Microextraction	HPLC-MS

[a] Average of triplicate spiked samples.
[b] Method detection limit.
[c] Method 6231B (APHA-AWWA-WEF 1998).

3. Results and Discussion

3.1. Pilot experiment

First, the results of two runs of the pilot experiments are presented. The experiments were conducted on one packed soil column with bromide and contaminant solution, and the experimental conditions are listed in Table 7.

Table 7. Experimental Conditions of the Pilot Transport Experiment

Run ID	Chemicals	Height (cm)	Diameter (cm)	Volume (cm^3)	Area (cm^2)	Bulk density (g/cm^3)	Flux (cm/h)	Pulse (pv)[a]
P2S2_Br	Br$^-$	6.0	7.6	344.6	45.3	1.10	0.2009	4.1
P2S2_Con	Br$^-$ + six contaminants	6.0	7.6	344.6	45.3	1.10	0.2075	12.8

[a]Since the real value of the water content was not known at the time, the pore volume (pv) calculation is based on an estimated value of $\theta = 0.6$.

Figure 4 shows the bromide BTC based on data fitted with the advection dispersion equation (ADE) using the WS_1D_INV code (Nakhei and Vogel 1997). The inverse method is based on the HYDRUS 5.0 code (Vogel et al. 1996), and the parameter optimization function uses the Levenberg-Marquardt algorithm. The BTC showed nearly ideal behavior; there were no early breakthrough and no significantly prolonged tailing. Slow approximation of equilibrium in the first part of the experiment is likely to have been caused by physical nonequilibrium caused by the aggregate-conserving technique of column packing. There was no decrease of concentration after the flow interruption conducted during the desorption phase of the experiment, which confirms the conservative character of bromide transport in column. In figure 4, the solid gray line represents the input concentration of bromide and the circles represent the output concentration. The best fit was achieved at dispersivity, $D = 0.188$ cm^2/h.
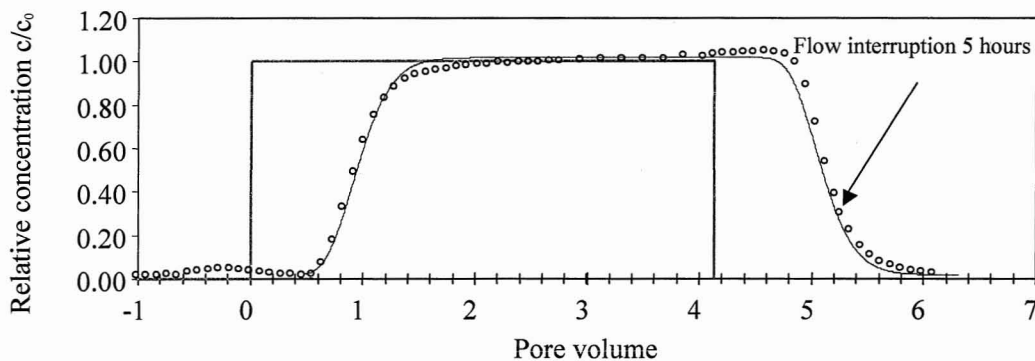
Figure 4. Pilot Experiment for bromide breakthrough

3.2. Contaminant transport

Figure 5 shows the BTC for atrazine and the bromide tracer based on data obtained during the pilot study. Although all contaminants were added in this pilot experiment, only atrazine shows significant breakthrough. Traces of octylphenol were detected at the 8th pore volume after application (not shown in the figure). Concentrations of the rest of the contaminants in the effluent were below detection limits, even after the application of the 12.8 pore volume pulse of input concentration. In figure 5, the solid gray line represents the input pulse into the column.
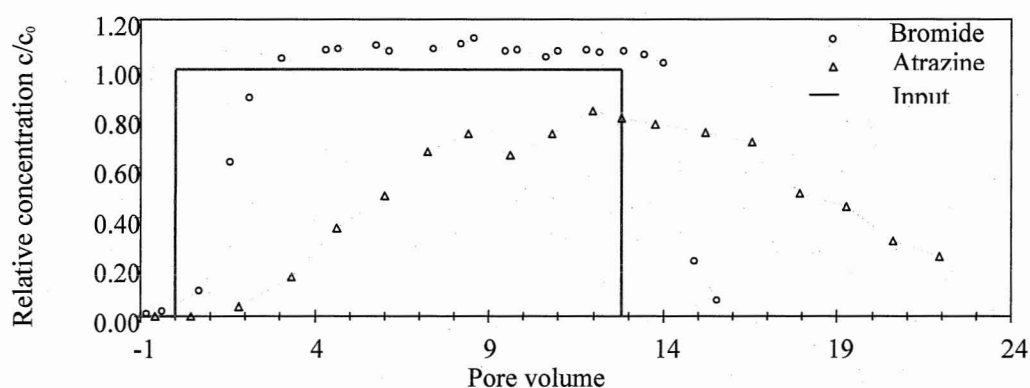
Figure 5. Pilot experiment for atrazine and bromide breakthrough

3.3. Main breakthrough experiments

Table 8 shows the parameters for the experiments involving AGW and R-1 water as the background solution to which the seven contaminants were added as a pulse. The breakthrough of these contaminants, as expected, was a function of the soil and the contaminant. The breakthrough concentrations were lower for the TOP soils than for the SAP soils.

Table 8. Experimental Conditions of Simultaneous Infiltrations of Contaminants

Soil Column	Water Type	Height	Diameter	Pulse Duration	Pulse volume	Experiment Duration	Total Effluent Volume
		(cm)	(cm)	(days)	(cm^3)	(days)	(cm^3)
TOP1	AGW	7.6	4.7	25.87	4,851.9	38.21	7,015
TOP2	AGW	7.6	4.7	25.87	4,650.3	38.21	6,809
SAP1	AGW	7.6	4.7	25.87	4,737.8	38.21	6,989.8
TOP3	R-1	7.6	4.7	23.98	3,050.4	23.98	3,050.4
TOP4	R-1	7.6	4.7	23.98	854.2	23.98	854.2
SAP2	R-1	7.6	4.7	23.98	3,110.2	23.98	3,110.2

Figure 6 shows the BTC for bromide for the two TOP columns. Although the concentrations fluctuate slightly, the respective shapes of the two breakthrough curves are similar, and 50% concentration is reached in each case after the passage of 1 pore volume of solution.
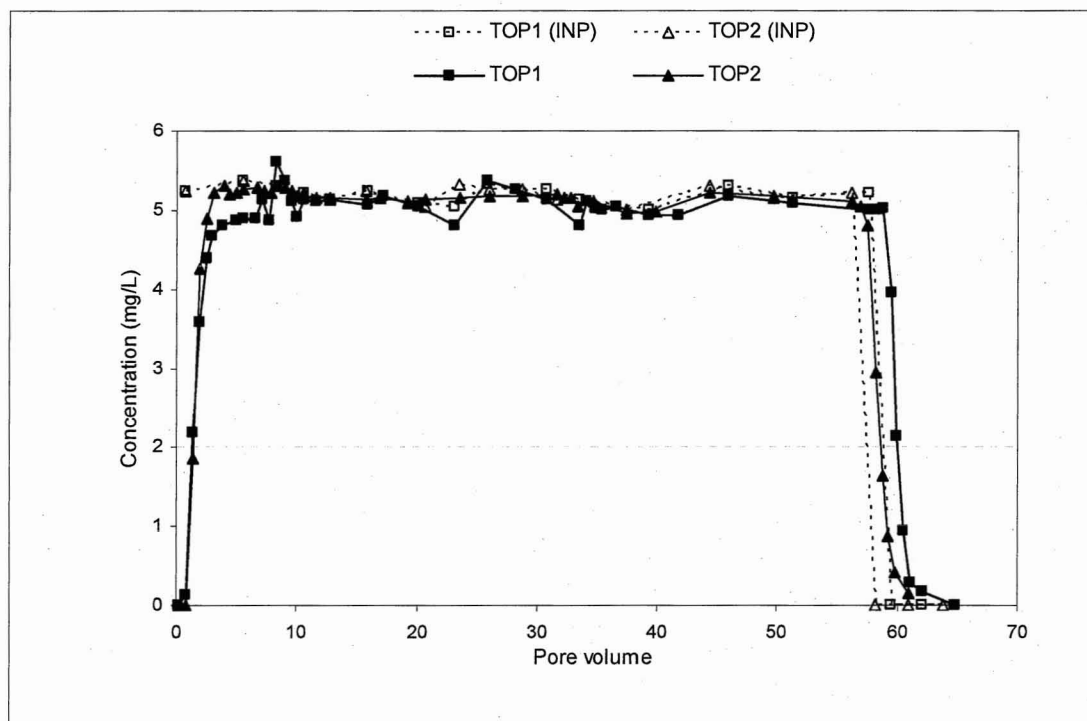
Figure 6. BTC of bromide in TOP soil with AGW as background, $C_0 = 5$ mg/L

For saprolite (e.g., soil column SAP2), the breakthrough was even more delayed. Nearly 50% of the input concentration was detected after passing approximately 2.7 pore volumes (Figure 7). Ion exchange at the iron oxide mineral surfaces may be seen as the mechanism for sorption. As presumed, there is no effect of the flow interruption on the bromide concentration in the effluent, because bromide does not undergo degradation.

NDMA breakthrough data showed high mobility in both the TOP and SAP columns. The breakthrough of NDMA in both soils was nearly identical. Approximately 50% of the input concentration was detected in the effluent after passing 1 pore volume of AGW (see Figure 8) spiked with NDMA. Its concentration in the effluent decreased slightly after the flow interruption that took place after 94.9 hours in both TOP and SAP columns. This implies that slow degradation took place. NDMA was the most mobile compound among the seven contaminants.
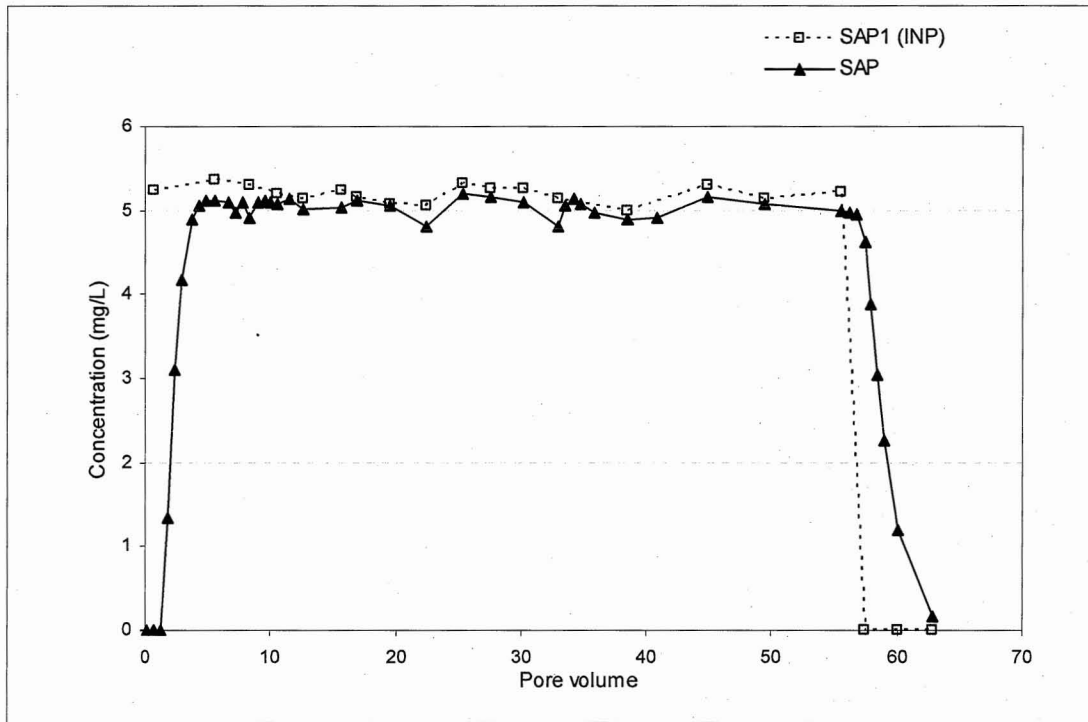
Figure 7. BTC of bromide in SAP for AGW, $C_0 = 5.0$ mg/L
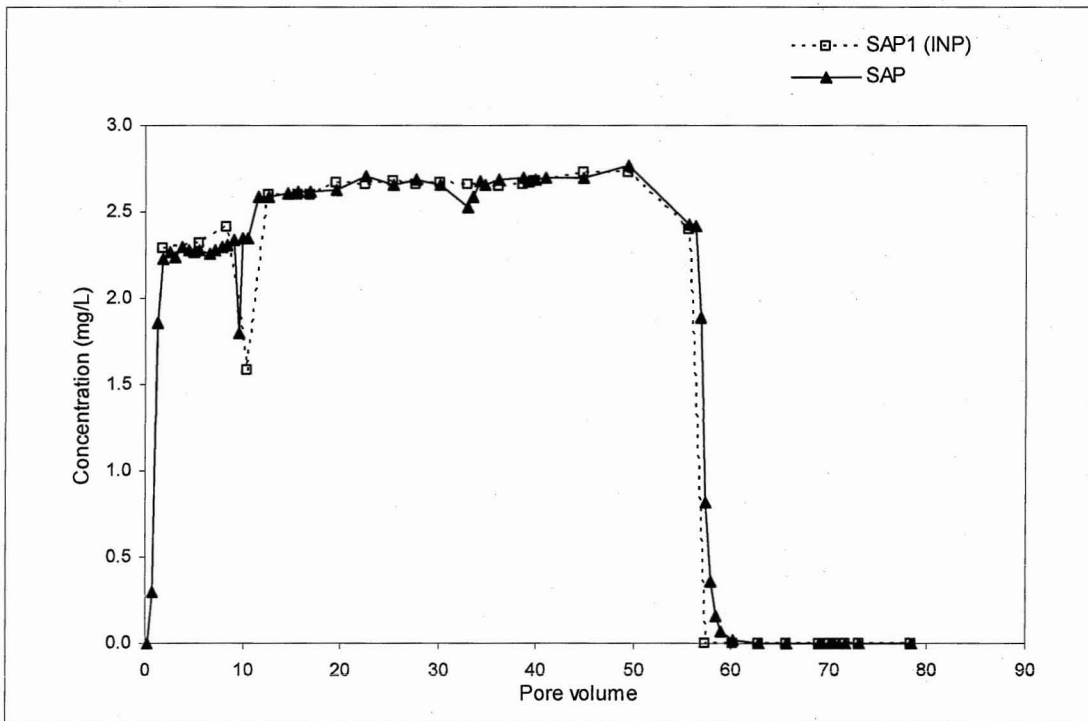
Figure 8. BTC of NDMA in SAP for AGW, $C_0 = 2.5$ mg/L

Atrazine appeared to be a moderately sorbing compound in TOP column (Figure 9), while in SAP column the sorption was nearly negligible. The results were very similar between AGW and R-1 water (see Appendix A.5). The concentration of atrazine in the effluent reached the input concentration after passing approximately 4 pore volumes of spiked water through TOPs. In SAP column, the breakthrough showed near ideal tracer properties, since 50% of the input concentration appeared after passing 1 pore volume of solution. The flow interruption caused a small decrease in concentration in the effluent, showing a slow rate of atrazine degradation in TOPs.
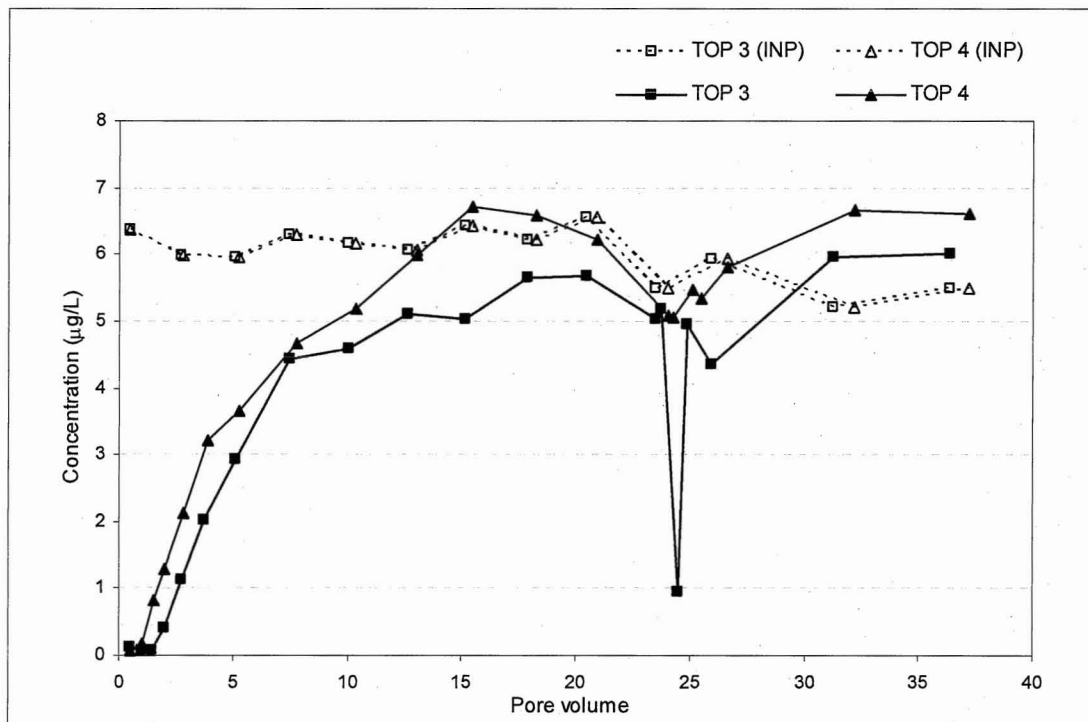
Figure 9. BTC of atrazine in TOP in R-1 water, C_0 =0 6 µg/L

The shape of the breakthrough curves for lindane was similar to that for atrazine in TOP column (Figure 10), but its breakthrough was about 10 times slower. Again, lindane is much more mobile in the SAP than the TOP column.

Passing water with estrogen compounds resulted in very low breakthrough concentrations. Concentration was barely at the analytical detection limit for the TOP columns. The concentration of estrone effluent from saprolite columns reaches about 50% of the input concentration at the end of the concentration pulse (Figure 11). Fluctuation of the detected concentrations of estrogen compounds over time makes it difficult to estimate its sorption properties accurately. However, negligible concentration in the effluent is a clear indication that estrogens have limited mobility in TOP column. Breakthrough of the compound in SAP column is faster than in TOP column.
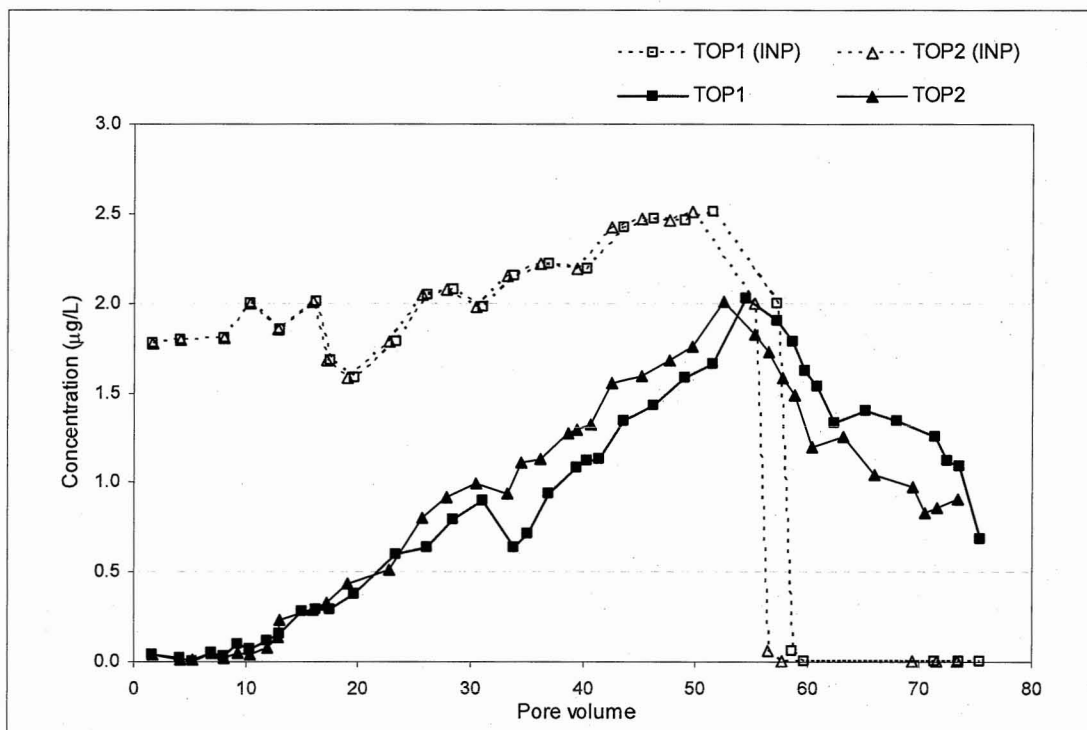
Figure 10. BTC of lindane in TOP in AGW, $C_0 = 2$ µg/L
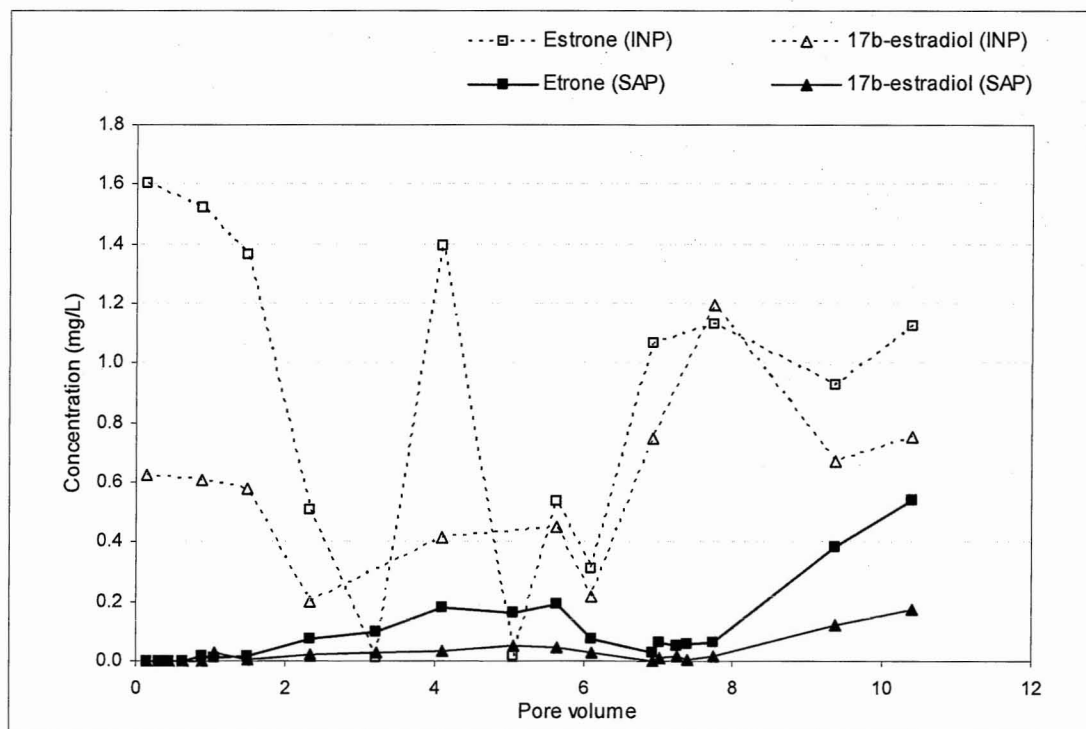
Figure 11. BTC of estrone and 17β-estradiol in SAP in R-1 water, $C_0 = 0.6$ mg/L

Most analytical problems were encountered with octylphenol and nonylphenol. These compounds often degraded during sample preparation and analysis. The effect of possible sample degradation was compensated by regular sampling of the water entering the soil columns (denoted as INP samples) and using the same fraction collector for sampling the input. The concentration of appropriate INP samples is plotted in each BTC graph for the purpose of comparison. Using a GC-MS and its internal library, it was found that the standard contained multiple peaks representing multiple compounds. Although the standard was available from a commercial source, its purity is questionable. The LC-MS method did not involve verification of the purity of the standard. As a result, this problem was not revealed until we were far ahead into various experimental tasks. Also, leaching of phenolic compounds from the bulk soil is a possibility during sample extraction. Breakthrough curves are presented in Appendix A.5.

3.4. Parameter optimization

Inverse numerical modeling was performed to obtain the parameters for the fate and transport of the studied contaminants in the TOP soil. Simulations were conducted using HYDRUS 1D, version 2.02 (Šimůnek et al. 1998). HYDRUS 1D is a software package was used to simulate the one-dimensional movement of water, heat, and multiple solutes in variably saturated media. Modeling of unsaturated water is based on numerical solution of the Richards equation. The model involves two-site and two-region concepts for simulations of transport under nonequilibrium sorption. In the literature, the nonequilibrium concept can be found, for example, in (Beigel and Pietro 1999). Here, only brief introductions are given. The two-site, two-region bicontinuum model has been formulated to account for either sorption-related or transport-related nonequilibrium during solute transport. The two-site nonequilibrium concept assumes that sorption sites in soils can be classified into two fractions. In the first fraction, sorption is instantaneous and is described by an equilibrium sorption isotherm (Type 1, equilibrium). In the second fraction, sorption is time-dependent and follows first-order kinetics (Type 2, kinetic). In this case, the rate-limiting step for Type 2 sites would be either chemical (chemisorption) or diffusive (intraparticle or intrasorbent diffusive mass transfer), as discussed by (Brusseau et al. 1991). The two-region approach assumes that the liquid phase can be partitioned into mobile (flowing, macropore domain) and immobile (stagnant, matrix, or micro-pore domain) regions. The exchange between the two liquid regions is modeled by a first-order kinetic equation. Flow occurs only in the mobile region. Sorption is assumed to be instantaneous on all sorption sites, and the sorption rate is limited by the diffusion of the solutes to the exchange sites in the stagnant phase.

HYDRUS 1D includes an inverse parameter optimizer. The optimizer is based on minimizing the objective function using the Levenberg-Marquardt algorithm. All of these parameters are described in detail in HYDRUS 1D.

Simulations were performed individually for each of the seven contaminants in the experiment conducted on column TOP1. The experiment was simulated as unsaturated flow with solute transport. Small variations of the flow rate and the flow interruptions were introduced into the model as prescribed flow-boundary conditions at the top. For NDMA, atrazine, and lindane the best results (lowest objective function) were achieved using the nonequilibrium model. The bottom flow-boundary condition was set to a constant water pressure head of -10 cm. The soil water retention curve parameters (given in Table 4) were used for the simulations. The chemical pulse was simulated by a prescribed concentration at the upper boundary. For all compounds except atrazine, the concentration was set constant in the model during the period of pulse application. The level of the concentration at the boundary was calculated as the arithmetic mean concentration of a particular compound in the influent water samples. Atrazine showed fluctuations of the concentration in input water during the pulse, and these were included in the model as a time-variable prescribed concentration at the boundary. The aim of solute transport modeling was to find such a set of the sorption and degradation parameters that would produce the closest fit of the observed and modeled concentrations in the effluent over time. To obtain such a set, a combination of manual and automated optimizations using the built-in function of HYDRUS 1D was invoked. In most cases the fitting was an iterative procedure, which involved manual adjustment of one or more parameters (fixed parameters) and automated optimization of one or more parameters using the built-in optimizer (free parameters). The result of inverse modeling is a set of transport parameters given in Table 9. Simulated versus modeled breakthrough curves and residual concentrations of compounds are shown in Appendix A.4. The specific modeling approach for each compound was as follows:

NDMA

The hydrodynamic dispersion coefficient **Disp** for soil column TOP1 was estimated from the NDMA data. Unlike bromide, the NDMA BTC has negligible sorption. At 1 pore volume of solution passage, the relative concentration (measured divided by the supplied) was 0.5, indicating no sorption or negligible sorption. The **Disp** parameter estimation was performed using the HYDRUS 1D built-in parameter optimization option in combination with manual adjustments. The initial guess of the solute transport parameters for NDMA

was obtained from literature[2]. The best fit was obtained by setting four parameters as free parameters (***Disp, Kd, SinkWater1, SinkSolid1***) in the code.

ATRAZINE

Special care was taken to simulate the decrease of the concentration after the first long flow interruption. The decrease was mainly due to degradation of the compound inside the soil columns during the no-flow period. Due to fluctuations in measured input concentrations, these values were included in the model as upper prescribed concentrations at the upper boundary. The first set of parameters as initial guesses were obtained from a freely available database[3]. The trial-and-error method led to a set of fixed and optimized parameters which gave satisfactory fit of observed data. The best fit was produced by simulation using the nonequilibrium transport model. The final inverse model runs involved optimization of two free parameters (***Kd*** and ***Alpha***).

LINDANE

Lindane, a moderately sorbing compound, produced a BTC with slow rise and long tailing. The changes of the concentration were significant during first- and second-flow interruptions. The initial guess of parameters comes from free sources[4]. The final set of free parameters included ***Fract, ThImob, Beta*** and ***Alpha***. The modeling result is shown in Table 9. The fitted curve to the breakthrough data is shown in Figure 12.

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[2] http://www.inchem.org/documents/cicads/cicads/cicad38.htm#5.4

[3] http://pmep.cce.cornell.edu/facts-slides-self/facts/pchemparams/gen-pubre-atrazine.html accessed in January 2005

[4] http://www.the-piedpiper.co.uk/th13(j).htm, accessed in January 2005
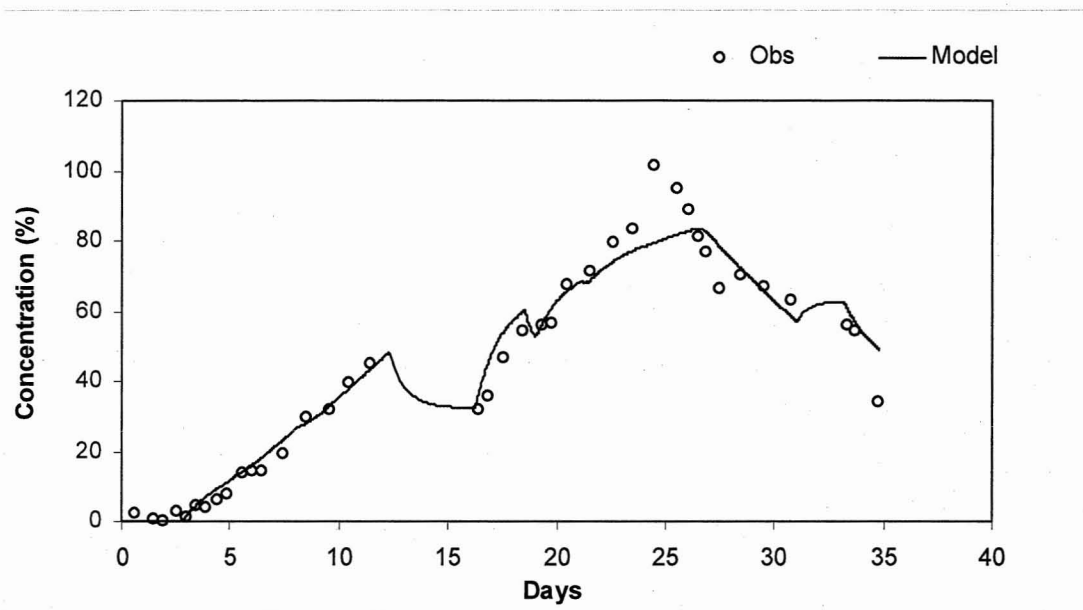
Figure 12. Lindane BTC. Observed points (circles) were fitted with HYDRUS 1D simulation results

ESTRONE, 17β-ESTRADIOL, NONYLPHENOL, and OCTYLPHENOL

17β-estradiol, estrone, and the phenols did not produce significant BTCs. Therefore the residual concentrations were taken into account for parameter optimization. Model fitting for these four compounds was done manually. The goal of the optimization was to minimize the difference between the compound residuals extracted from the soil and the calculated solid phase that was adsorbed from the pore water to the solids during the transport experiments. At the same time, the predicted concentration had to fit the observed (low) levels. The soil column for this purpose was divided into three portions as described in subsection 2.6. In HYDRUS 1D, the flow domain was divided into three virtual subregions and the total quantity of the compound was calculated at the end of the simulation. The respective residual concentrations measured for octyphenol and nonylphenol gave values exceeding the total load of the column with the compound. Due to this discrepancy, parameter optimization could not be performed, and modeling was done using only the literature-reported parameters[5] (Jacobsen et al. 2004); (Hesselse et al. 2001).

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[5] http://www.ospar.org/documents/dbase/publications/p00173_octylphenol.pdf

Table 9: HYDRUS 1D Parameters for Modeling of AGW Experiment TOP1 Column Breakthrough Curves

Compounds	Optimized parameters	Parameters									
		Bulk.D.	Disp.	Fract.	ThImob	Kd	Beta	Henry	SinkWater1	SinkSolid1	Alpha
NDMA	D+SinkW+Kd+Im	1.10E+00	9.52E-01	1.00E+00	1.00E-01	4.43E-03	1.00E+00	0.00E+00	1.49E-01	8.97E-03	4.88E-04
Atrazine	Kd+alpha	1.10E+00	9.71E-01	7.00E-01	3.00E-01	3.52E+00	9.00E-01	0.00E+00	1.00E-01	4.24E-04	2.31E-01
Lindane	fract+ThImob+Kd+beta+alpha	1.10E+00	9.70E-01	2.29E-01	4.01E-02	1.12E+00	6.14E-01	1.00E-02	3.85E-03	5.21E-03	6.25E+00
Estrone	manual fit	1.10E+00	9.71E-01	0.00E+00	0.00E+00	1.80E+02	1.00E+00	0.00E+00	2.70E-01	2.70E-01	8.00E-01
Estradiol	manual fit	1.10E+00	9.71E-01	5.00E-02	0.00E+00	1.80E+02	1.00E+00	0.00E+00	1.90E-01	1.90E-01	1.15E+01
Octylphenol	literature values	1.10E+00	9.71E-01	1.00E+00	0.00E+00	2.74E+01	1.00E+00	0.00E+00	1.73E-02	1.16E-02	0.00E+00
Nonylphenol	literature values	1.10E+00	9.71E-01	1.00E+00	0.00E+00	1.70E+02	1.00E+00	0.00E+00	6.93E-02	6.93E-02	0.00E+00

Bulk.D.   Bulk density, r (g/cm^3)

Disp   Longitudinal dispersivity, DL (cm)

Fract   Dimensionless fraction of adsorption sites classified as Type-1, i.e., sites with instantaneous sorption when the chemical nonequilibrium option is considered (-). Equal to 1 if equilibrium transport is considered. Dimensionless fraction of adsorption sites in contact with mobile water when physical nonequilibrium option is considered [-]. Equal to 1 if all sorption sites are in contact with the mobile water.

ThImob   Immobile water content. Set equal to 0 when the physical nonequilibrium option is not considered.

Kd   Adsorption isotherm coefficient, k (cm^3/g)

Beta   Adsorption isotherm coefficient, b (-)

The sorption isotherm relating concentration on solids **s** and **c** is described as generalized non-linear expression:

$$s = Kd \cdot c^{Beta}$$

If **Beta = 1** the sorption isotherm is linear

If **Beta is different from 1** the expression becomes **Freundlich isotherm**

Henry   Equilibrium distribution constant between liquid and gaseous phases, kg (L^3/kg)

SinkWater1 First-order rate constant for dissolved phase, mw (1/days)

SinkSolid1 First-order rate constant for solid phase, ms (1/days)

Alpha   First-order rate coefficient for one-site or two-site nonequilibrium adsorption, mass transfer coefficient for solute exchange between mobile and immobile liquid regions, w (1/days)

The units used for the simulation were centimeters (cm), days, grams, and mass units for the expression of concentration C expressed in micrograms (μg), which for length units expressed in centimeters results in expressing of the aqueous concentration in micrograms per milliliter (μg/mL) and solids concentration in micrograms per gram (μg/g) or part per million (ppm).

A cautionary note: K_d values are frequently reported as having units, and a dimensional analysis of the Freundlich equation suggests that K_d will vary in a nonlinear way if C units are converted. If Freundlich parameters are used, be sure to note and apply the same units for mass expression of concentration.

4. Conclusions

Column experiments with leaching of bromide and seven contaminants were conducted under an unsaturated steady-state flow condition. Analytical methods were either modified or developed for all contaminants in order to reliably detect these compounds in samples of small volumes. With the exception of atrazine and lindane, the concentrations of most of the contaminants were increased by several orders of magnitude to get a breakthrough. The following are general conclusions of the study:

- Producing breakthrough of the estrogenic (17β-estradiol and estrone) and phenolic (octylphenol and nonylphenol) compounds in small (3-inch long) soil columns was difficult even when the feed solution concentration contained these chemicals near their solubility limit.

- It was more difficult to obtain a breakthrough of chemicals in surficial (B horizon, referred to as TOP here) soil than in SAP, the saprolite. This could partly be due to lower amounts of organic carbon in the SAP.

- NDMA moved like a tracer. Bromide in saprolite showed slight sorption.

- Both atrazine and lindane showed moderate sorption behavior.

- Estradiol and estrone did not move appreciably in surficial soils to produce a breakthrough. Although traces of these compounds were found in the column effluent, the measured concentrations were low and often erratic in the SAP.

- The concentrations of octylphenol and nonylphenol in the effluent were also low. However, the feed solution concentration varied erratically, possibly due to losses during sample collection and analysis and the impurities present in the standards.

- Residues of estradiol, estrone, and the phenols were found predominantly in the upper one-third of the TOP columns after the experiments were finished. The presence of very low amounts of residues in rest of the column indicate low mobility of these compounds in B horizon soils.

- Flow interruption during the leaching experiment enabled us to estimate the degradation parameters for some chemicals such as atrazine.

- The column experiments did not account for microbial activity normally encountered in the organic-rich TOP soils (A horizon). Thus the conditions for producing breakthroughs were extreme. Such conditions are not expected to occur in the field where R-1 water is applied to the TOP soil of the A horizon at agronomic rates.

5. Acknowledgments

6. References

APHA-AWWA-WEF. (1998). " Standard Methods for the Examination of Water and Wastewater." American Public Health Association, American Water Works Association, Waters Environment Federation, 6-33-6-35.

Baronti, C., Curini, R., D'Ascenzo, G., Corcia, A. D., Gentili, A., and Samperi, R. (2000). "Monitoring Natural and Synthetic Estrogens at Activated Sludge Sewage Treatment Plants and in a Receiving River Water." *Environ. Sci. Tech.*, 34(24), 5059 - 5066.

Beigel, C., and Pietro, L. D. (1999). "Transport of Triticonazole in Homogeneous Soil Columns: Influence of Nonequilibrium Sorption." *Soil Sci. Soc. Am. J.*, 63, 1077–1086.

Brown and Caldwell. (2005). "Assesment of Recycled Water Irrigation in Central Oahu, Final Report." Honolulu Board of Water Supply, Honolulu.

Brusseau, M. L., Jessup, R. E., and Rao, P. S. C. (1991). "Nonequilibrium sorption of organic chemicals: Elucidation of rate-limiting processes." *Environ. Sci. Tech.*, 25(1), 134–142.

Casey, F. X. M., Larsen, G. L., Hakk, H., and Simunek, J. (2003). " Fate and transport of 17b-Estriadol in soil – water systems." *Environ. Sci. Tech.*, 37(11), 2400-2409.

Corcia, A. D., Cavallo, R., Crescenzi, C., and Nazzari, M. (2000). "Occurrence and Abundance of Dicarboxylated Metabolites of Nonylphenol Polyethoxylate Surfactants in Treated Sewages." *Environ. Sci. Tech.*, 34(18), 3914-3919.

Croley, T. R., Hughes, R. J., Koenig, B. G., Metcalfe, C. D., and March, R. E. (2000). "Mass spectrometry applied to the analysis of estrogens in the environment." *Rapid Commun. Mass Spectrom*, 14(13), 1087-1093.

Das, B. S., Lee, L. S., Rao, P. S. C., and Hultgren, R. P. (2004). "Sorption and degradation of steroid hormones in soils during transport: Column studies and model evaluation." *Environ. Sci. Tech.*, 38(5).

Fortin, J., Flury, M., Jury, W. A., and Streck, T. (1997). "Rate-limited sorption of simazine in saturated soil columns." *Journal of Contaminant Hydrology*, 25(219-234).

Gavenda, R. T., Green, R. E., and Schneider, R. C. (1996). "Leaching of pesticides in selected Hawaii Oxisols and Andisols as influenced by soil profile characteristics." University of Hawaii.

Hesselse, M., Jensen, D., Skals, K., Olesen, T., Moldrup, P., Roslev, P., Mortensen, G. K., and Henriksen, K. (2001). "Degradation of 4-Nonylphenol in Homogeneous and Nonhomogeneous Mixtures of Soil and Sewage Sludge." *Environ. Sci. Tech.*, 35(18), 3695-3700.

Jacobsen, A. M., Mortensen, G. K., and Hansen, H. C. B. (2004). "Degradation and Mobility of Linear Alkylbenzene Sulfonate and Nonylphenol in Sludge-Amended Soil." *J. Environ. Qual.*, 33, 232-240.

Johnson, G. R., Gupta, K., Putz, D. K., Hu, Q., and Brusseau, M. L. (2003). "The effect of local-scale physical heterogeneity and nonlinear, rate-limited sorption/desorption on contaminant transport in porous media." *Journal of Contaminant Hydrology*, 64(1-2), 35.

Kamra, S. K., Lennartz, B., Van Genuchten, M. T., and Widmoser, P. (2001). "Evaluating non-equilibrium solute transport in small soil columns." *Journal of Contaminant Hydrology*, 48(3-4), 189.

Klute, A. (1986). " Methods of Soil Analysis, Part 1 Physical and Mineralogical Methods." Water Retention: Laboratory Methods: Agronomy, American Society of Agronomy, Inc. Soil Science Society of America, Inc. Madison, Wisconsin USA, 635-662.

Miller, M. E., Green, R. E., Peterson, F. L., Jones, R. C., and Loague, K. (1988). "Hydrologic characteristics of subsoil and saprolite and their relation to contaminant transport, central O'ahu, Hawaii." Water Resources Research Center.

Muirhead, W. M., Kawata, E. M., and Crites, R. W. "Assessment of Recycled Water Irrigation in Central Oahu." *WEFTEC Conference.*

Nakhei, M., and Vogel, T. (1997). "WS_1D_INV code for inverse and forward solution of one-dimensional water flow and solute transport in variably saturated porous media." Civil Engineering CTU, Prague, Czech Republic.

Ni, Y., Liang, X., Chen, J., Zhang, Q., Ma, L., Wu, W., and Kettrup, A. (2004). "Investigation on the influence of methanol on adsorption and leaching of pesticides with soil column liquid chromatography." *Chemosphere*, 56(11), 1137.

Padilla, I. Y., Yeh, T.-C. J., and Conklin, M. H. (1999). "The effect of water content on solute transport in unsaturated porous media." *Water Resources Research*, 35(11), 3303-3313.

Petrovic, M., Diaz, A., Ventura, F., and Barceló, D. (2001). "Simultaneous Determination of Halogenated Derivatives of Alkylphenol Ethoxylates and Their Metabolites in Sludges, River Sediments, and Surface, Drinking, and Wastewaters by Liquid Chromatography-Mass Spectrometry." *Analytical Chemistry*, 73(24), 5886-5895.

Sanda, M., Ray, C., Dusek, J., Loo, B., and Green., R. "Evaluating the transport of pesticides in tropical soils in Hawaii." *World Water & Environmental Resources Congress*, Salt Lake City, Utah.

Šimůnek, J., Šejna, M., and van Genuchten, M. T. (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, Colorado.

The Merck Index. (2001). 10th edition Merck & Co., Inc. N.J., U.S.A

Vogel, T., Huang, K., Zhang, R., and van Genuchten, M. T. (1996). "The Hydrus code for simulating one-dimensional water flow, solute transport, and heat movement in variably-saturated media. Version 5.0." U.S. Salinity Lab. ARS, USDA, Riverside, CA.

Appendix: Column Leaching Experiment Data

Data for sieve analysis (Figure A1), water retention parameters (Table A1), water flow rate in column TOP1 (Figure A2), simulation results for various contaminants in AGW and R-1 waters through the column (Figures A3 through A12), and breakthrough curves of the seven contaminants and bromide (Figures A13 through A35) are presented in this appendix.
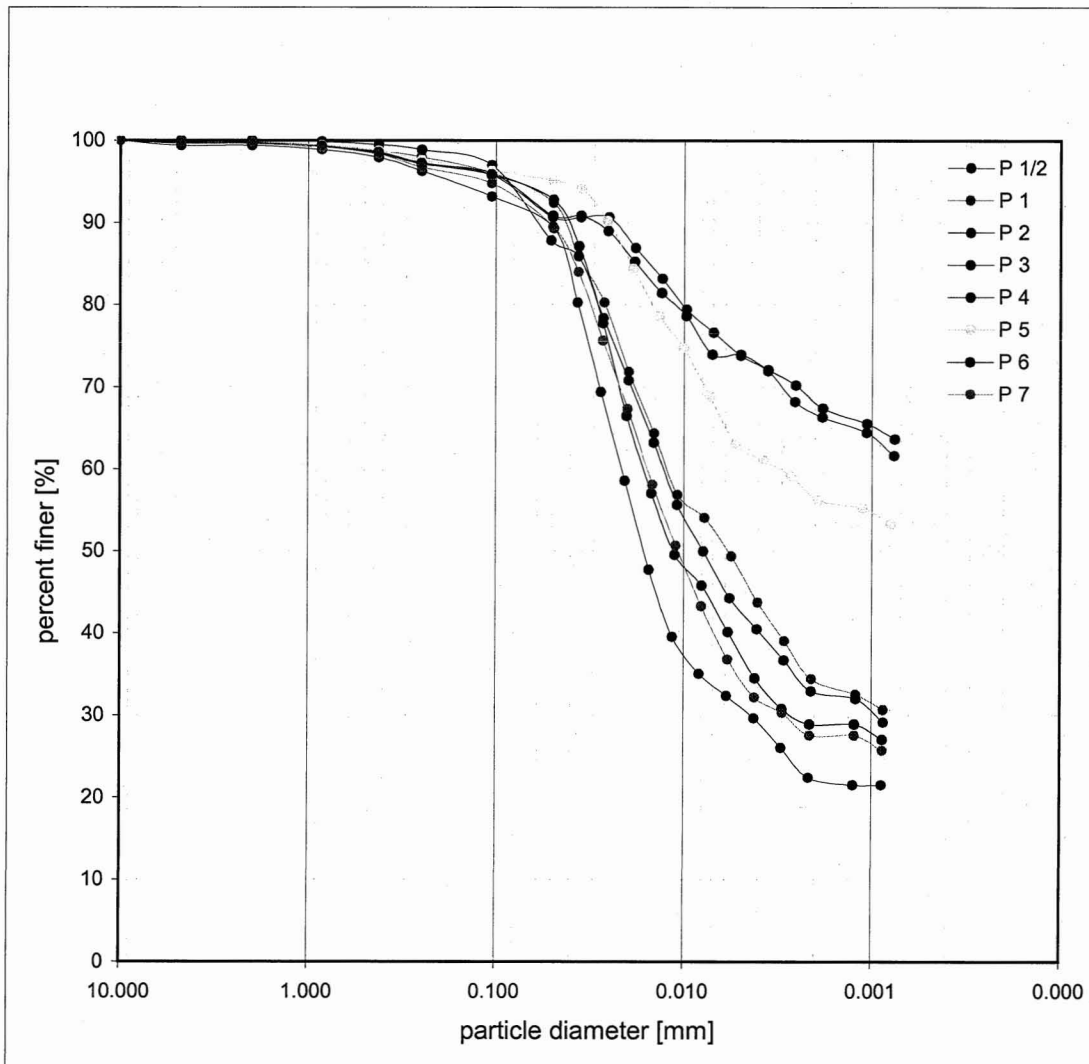
Figure A1. Sieve analysis data for Poamoho soil from the depth ranges of 0.5 ft to 7 ft.

Table A1. Data used to generate the retention curves for the TOP and SAP columns

Soil	Name	Soil water content (-) at the suction pressure head (mBar)							bulk	particles
	sample	1.0	10.0	100.0	500.0	1000.0	3500.0	15000.0	density	density
		-	-	-	-	-	-	-	g/cm³	g/cm³
TOP	A	0.68	0.66	0.46	0.38	0.35	0.32	0.31	1.10	3.47
	B	0.65	0.63	0.45	0.37	0.35	0.32	0.31	1.09	3.08
	C	0.68	0.65	0.47	0.38	0.35	0.32	0.31	1.09	3.41
SAP	D	0.64	0.65	0.51	0.44	0.41	0.37	0.34	1.06	2.98
	E	0.65	0.64	0.52	0.44	0.41	0.37	0.35	1.07	3.05
	F	0.66	0.64	0.51	0.44	0.41	0.37	0.35	1.07	3.10
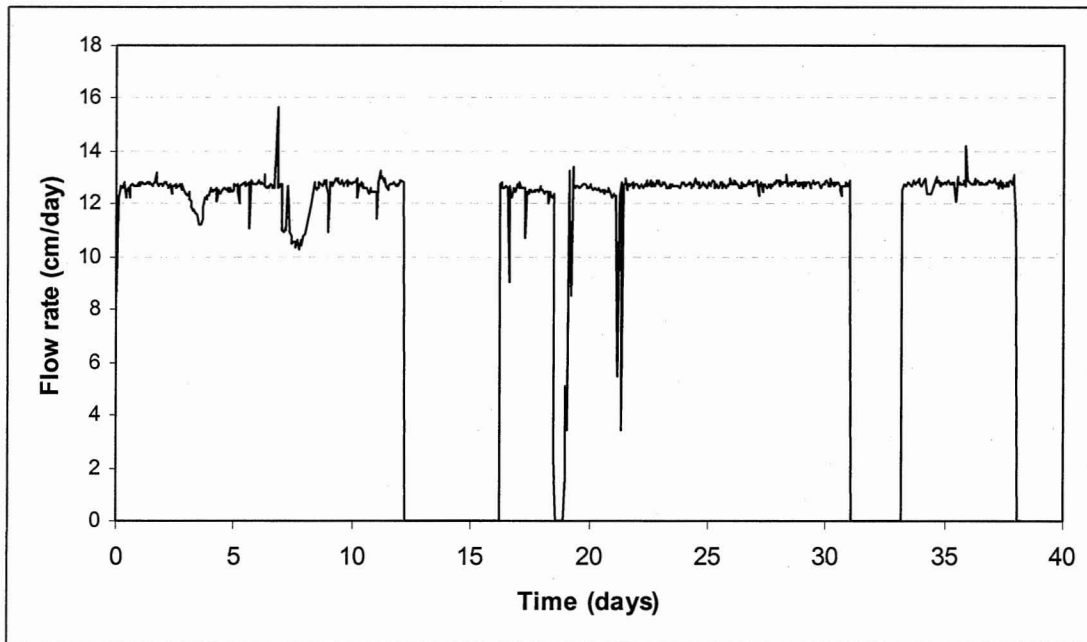
Figure A2. Flow rates in TOP1 column. During the period of flow interruption, the flow rate is zero.
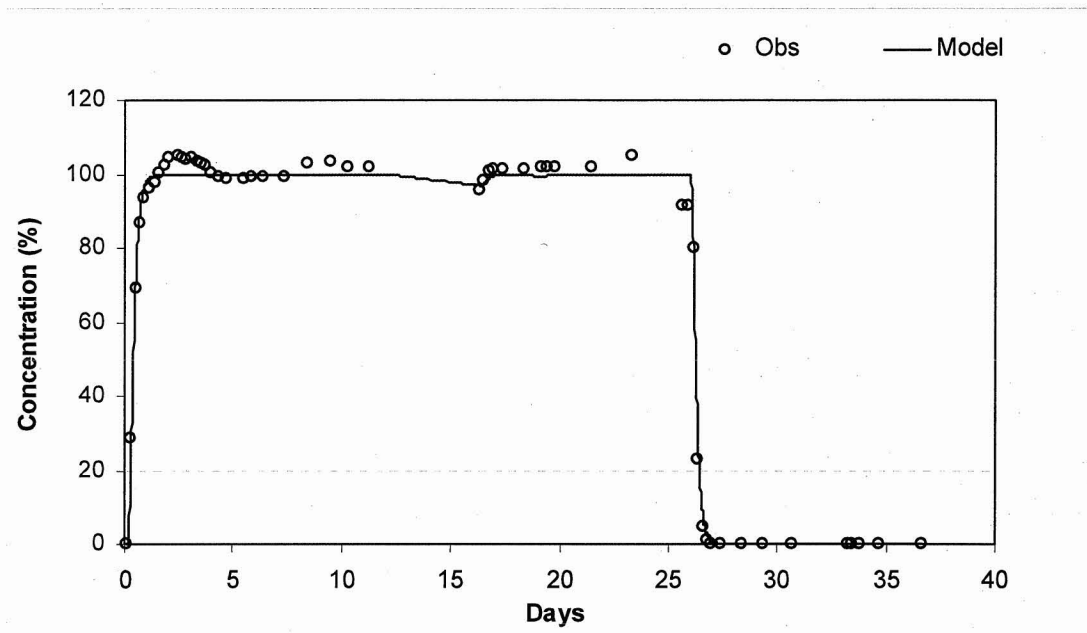
Figure A3. Simulated and observed breakthrough of NDMA in TOP1
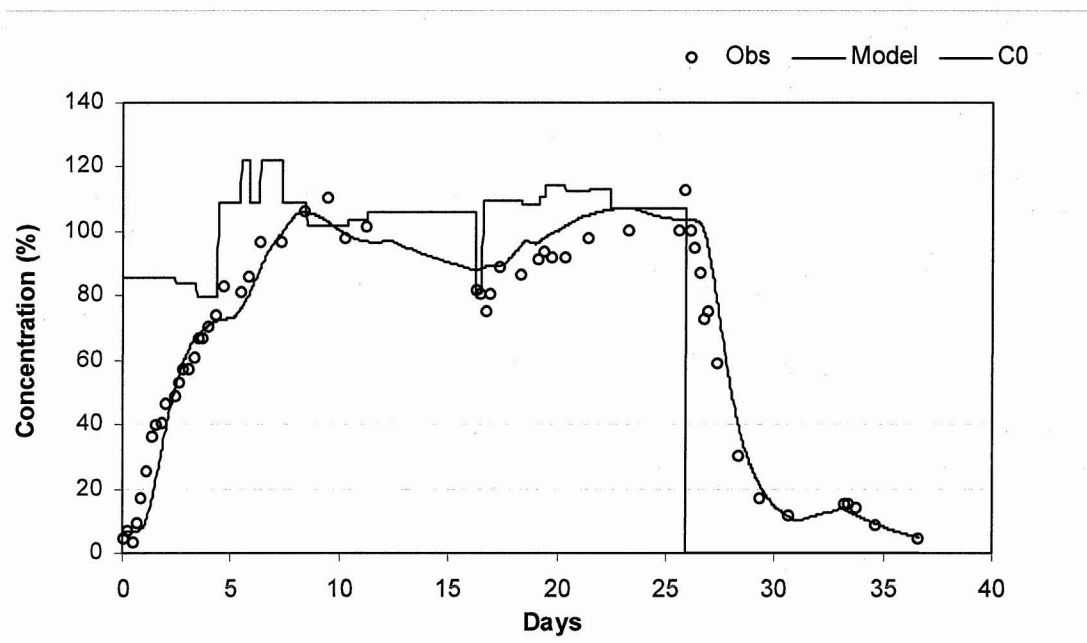
Figure A4. Simulated and observed breakthrough of atrazine in TOP1
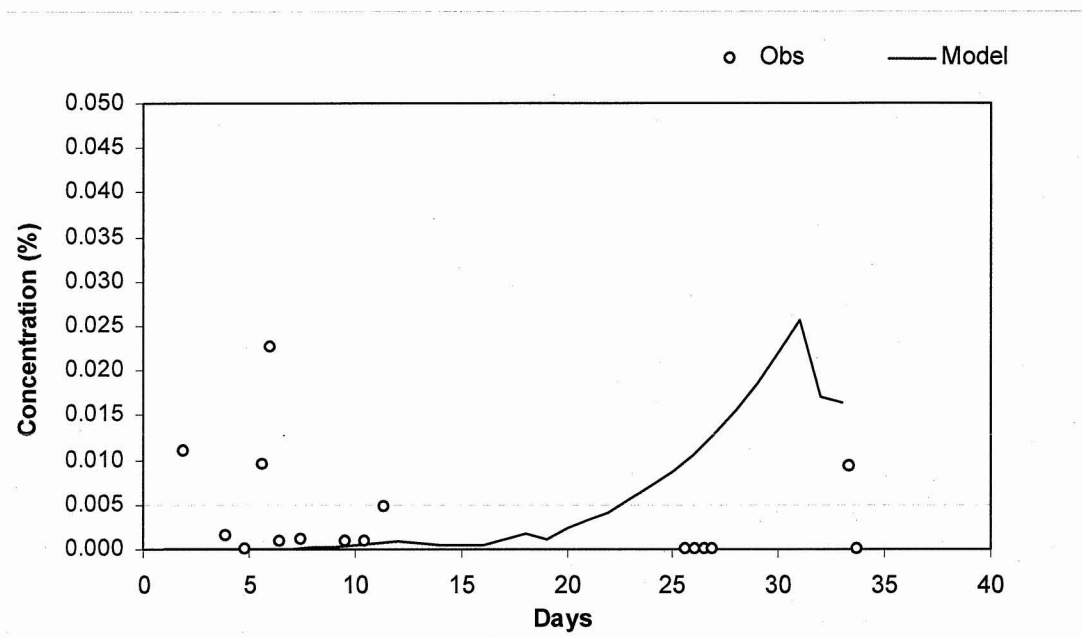
Figure A5. Simulated and observed breakthrough of 17β-Estadiaol in TOP1
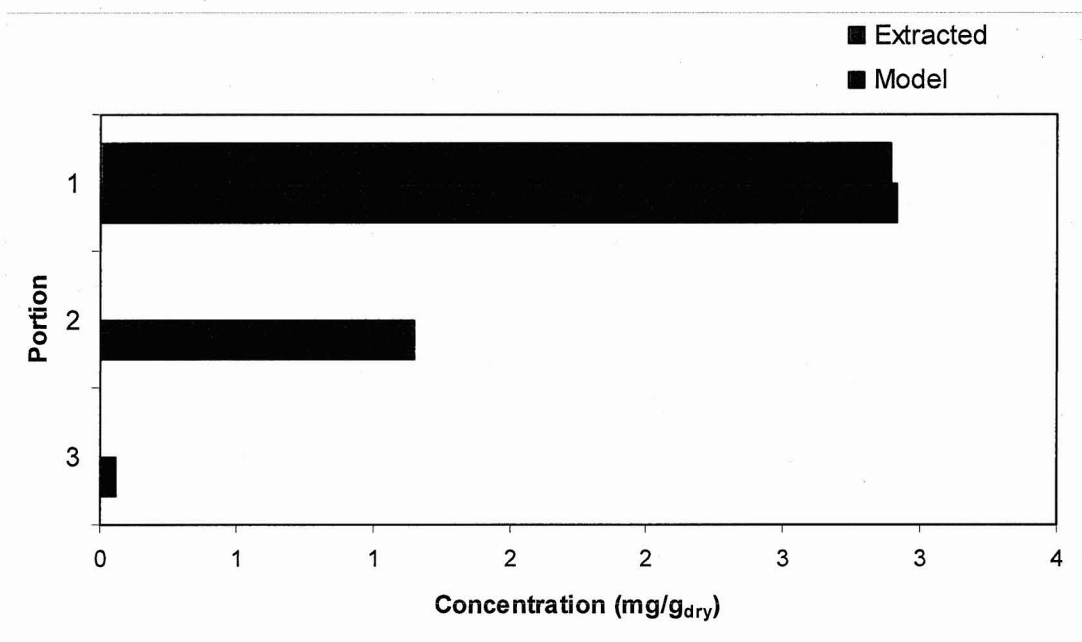
Figure A6. Simulated and measured 17β-Estadiaol residual in soils at the end of the experiment
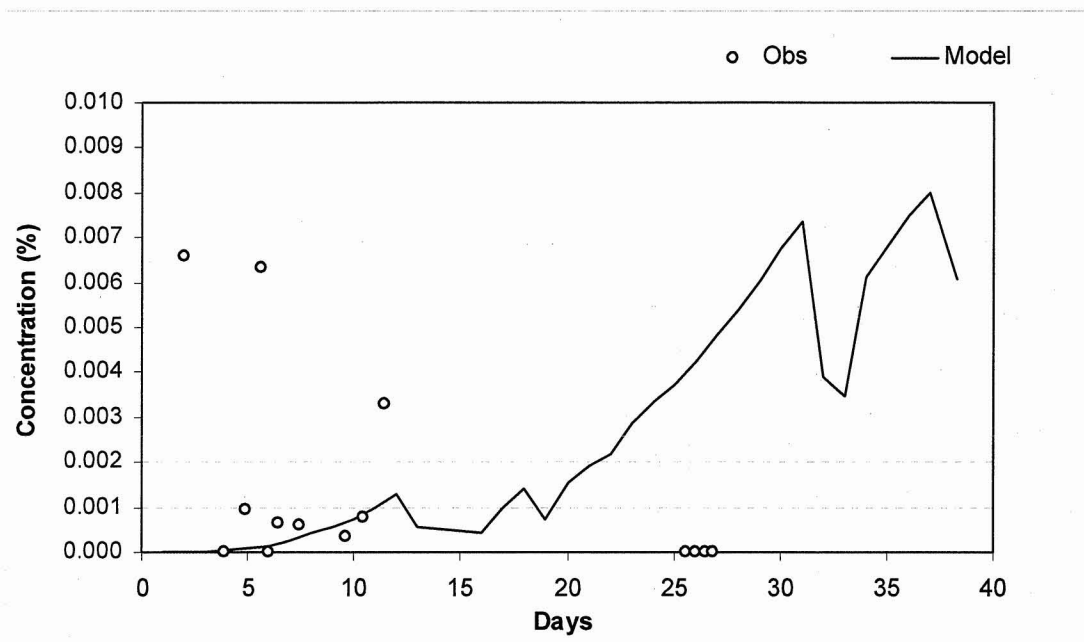
Figure A7. Simulated and observed breakthrough of estrone in TOP1
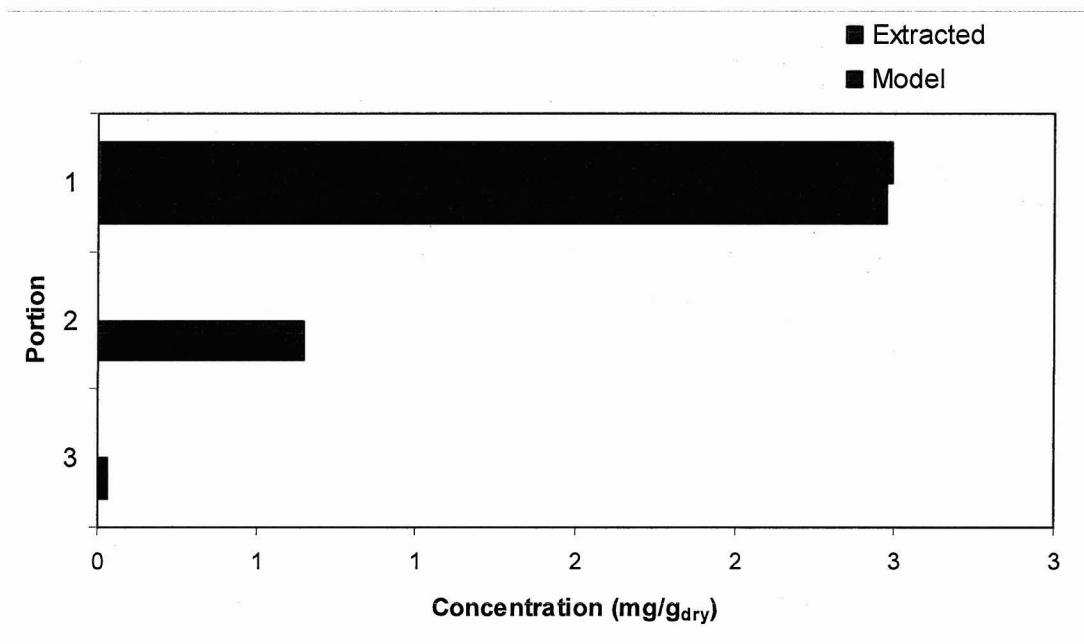
Figure A8. Simulated and measured estrone residual in soils at the end of the experiment
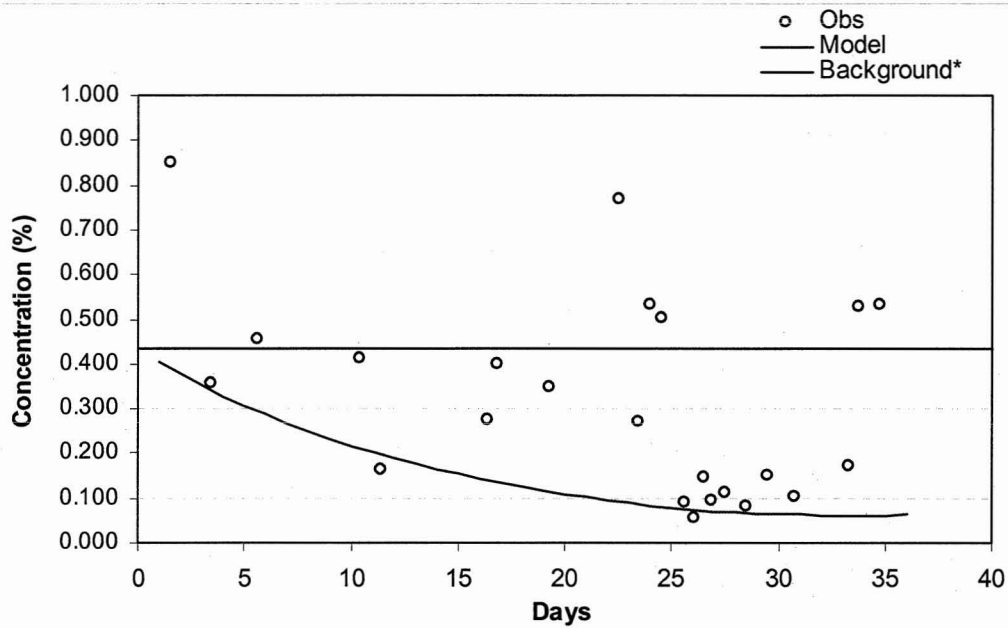
Figure A9. Simulated and observed breakthrough of nonylphenol in TOP1
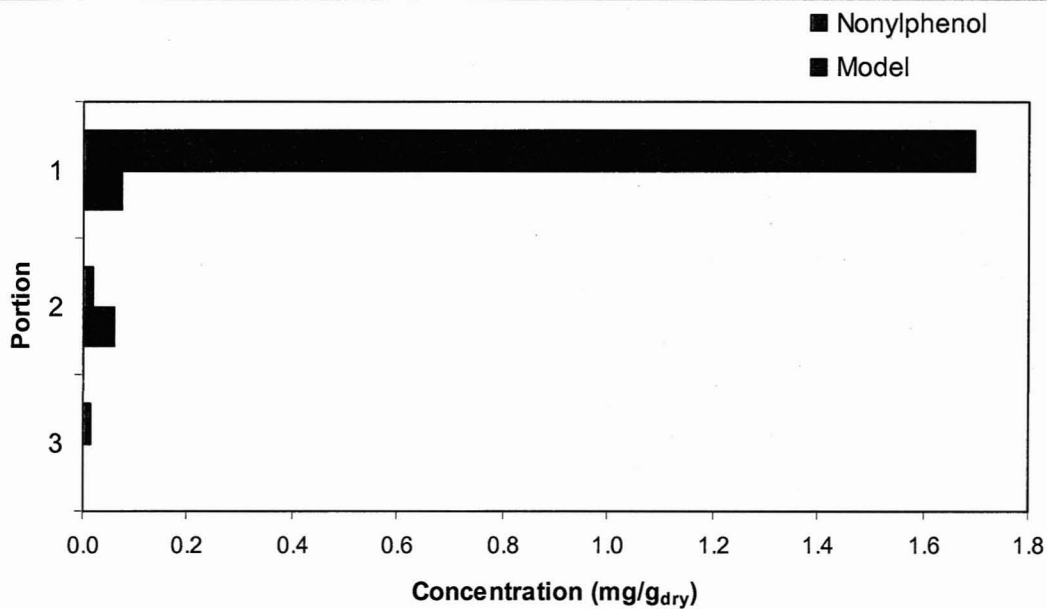
Figure A10. Simulated and measured nonylphenol residual in soils at the end of the experiment

*Background concentration detected in effluent before compound application
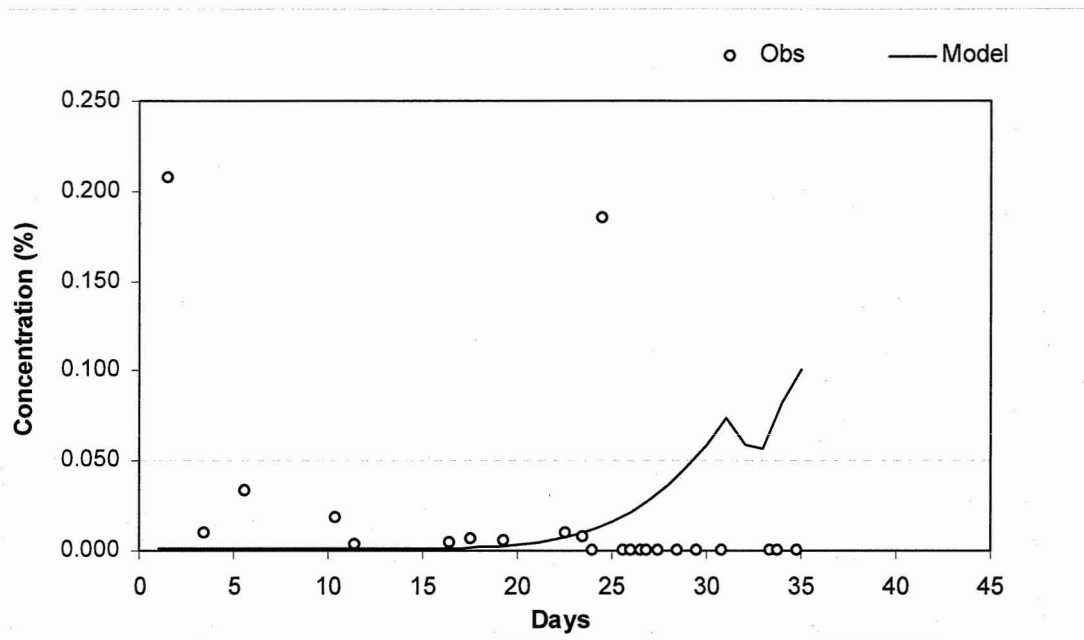
Figure A11. Simulated and observed breakthrough of octylphenol in TOP1
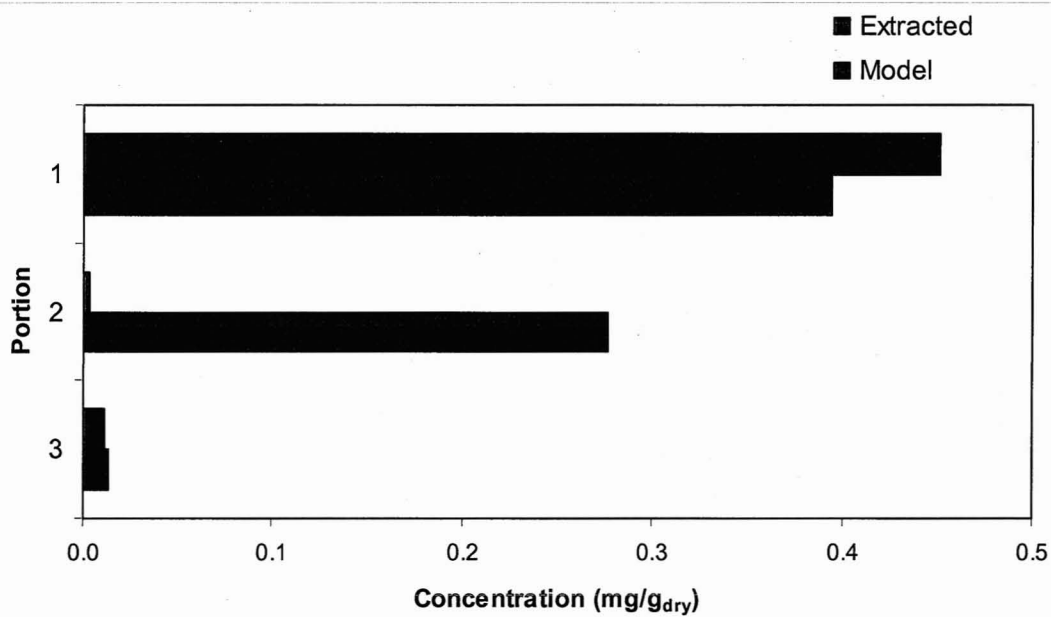
Figure A12. Simulated and measured octylphenol residual in soils at the end of the experiment
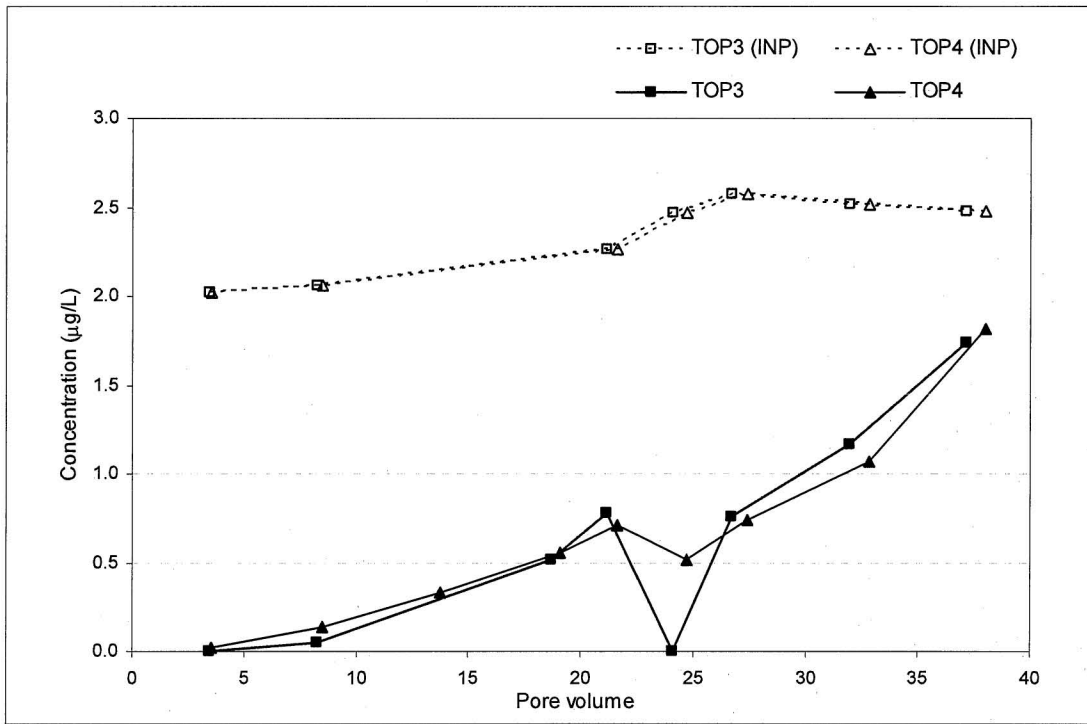
Figure A13. BTC of lindane in TOP in R-1 water, $C_0 = 2.0$ μg/L
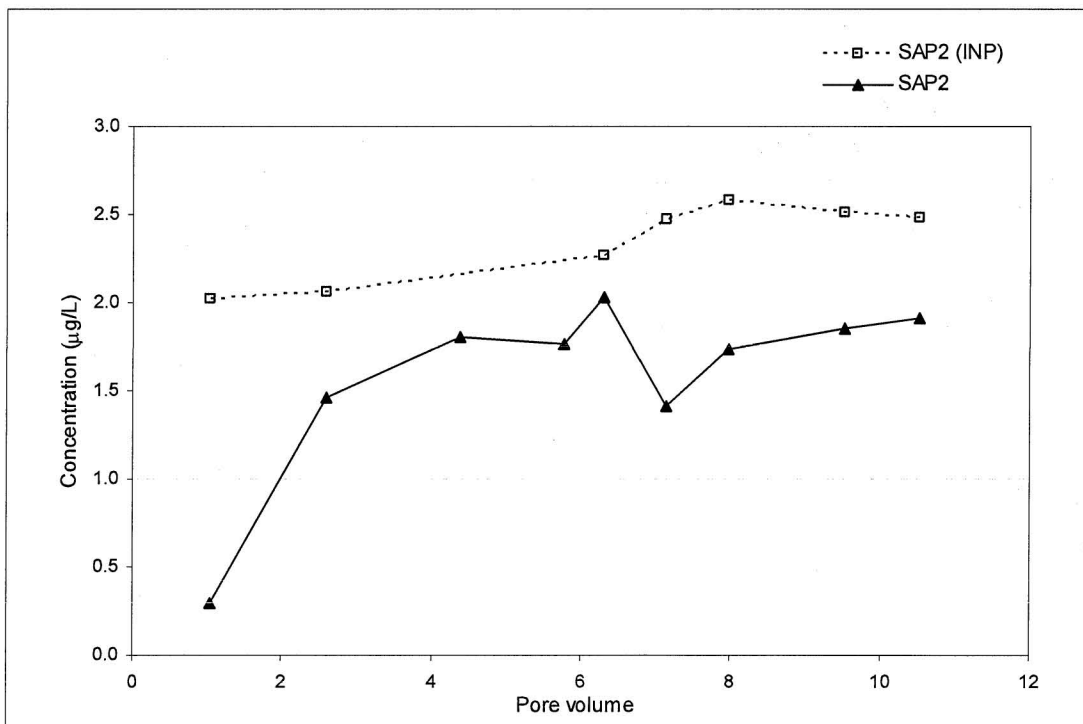
Figure A14. BTC of lindane in SAP in R-1 water, $C_0 = 2.0$ μg/L
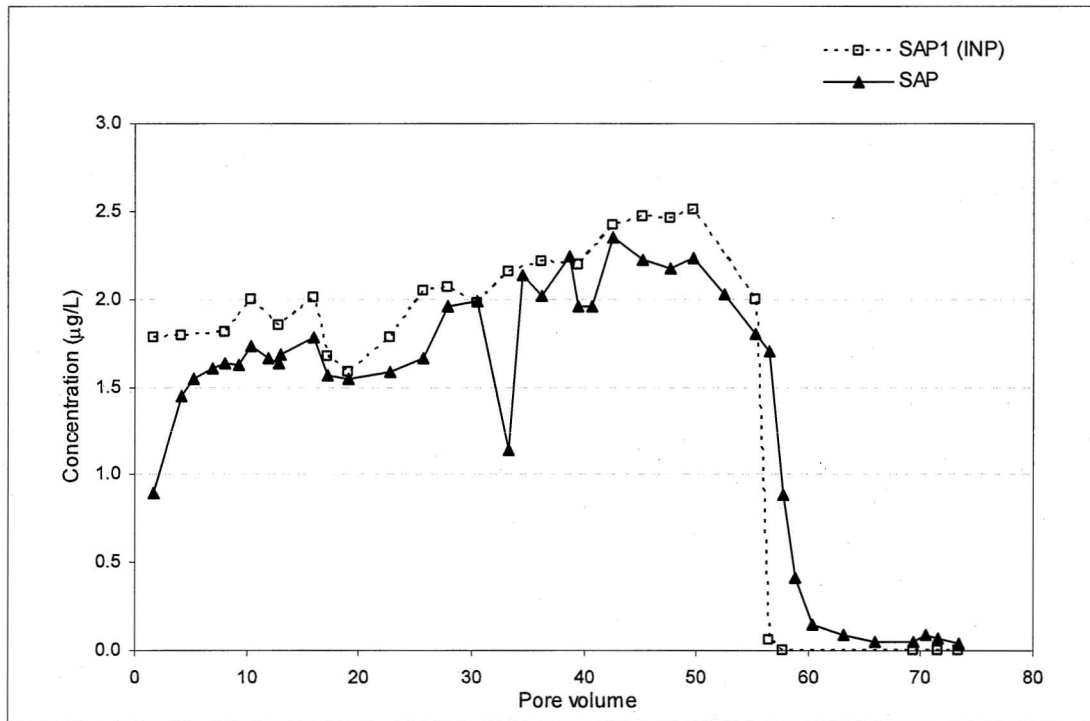
Figure A15. BTC of lindane in TOP in AGW, $C_0 = 2.0$ µg/L
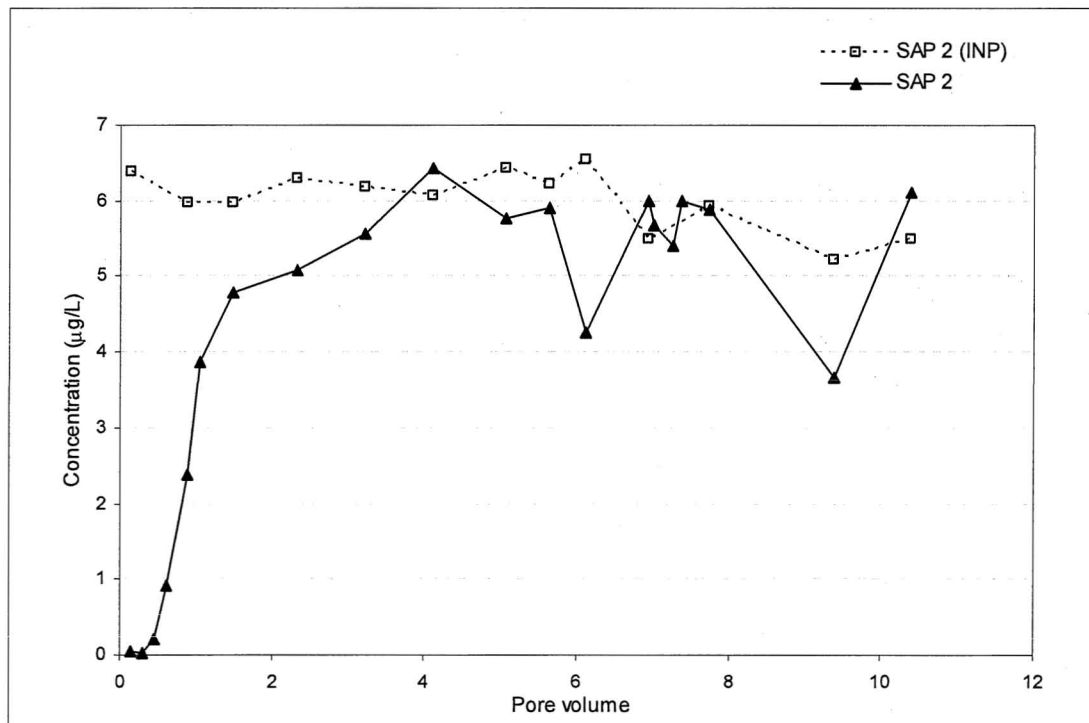
Figure A16. BTC of atrazine in SAP in AGW, $C_0 = 8.0$ µg/L
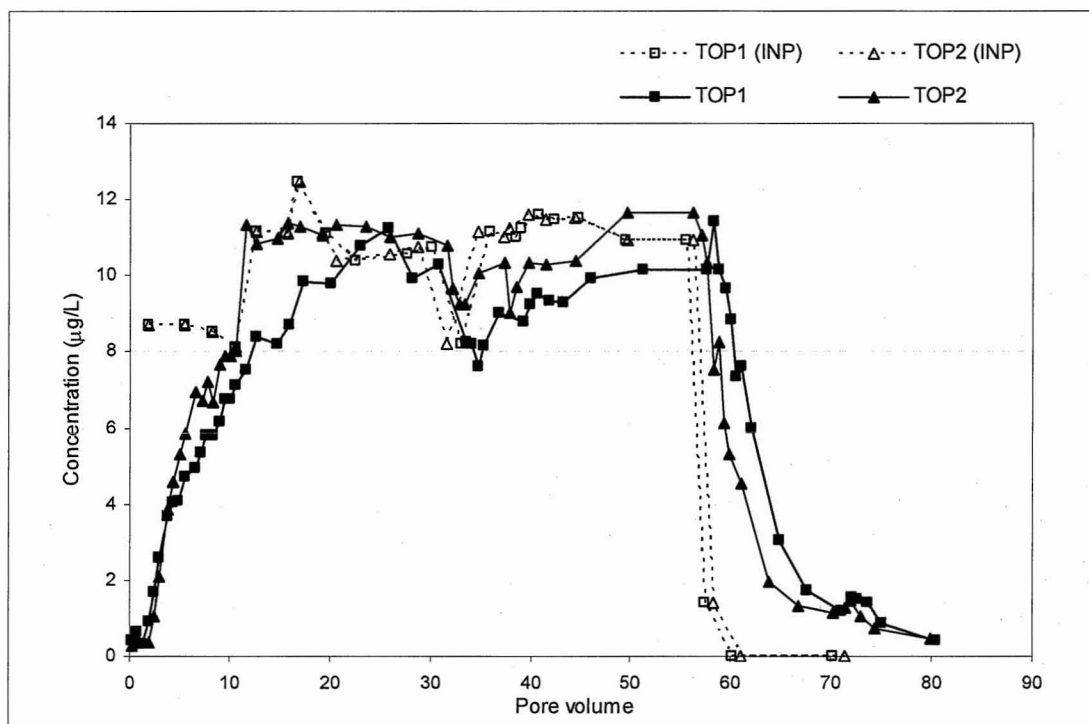
Figure A17. BTC of atrazine in TOP in AGW, C_0 = 8.0 µg/L
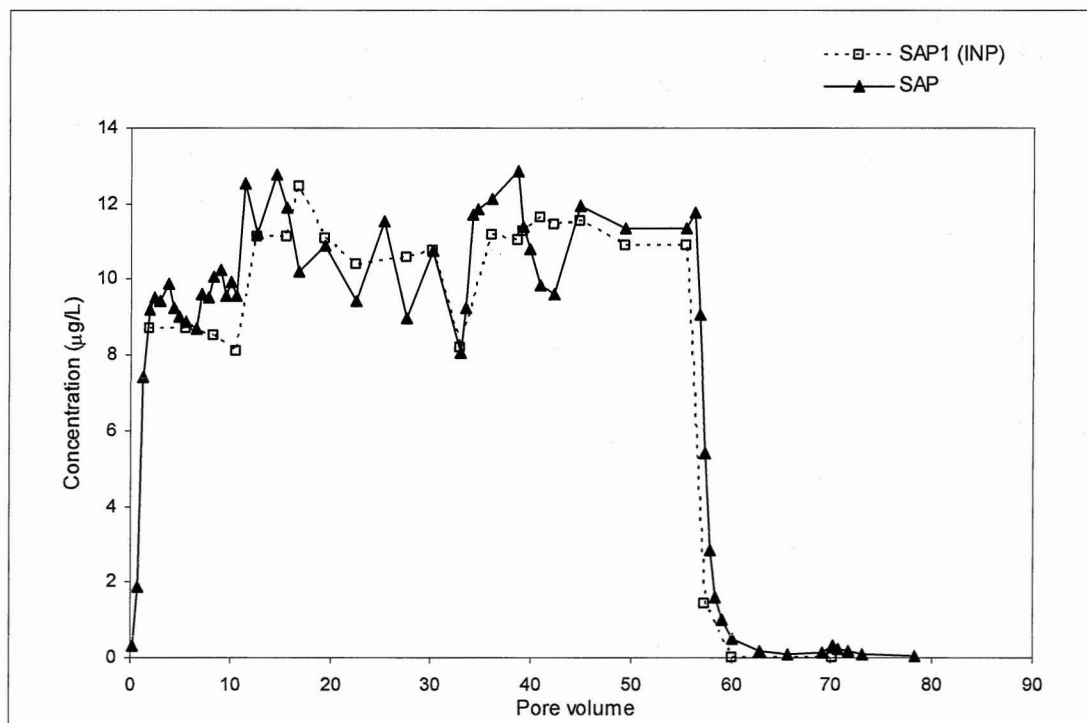
Figure A18. BTC of atrazine in SAP in AGW, C_0 = 8.0 µg/L
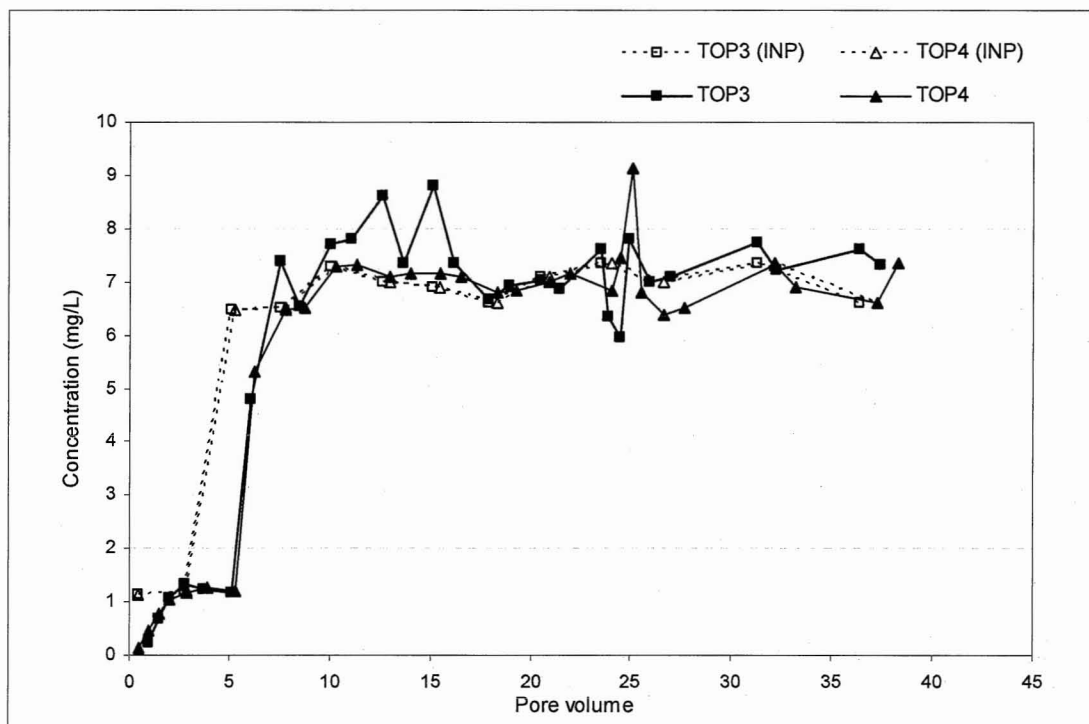
Figure A19. BTC of bromide in TOP in AGW, $C_0 = 5.0$ mg/L
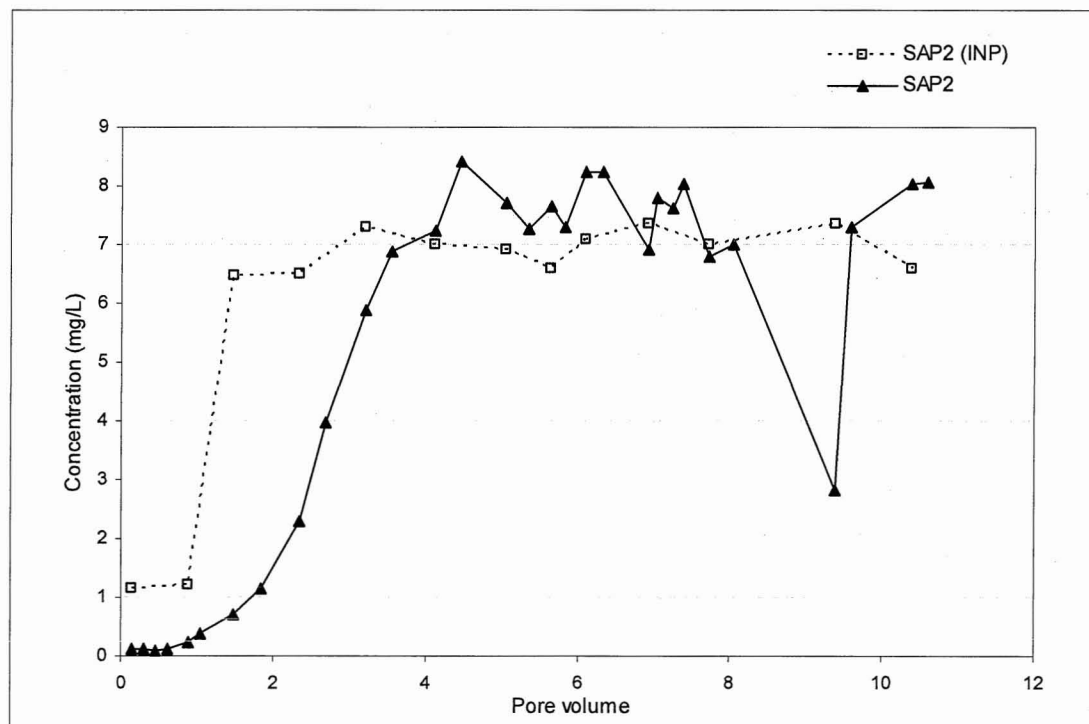
Figure A20. BTC of bromide in SAP in AGW, $C_0 = 5.0$ mg/L
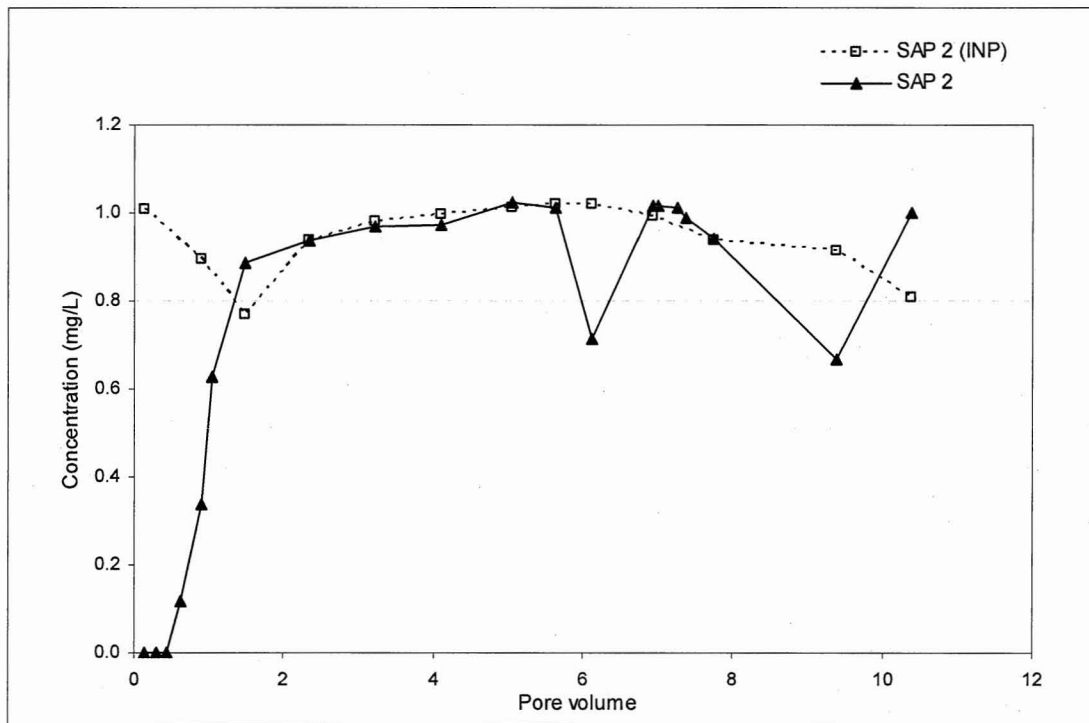
Figure A21. BTC of NDMA in TOP in R-1 water, C₀ = 1.0 mg/L
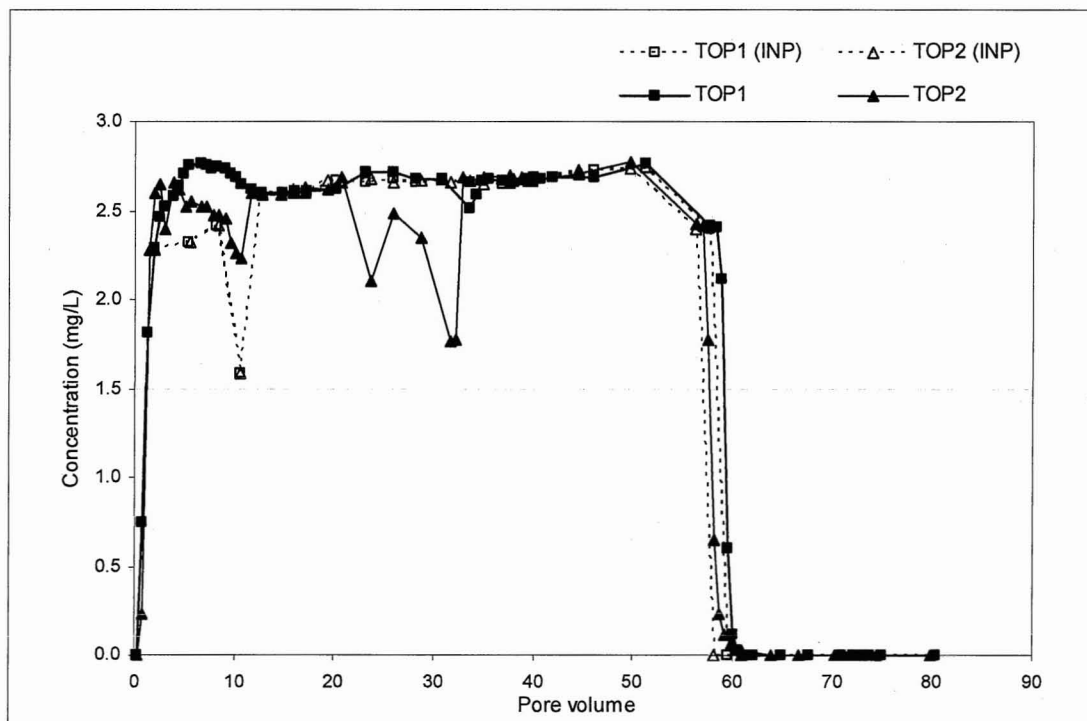
Figure A22. BTC of NDMA in TOP in AGW, C₀ = 2.5 mg/L
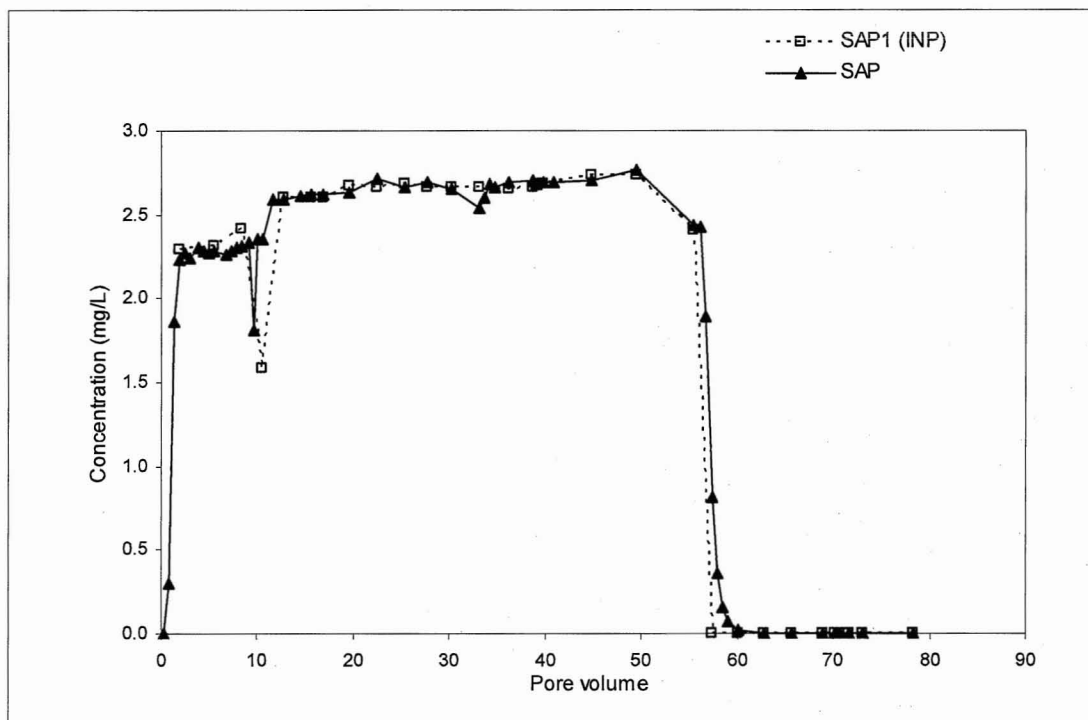
Figure A23. BTC of NDMA in SAP in AGW, C_0 = 2.5 mg/L
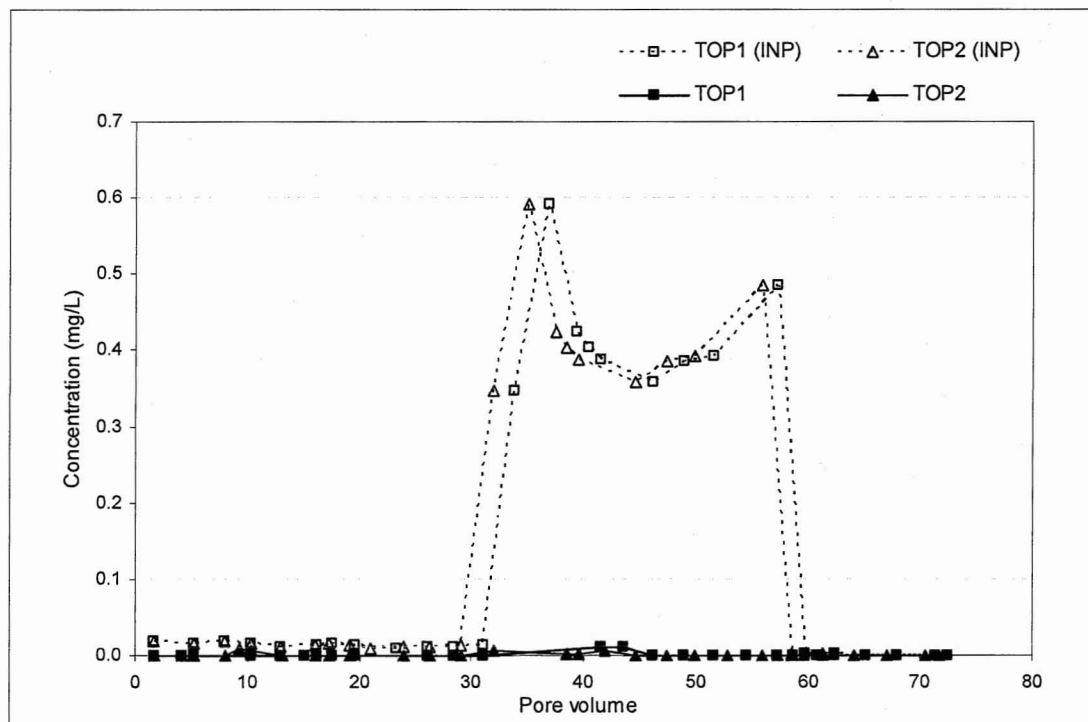
Figure A24. BTC of estrone in TOP in AGW, C_0 = 5.0 mg/L
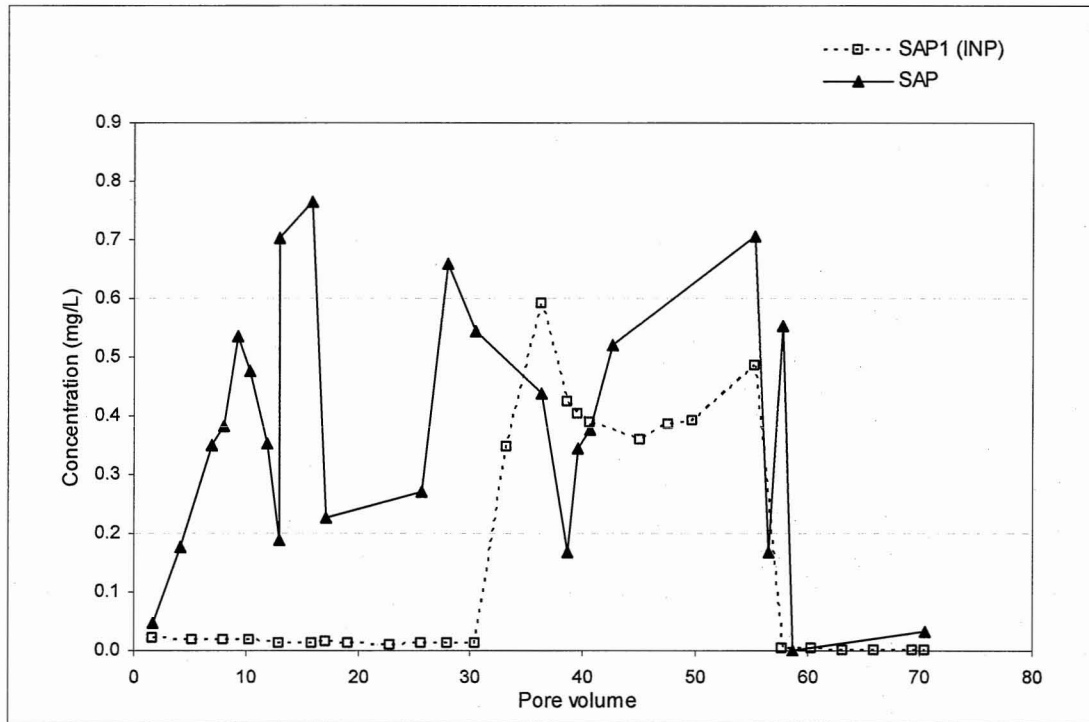
Figure A25. BTC of estrone in SAP in AGW, C_0 = 5.0 mg/L
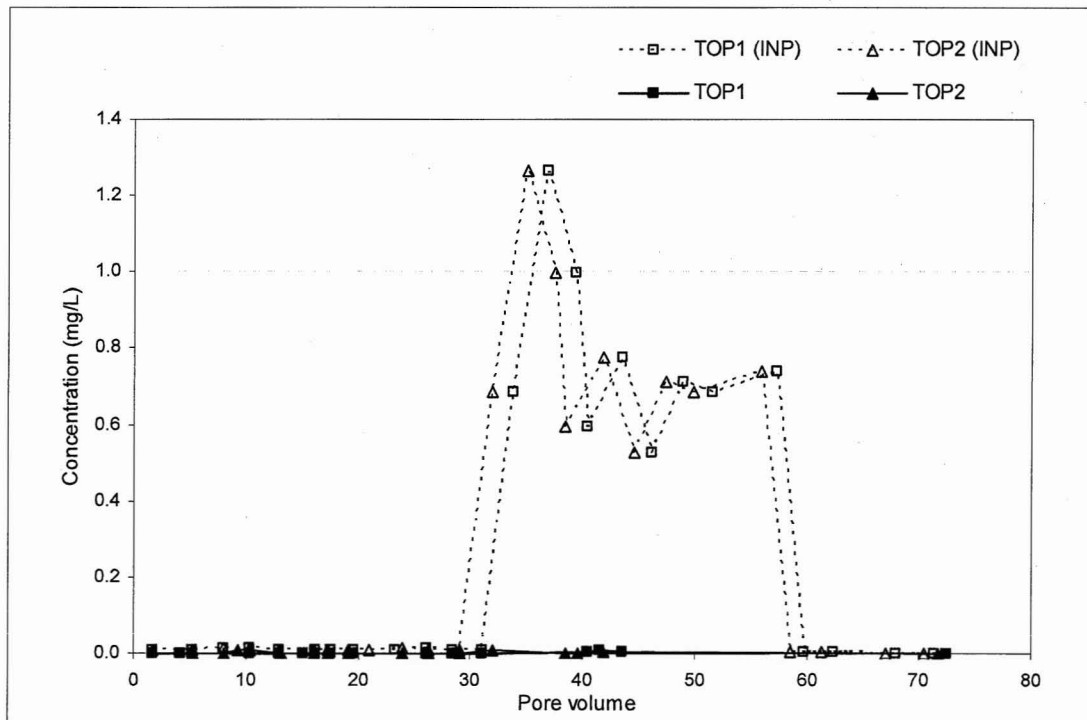
Figure A26. BTC of 17β-estradiol in TOP in AGW, C_0 = 5.0 mg/L
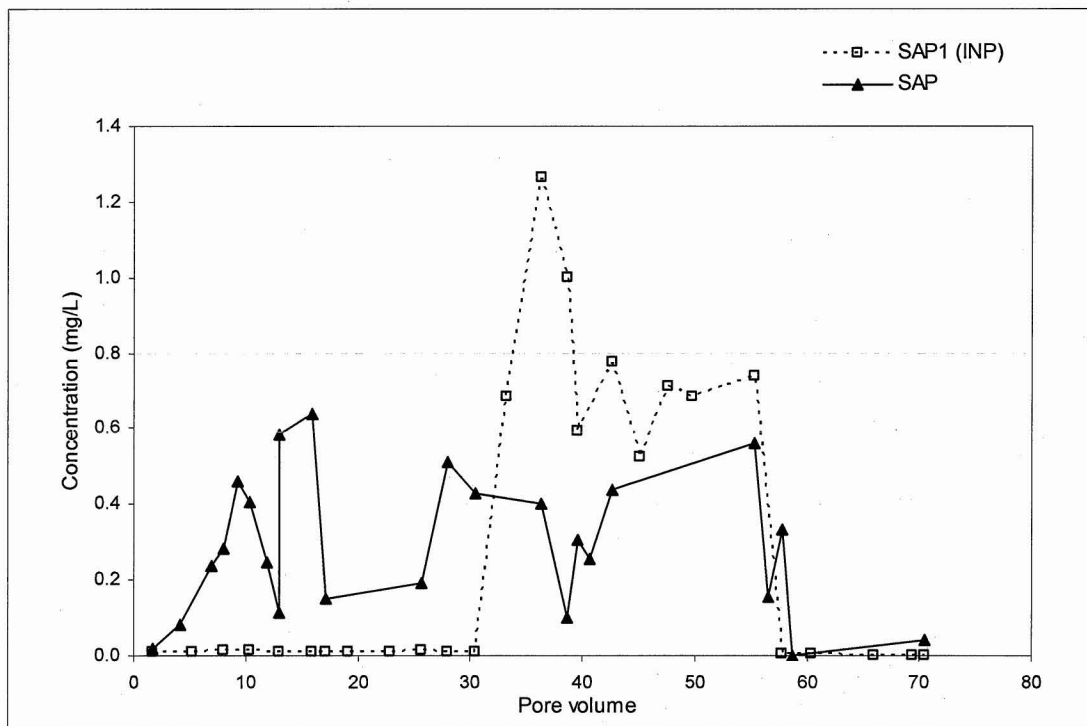
Figure A27. BTC of 17β-estradiol in TOP in AGW, C₀ = 5.0 mg/L
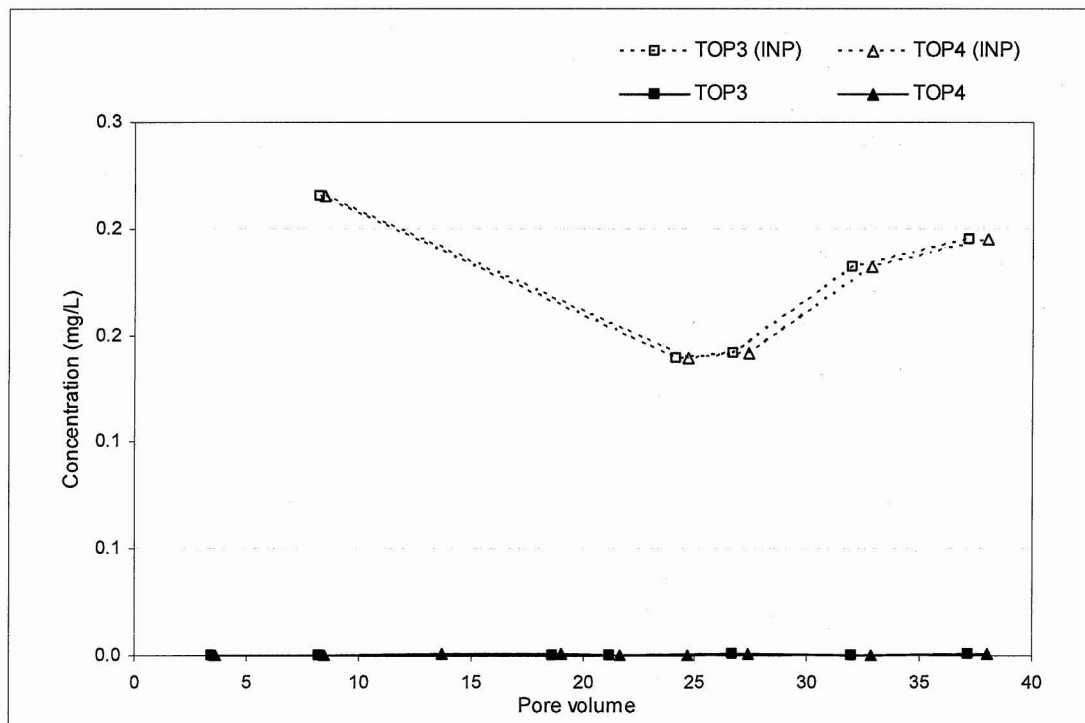
Figure A28. BTC of nonylphenol in TOP in R1 water, C₀ = 0.6 mg/L
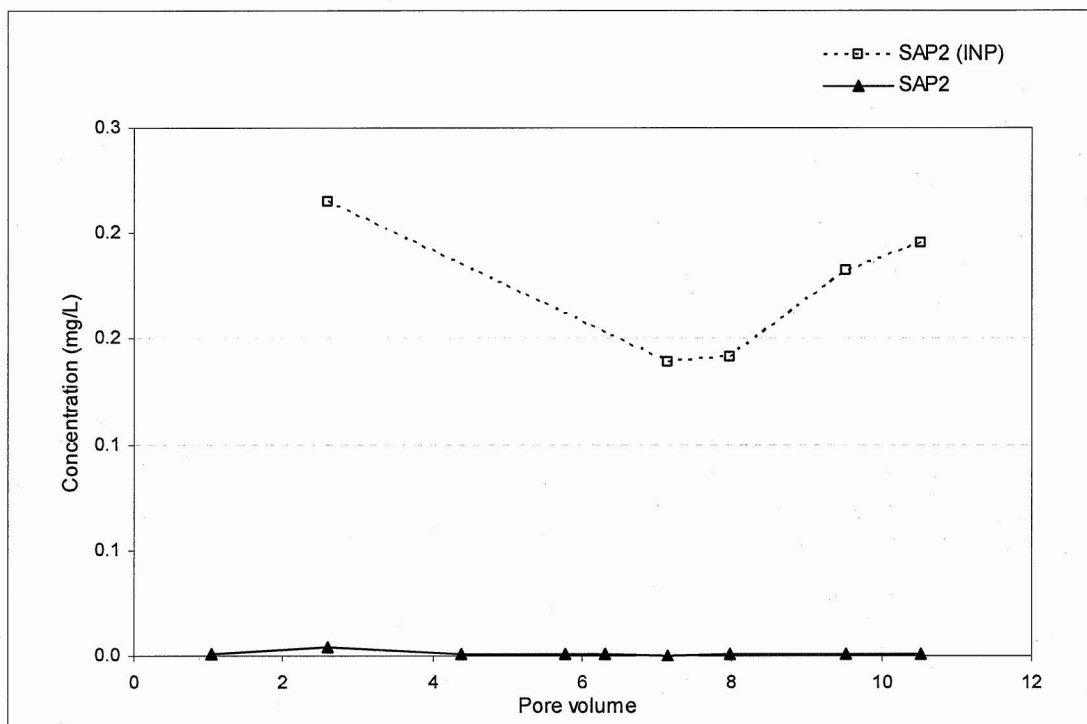
Figure A29. BTC of nonylphenol in SAP in R1 water, $C_0 = 0.6$ mg/L
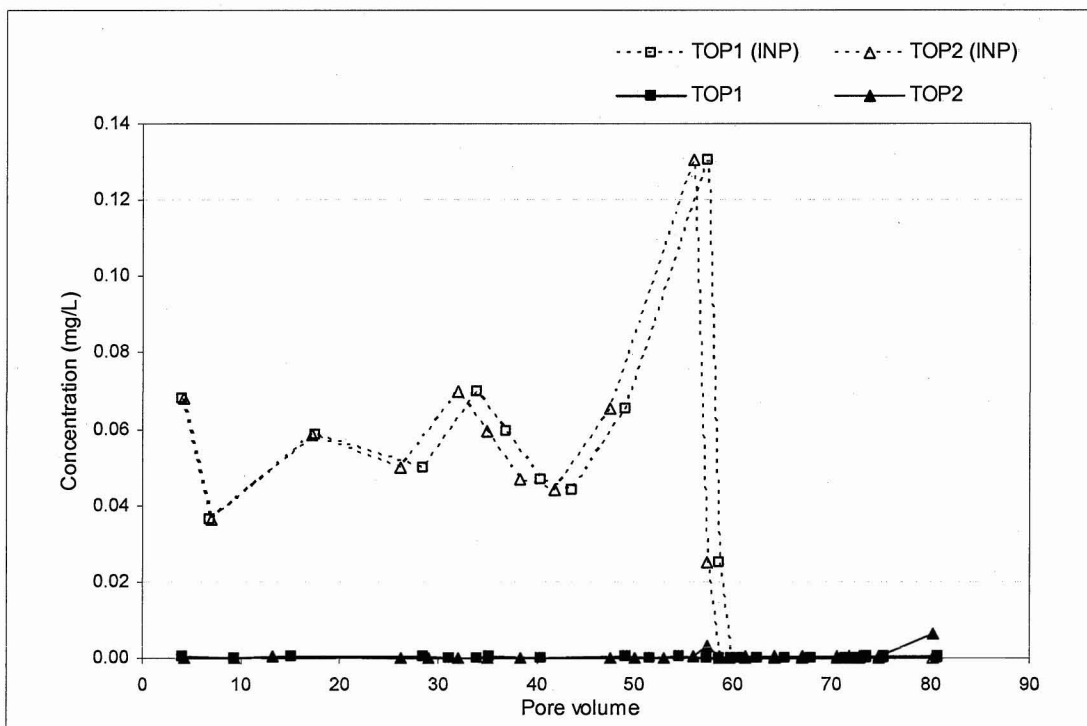
Figure A30. BTC of nonylphenol in TOP in AGW, $C_0 = 0.2$ mg/L
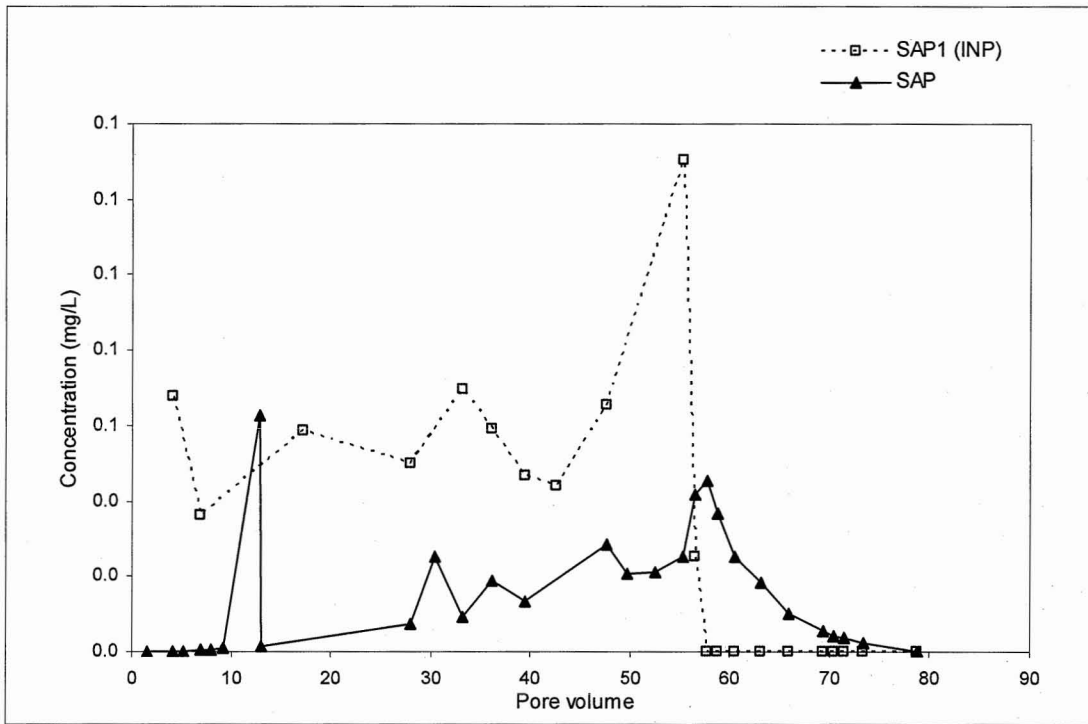
Figure A31. BTC of nonylphenol in SAP in AGW, C_0 = 0.2 mg/L
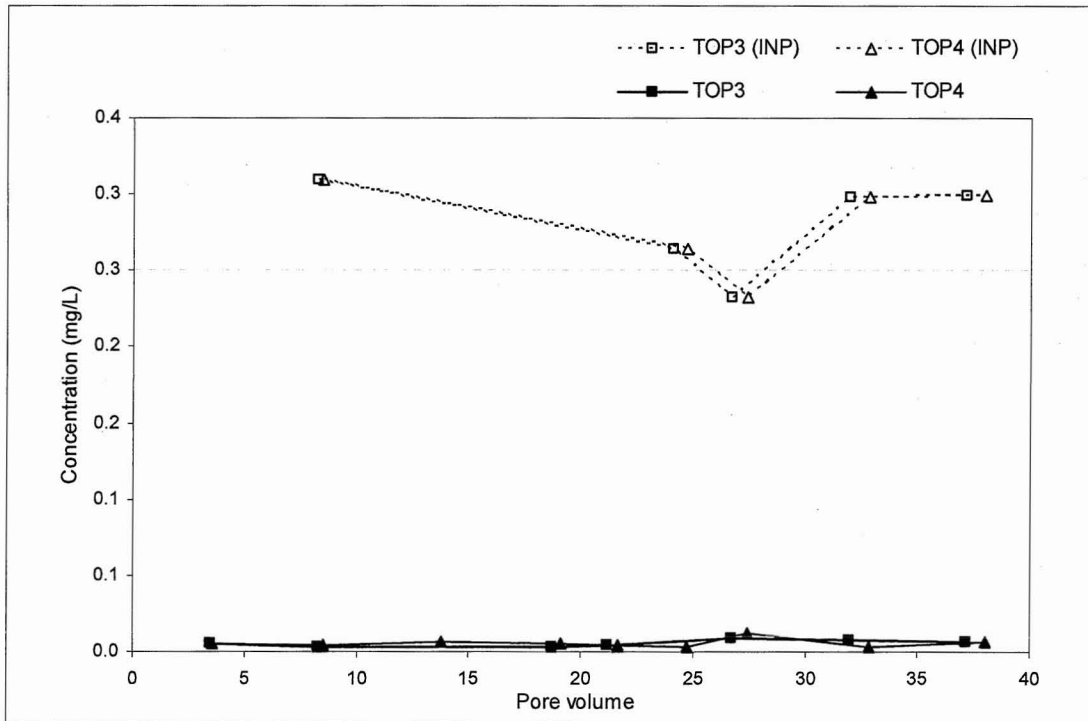
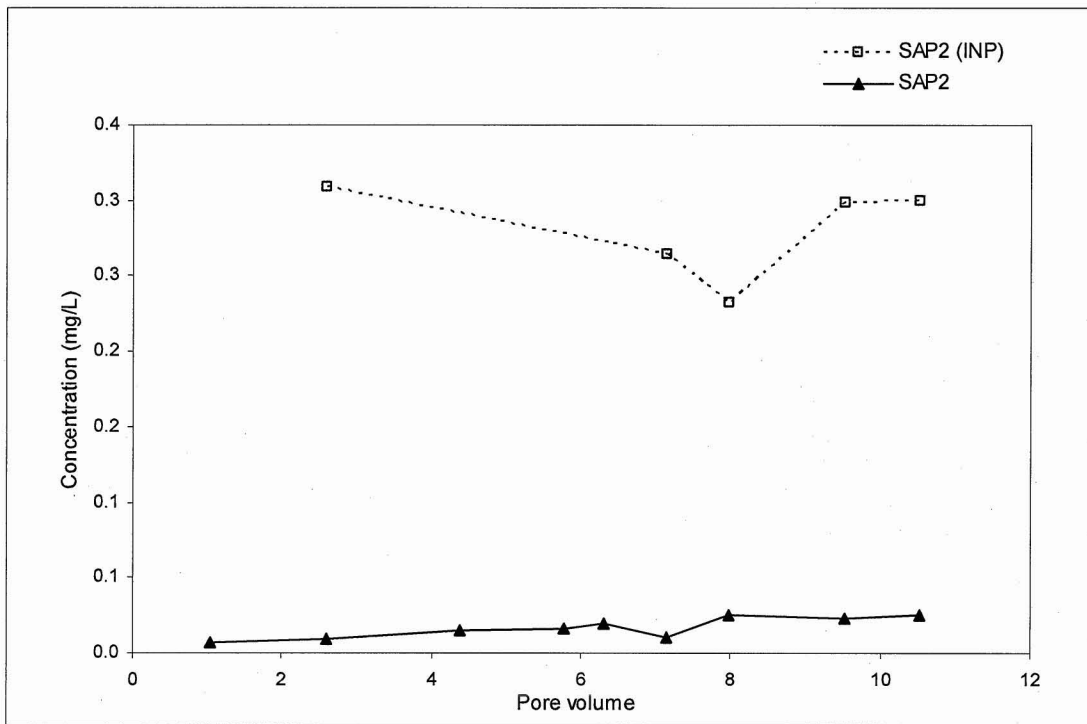**Figure A32. BTC of octylphenol in TOP in R-I water, C_0 = 0.6 mg/L**

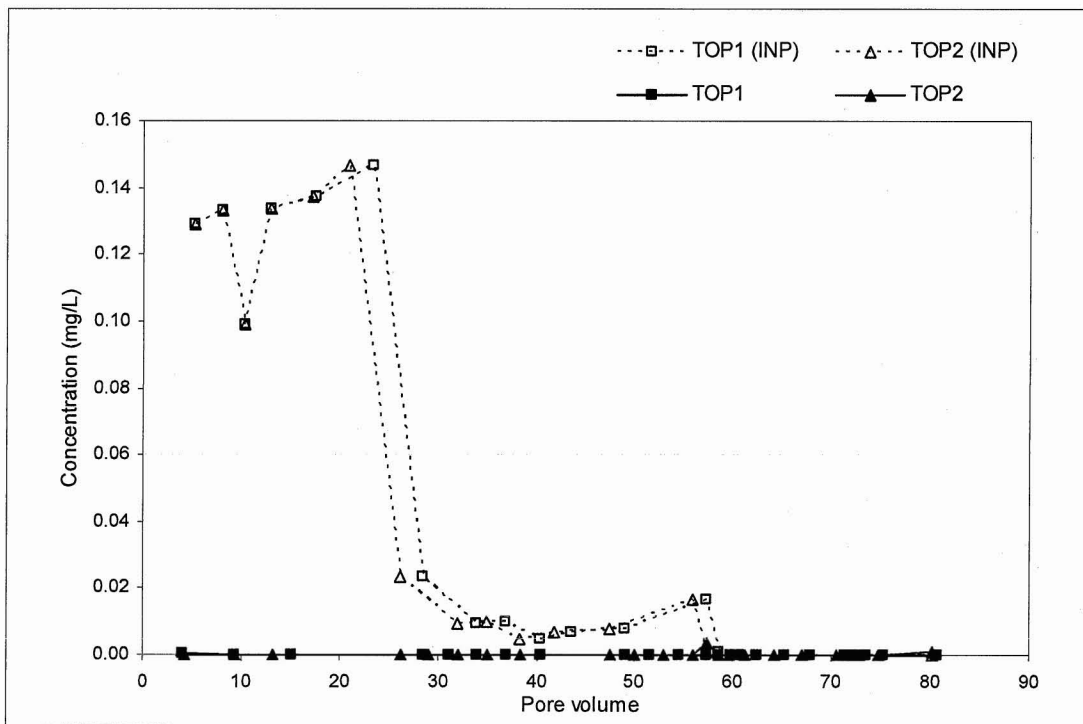**Figure A33. BTC of octylphenol in SAP in R-I water, $C_0 = 0.6$ mg/L**

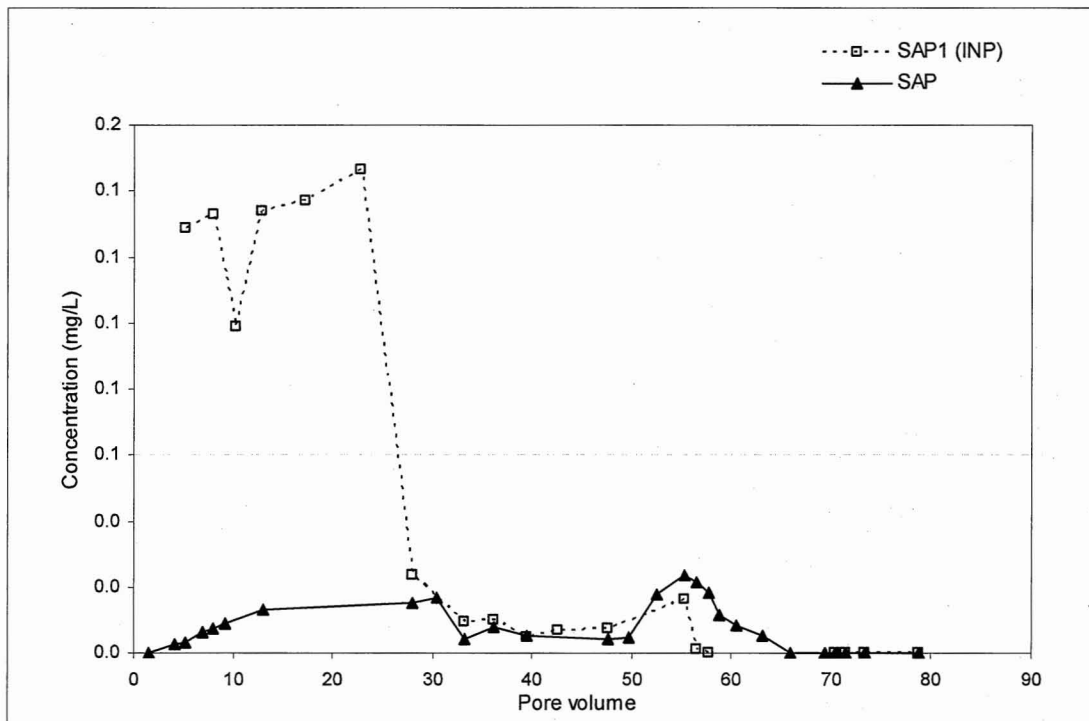**Figure A34. BTC of octylphenol in TOP in AGW, $C_0 = 0.4$ mg/L**

Figure A35. BTC of octylphenol in SAP in AGW, C_0 = 0.4 mg/L