Sorption of Organic Compounds on Oil Shale Materials and Sorption of Selected Chemicals on a Western Soil

by

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(ABSTRACT)

The sorption capacity of a raw shale (Anvil Points), three spent shales, (Antrim, Oxy 6, and Run 16), and a western soil for three organic compounds (2-Hydroxynaphthalene, 1,2,3,4-Tetrahydroquinoline, and 2,3,5-Trimethylphenol) was evaluated by batch and column sorption studies. In addition, the sorption capacity of the western soil for selected inorganic agents (arsenic, cadmium, calcium, potassium, iron, ammonium, fluoride, and sulfate) was also determined.

The results of the study showed that the sorption capacity of oil shales for organic compounds varied with the retorting conditions of spent shales, the characteristics of sorbates, and the number of different sorbates present. The overall sorption capacity of the oil shales and the soil were greatly enhanced in multi-sorbate solutions. On the other hand, mutual inhibition for sorption of individual compounds was evident throughout the study.

The western soil, in general, exhibited a better sorption capacity for organic compounds than Anvil, Oxy 6, and Run 16 shale, yet Antrim shale appeared to be the best sorbent. Sorption of inorganic ions by soil was closely related to the pH of the solution, and was greatly affected by the interactions between ion species in multi-sorbate solutions. The soil had good affinity for arsenic, cadmium and iron, but little sorption capacity for ammonium and sulfate. Desorption of calcium and potassium from the soil was evident.

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Chapter I

INTRODUCTION

Recognition of the increased demand of energy while petroleum supply is predicted to be exhausted by the year of 2050 [38] has resulted in substantial efforts in developing alternative energy sources. One of the substitute resources which are anticipated to supply a sizable portion of the energy requirement of the United States in the next century is oil shale. Oil shale is one of the largest undeveloped energy resource in this country. Approximately 75% of the world's known reserves of oil shale are distributed in the Green River Formation in Colorado, Utah, and Wyoming and in other areas of the country as shown in Figure 1. The oil shale reserves in the United State are, if 100% recovery is assumed, capable of providing 600 billion barrels of oil from high grade shale (oil yields more than 25 gal/ton) and 1600 billion barrels of oil from low grade shale (oil yields less than 25 gal/ton), which are sufficient to supply the oil demand of the U.S. for approximately 100 years [96].

The oil shale development includes two dimensions: (1) attempts to develop and improve processing technology and (2) attempts to handle the processing wastes in an environmentally acceptable manner. Both dimensions are critical to the success of developing oil shale as a petroleum substitute. Current production cost for 1 barrel synthetic fuel from

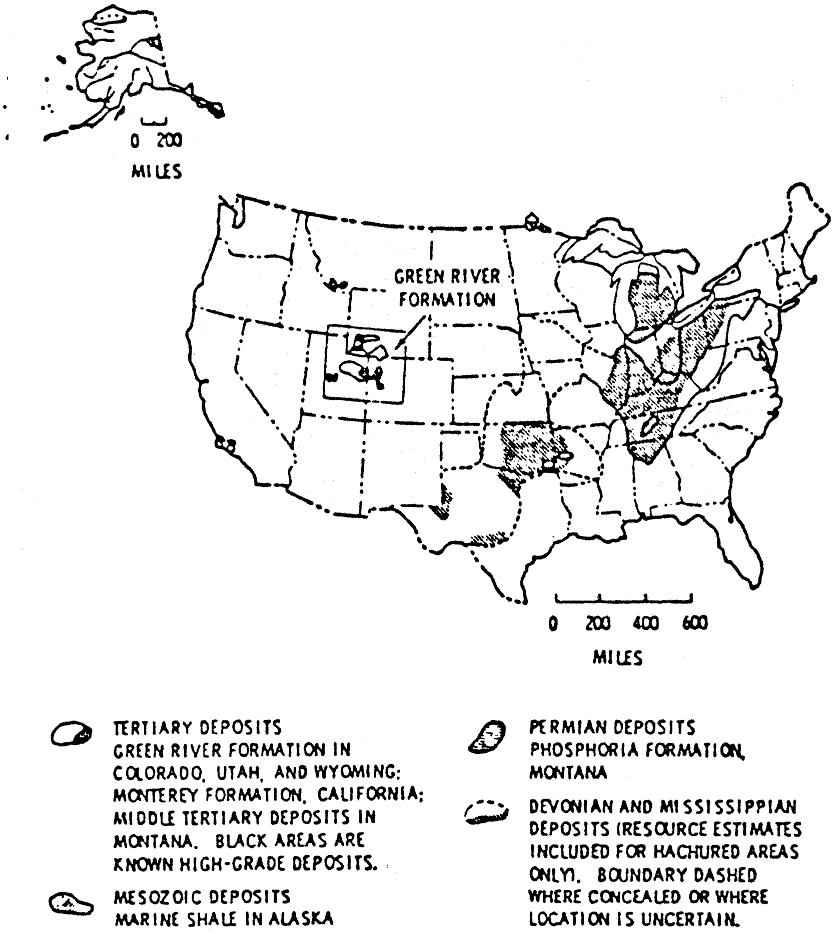

Figure 1. Oil shale deposits of the United States

shale is nearly twice as much as that needed for 1 barrel of oil from crude oil, which makes other alternatives, for example, burning coal and converting residual oil, more attractive [50]. In the case of technological dimension, therefore, more cost-effective technologies in mining, processing, and upgrading are expected. Besides technological and economical concerns, proper evaluation of environmental impacts from oil shale development activities is a major prerequisite to commercialization of shale oil production. For current processing technology, retorted shale and retort water constitute the major waste management issues.

Disposal of spent shale is one of the most serious environmental impacts associated not only with surface retorts but also with modified *in situ* (MIS) retorts. In the case of MIS process, the mined out shale is subject to be retorted on surface, and is eventually disposed on land as well. Potential problems related to spent shale disposal include:

1. Selection of disposal sites.

2. Stabilization of spent shale embankments.

3. Surface and ground water contamination by erosion, runoff, and percolation through spent shale with subsequent effects of potential toxic minor elements, and organic compounds in the leachate.

4. Air pollution by wind erosions of oil shale, auto ignition and, if disposed of on the surface, fugitive dust emissions.

Co-disposal of process waters with spent shale is part of the retort water management strategy that reduces the large quantity of external water required for moisturization of spent shale from retorts, and lowers the cost for retort water treatment. This approach has currently been undertaking in other countries having commercial oil shale plants [50]. However, under current EPA policy and the Resource Conservation and Recovery Act (RCRA), the co-disposal option is not allowed because of the uncertainty of what environmental impact would be imposed from the combination of these two wastes. Therefore, whether spent shale can be an effective adsorbent for the materials present in retort water becomes a key issue in determining the feasibility of the co-disposal option.

The primary objective of this project was to evaluate the sorptive behavior of three organic compounds in the presence of four shales (Antrim, Anvil Points, Oxy 6, and Run 16) and a western soil. An attempt was made to evaluate competitive sorption effects of chemical species on shales and soil. The study was undertaken with single- and multi-component solutions and a series of batch and continuous-flow column experiments. Similar work was also conducted to assess the adsorptive capacity of the western soil with several inorganic anions and cations.

Chapter II

LITERATURE REVIEW

2.1 Description of Oil Shale

The term oil shale refers to a seporopelite of which the mineral portion is associated with high molecular weight organic matter that, on destructive distillation, yields shale oil. Oil shale was formed by the contemporaneous deposition and lithification of fine-grained mineral debris and organic degradation products derived from the breakdown of algae, spores or pollen. Gavin [34] defined oil shale as: "a compact, laminated rock of sedimentary origin, yielding over 33% of ash and containing organic matter that yields oil when distilled, but not appreciably when extracted with the ordinary solvents for petroleum."

Oil shales are classified as marlstones, mixture of calcium and magnesium carbonates with small amount of quartz and silicates which contains nearly 86% mineral matter and 14% organic matter [82]. A typical composition of oil shale is shown in Table 1. Because of the nature of their complex formation, oil shales exhibit considerable variability in organic content and in inorganic minerals.

Table 1. Average chemical composition of Green River oil shale

Mineral Composition	Wt. %	Organic Matter	Wt. %
Pyrite (FeS_2)	0.86	Bitumen	2.76
Analcite ($NaAlSi_2O_6 \cdot H_2O$)	4.3	Kerogen	11.04
Quartz (SiO_2)	8.6		
Clay ($KAl_4Si_7AlO_{20}[OH]_4$)	12.9		
principally, illite			
Feldspar ($KAlSi_3O_8$)	16.4		
& Plagioclase ($NaAlSi_3O_8$ - $CaAl_2Si_2O_8$)			
carbonates ($CaMg[CO_3]_2$)	43.1		
principally, dolomite & calcite			

Source: [112]

Shale oil is recovered from kerogen, the major organic constituent in oil shale. Kerogen is a polymeric hydrocarbon with high molecular weight (> 3,000), thermally unstable and not extractable by ordinary organic solvents. The composition of kerogen has not been fully understood. When temperature is higher than 250°C, kerogen decomposes to gaseous and liquid products. Most of the organic matter in oil shale is vaporized at 500 to 600°C.

2.2 Processing of Oil Shale

In order to obtain oil from oil shale, organic matters must be decomposed and separated from minerals. Currently, oil shale is decomposed thermally by gas combustion (with air) and pyrolysis (without air). Retorting technology of oil shale is classified either as *ex situ* or as *in situ*. The major differences between *ex situ* and *in situ* processes are the heating temperature and the heating pattern involved in shale retorting processes. By comparing advantages versus disadvantages of *in situ* and *ex situ* processes, Yen [111] indicated that the *in situ* process was more economic and more environmentally desirable because most of the operations were conducted underground which minimized the mining and waste disposal problems.

2.2.1 Ex Situ (Surface) Retorts

Surface retorting processes consist of mining, crushing and heating the shale at high temperature. Oil shale is thermally decomposed in above-ground retorts at 500-750 °C until the organic matter is vaporized [107]. Surface retorting processes can be further divided into two categories: (1) direct heating process and (2) indirect heating process, based on the method used for heat exchange.

In the direct heating process, heat is supplied by hot gases from controlled combustion of a part of carbonaceous matters in the shale. This category includes Paraho-direct, Union A, and the Superior Oil Circular-grade retort. The indirect processes involve the use of an external heat carrier, e.g., heated gas or solid, that circulates through the unit to provide sufficient heat for shale retorting. Examples are Fisher Assay, TOSCO II, Lurgi-Ruhrgas, Union B, and Paraho-indirect process.

2.2.2 In Situ (Subsurface) Retorts

In situ retorts are processes by which oil shale is thermally decomposed in the shale formation. The maximum retorting temperature may exceed 1000 °C [24]. *In situ* processes can be subdivided into true *in situ* (TIS) processes and modified *in situ* processes (MIS). In true *in situ* process, an external fuel source is used to ignite the material underground and controls the burnings. The permeability of gas and liquid flow is enhanced by creating void space without shale removal by using surface uplift or other means.

The Modified *in situ* process involves underground pyrolysis of large chambers of fractured shale. Chambers are constructed by mining out 20% to 40% of the formation to create sufficient voids. The balance is fractured with explosives for *in situ* retorting. Subsequently, the mined out shale is retorted at surface facilities.

2.3 Retorting Wastes Generation

When synthetic fuels are produced from oil shale retorting, large quantities of wastes are generated, and must be handled and be disposed of in an environmentally acceptable manner. These wastes include spent shale (retorted shale), retort process waters, low grade or off-size shale, overburdens, offgases, and scrubber wastes. Of these wastes, retorted shale and process waters constitute major waste management problems due to their great amount and large volume.

2.3.1 Spent Shale

Both *ex situ* and modified *in situ* processes produce significant quantities of solid wastes. As high as 96% of the total solid waste may be constituted by spent shales (Table 2). During retorting processes, the weight of shale may decrease 15% to 20% because of the vaporization of organic matter. On the other hand, the volume of spent shale may be 10% to 40% greater than that of unmined shale due to an increase in void space during mining, crushing, and retorting [77]. A one million barrel per day oil shale industry will generate up to 1.7 million tons of spent shale per day, and may require 500 to 700 hectors (ha) of land each year for spent shale disposal [15, 37].

2.3.2 Process Waters

Retorting processes produce two types of process waters, known as retort water and gas condensate, which are unique to the oil shale industry. These two waters originate from the combustion of organics in the retort, dehydration of minerals, input steam and local ground water (*in situ* processes). Water coproduced with shale oil in an oil-water emulsive state is referred to as retort water. The retort water is separated from oil by heat treatment and decantation. Gas condensate is the water phase leaving the retort in a vapor state with offgas, and is removed from the gas stream in a gas scrubbing system.

Because of the intimate contact with the oil and shale matrix at high temperature during the retorting process, retort water and gas condensate are chemically complex, containing

Table 2. Solid wastes from oil shale processing

Major wastes [1]	Quantity (ton/day) [2]	Wt. %
Raw shale dust	425	0.8
Spent shale	53,300	96.2
Scrubber sludge	860	1.6
Coke	800	1.4
Catalysts (ton/yr)	1,250	0.01
Other (ton/yr)	11,000	0.05
Total (ton/yr)	20.2 x 10^6	100

[1] Based on an oil production capacity of 50,000 barrel/day.
[2] Except as noted.
Source: [56]

high concentrations of organic and inorganic constituents. The quantities, type and composition of these waters are site specific, and will primarily depend upon retort operation conditions and product collection system design. Generally, retort water is more highly contaminated than gas condensate [26].

During shale retorting, an average of 0.4 barrels of retort water coproduced with shale oil has been reported [45]. Combined production of retort water and gas condensate varies with site and process. Retort water production from surface retorts ranges between 0.1 to 0.5 barrels of water per barrel of oil, while that from *in situ* processes may range from 0.4 to 10 barrels of water per barrel of oil [24]. As noted by Fox and Phillips [26], the high volume of water produced during *in situ* retorting was probably due to groundwater intrusion.

2.3.3 Offgas

Low BTU gas produced in oil shale retorting ranges from 70 to 14,000 scf/ton of raw shale. Due to the lower temperature, less gas per ton of shale is produced from surface retorts than from *in situ* retorts. Fruchter [31] found offgas composition varies significantly between different retorting processes (Table 3). The major gaseous pollutants determined in the offgas include NO_x , SO_x, F, As, Hg, CO, thiophene, and other volatile trace elements [31, 82].

Table 3. Composition of raw offgas

Constituent	Technology TOSCO II *Ex situ*	 Paraho Direct *Ex situ*	 Occidental Modified *In situ*	 Geokinetics True *In situ*
H_2	19.46	3.53	4.25	4.35
CO	3.26	1.60	0.77	4.34
CO_2	19.51	17.53	24.70	15.95
N_2	-	51.30	44.70	62.13
H_2O	-	19.20	22.80	-
O_2	-	0.74	0.08	5.10
NH_3	-	0.57	0.62	-
NO_x	-	-	-	0.006
H_2S	3.94	0.24	0.15	0.07
CH_4	19.36	1.86	1.16	2.47
Higher Hydrocarbons	34.49	3.41	0.77	< 1.00
Mol. wt. (g/mole)	29.05	28.40	28.49	-

Unit: Mole %, except as noted.
Source: [31]

2.4 Characteristics of Retorting Wastes

2.4.1 Spent Shale

The chemical and physical properties of spent shale vary greatly, depending on shale mineralogy and the retorting technology employed. High temperature during retorting results in considerable chemical and physical alterations of the shale. Besides temperature, other retorting parameters such as oxygen concentration and particle size are also important in determining the characteristics of spent shales [37, 109]. In the case of laboratory leaching study, Fransway [29] suggested using unsieved spent shale to simulate field situation because specific ion concentrations and electric conductivity (EC) tended to decrease with particle size.

The pH value and alkalinity of spent shale are closely related to the retorting temperature. Oil shale retorted at high temperature (600-800 °C) has a high pH value of 11-12. On the other hand, oil shale retorted at 500 °C produces spent shale with a lower pH value of 8-9 [84]. Alkalinity tends to increase with retorting temperature [78]. Color varies from black to light gray depending upon the severity of combustion [41]. In comparison with soil which may be considered saline if the EC of saturation extracts exceeds 4 mmho/cm, spent shale has a relatively high soluble salt content with EC ranging from 8 to 26 mmhos/cm [78].

Although most elements in raw shale were conserved in the spent shale [24], the mineral compositions may vary considerably under different process conditions as shown in Table 4. Dale and Fardy [18] conducted studies on the element partitioning of some Australian oil shale retorted under Fisher assay. Differences in partition were evident in comparison with the data obtained from Green River formation. During direct retorting of raw shale from Green River formation, 50-60% of Hg, N and organic C, 20% of S, and 5% of As and Se are redistributed to process products such as shale oil, retort water, and offgas, causing the depletion of these elements in the spent shale relative to the raw shale [32, 84]. As shown in Table 5, mobilities of trace elements in other types of oil shale, for example, Antrim and Moroccan shale, act quite different from that of Green River formation.

Fox *et al.* [24] have summarized the concentrations of some toxic elements in raw shale and spent shale from five retorting processes. Comparison of Table 6 and 7 shows that the elemental composition of some toxic elements in oil shale varies considerably during retorting process. The concentration of As, B, Cd, Mo, Sb and Se in spent shale were higher than those found in raw shale. Furthermore, different retorting processes produce spent shale with different compositions even if the same feedstock has been used.

Spent shale may contain up to 6% of organic pyrolytic products originating from the organic matters in raw shale. The quantity and quality of organic content in spent shale are largely affected by retorting conditions [107]. Oil shale retorted by direct combustion appears to have less organic residue than that produced by indirect heating process because of the higher temperature encountered in the direct process [58, 107]. For example, 2.6% organic carbon content was found in Paraho (direct) spent shale, and spent shales with 3-6% organic residues were produced by TOSCO II (indirect) process [64, 107, 109].

Because of the complexity of the retorting conditions and mineralogy, only a small portion of organic compounds in spent shale have been identified to date by extraction with organic solvents such as benzene and methylene chloride. These organics include naphthalenes, azarine, polycyclic aromatic hydrocarbons (PAH), and saturated normal hydrocarbons such as phytane, pristane and isoprenes [85, 109]. Some of these organic compounds, for example, benzo(a)pyrene and 7,12-dimethylbenzen(a)anthracene, are known to be highly carcinogenic [20].

2.4.2 Retort Water

Retort water is characterized by its high pH, high alkalinity and high levels of inorganic and organic content (Table 8). The pH value of retort water ranges from 8.5 - 9.5 [42]. Com-

Table 4. Selected elemental composition of raw and retorted shales

Constituent	Paraho		TOSCO	
	Raw Shale	Retorted Shale	Raw Shale	Retorted Shale
		(Unit: Wt. %)		
Org C		2.39		5.5
C	15.5	6.1		
H	1.50	0.17		
N	0.66	0.58		
S	0.60	0.48		
Ca	10.1	13.3	9.8	11.3
K	1.61	1.86	1.25	1.50
Mg	3.46	4.32	2.6	3.9
Na	1.69	2.19	1.43	1.74
Si	15.0	13.2	13.0	16.0
Al	3.77	4.83	3.4	4.2
Fe	2.07	2.40	1.89	2.45
		(Unit: ppm)		
F		1,660	1,020	1,490
As	44	59	70	82
Cu	40	56	48	62
Pb	27	35	30	41
Cd		0.57	1.05	0.98

Source: [109]

Table 5. Mobility of selected elements in oil shales

	Mobility, % [1]	
Constituent	Green River	Antrim
H	94.0	79
Org. C	79.0	38
Hg	70.0	46
N	49.0	16
Inorg. C	34.0	88
S	44.0	46
Cd	29.0	53
As	3.8	0.22
Na	0.19	0.15
Fe	0.084	0.0006
K	0.023	0.016
Al	0.0062	0.0002
Ca	0.003	0.008

[1] Weight percent of mass presented in raw shale.

Source: [27]

Table 6. Elemental abundance of selected toxic elements in raw shale

Element	Green River oil shale	LLNL SIS	Paraho Direct Mode	TOSCO Modified Fischer Assay
As	5-134	42	44	75
B	25-250	108	94	80
Cd	0.2-1.4	0.72	0.64	1.1
Cu	11-63	39	40	46
F	100-3200	990	-	1020

Unit: ppm.
Source: [24]

Table 7. Elemental abundance of selected toxic elements in spent shale

Element	Occidental Retort 3	LLNL Simulated *In situ* (1000 °C)[1]	Paraho Direct Mode (750 °C)[1]	TOSCO Modified Fischer Assay (500 °C)[1]
As	34	58	59	82
B	252	140	107	110
Cu	36	49	56	67
Cd	-	0.77	0.91	1.28
F	-	980	-	1420

[1] Maximum operating temperature.
Unit: ppm.
Source: [24]

positions of retort water produced from various retorting processes have been given elsewhere [26, 42]. Recent studies [22, 47, 59, 79] indicated that organic constituents in retort water are primarily polar, and $C_2 - C_{12}$ carboxylic acids comprised about 70% of the organic carbon present . Dobson *et al.* [22] believed these acids were probably in their ammonium salt forms due to the high ammonia content found in retort water. Other identified organic compounds include ketones, phenols, pyridines, hydroxypyridines, pyrroles, anilines, amines, indoles, quinolines and nitriles [22, 59]. Ho *et al.* [47] found that the dissolved organic constituents in retort water were quite stable during their four-month study.

The feasibility of treating retort waters with conventional techniques, e.g., gas stripping, ozonation, reverse osmosis, carbon adsorption, and biological treatment, have been thoroughly evaluated by many researchers [7, 26, 28, 42, 46, 83, 95]. A review of some proposed retort water treatment processes has been given by Mercer *et al.* [63]. Currently, there are no discharge standards for oil shale processing. Investigators from the oil shale industry have claimed that the retort waters can be effectively upgraded with extensive treatment to meet refinery effluent limitations [44, 88]. However, it has been challenged by researchers because no treatability data have been released to the public to justify these claims.

2.5 Leaching of Spent Shale

As mentioned previously, spent shale contains various constituents. Some of the constituents are toxic, and may be leached from a disposal pile into groundwater. A number of studies have been conducted on leaching of spent shales under laboratory and simulated *in situ* experiments [3, 33, 57, 92, 109]. The composition of spent shale leachate is summarized in Table 9. The leachability of spent shale can be influenced by several factors:

1. the mineralogy of oil shale;

Table 2. Concentration ranges for major components in retort waters

Parameter	Concentration (mg/L)[1]	
	Range	Mean
Sodium	2,300-2,800	2,600
Postassium	92-130	104
Magnesium	2.2-5.5	3.6
Calcium	7.6-12.0	11.0
Barium		0.6
Cadmium		0.1
Chromium		0.1
Lead		0.6
Chloride	370-490	392
Fluoride	29-32	31
Nitrate-N	2,700-7,600	3,160
Sulfate	1,380-1,480	1,430
Carbonate	1,300-1,700	1,480
Bicarbonate	5,500-6,200	5,800
Ammonia-N	1,000-1,800	1,320
Oil & grease	95-1,900	891
TDS (180 °C)	8,200-9,700	8,900
Total alkalinity (as $CaCO_3$)	7,100-7,400	7,190
pH (Standard pH units)	8.82-8.85	8.84
Conductivity (µmhos at 25 °C)	13,000-13,000	13,000
COD	13,000-18,000	14,000
Total carbon	2,610-6,220	4,040
Total Inorg. Carbon	840-1,200	1,040
Total Org. Carbon	1,500-4,380	2,390
Phenol		45
Organic-N		34
Color (Pt-Co units)		2,500

[1] Except as noted.

Source: [86, 95]

2. characteristics of retort operations;

3. characteristics of spent shale; and

4. the quality of leach water.

Mineralogical changes that occur during retorting may substantially alter the characteristics of the constituents in spent shales. During retorting, sodium, magnesium and calcium salts are produced through partial conversion of primary insoluble carbonates [82]. These soluble salts may be released by local water movement.

The composition of leachates varies as a function of water resident time rather than applied water volume. Garland and co-workers [33], after conducting field studies over a two-year period, claimed that the chemical state of elements in spent shales and chemical equilibrium between leach water and spent shale controlled the actual leaching processes. Weathering influence and microbial activity also impose long term effects on the organic and inorganic composition of leachates.

The pH change of aqueous leachate is closely related to complex solubility associations with amorphous residues, and is primary determined by the contact time between leach water and spent shale [108]. Short term studies have shown that the spent shale leachates are characterized by high pH values ranging from 7.8 to 12.7 and by high concentrations of total dissolved solids (TDS) [57, 89, 92, 109]. However, the concentrations of leachates decrease rapidly with leaching flow. Kuo *et al.* [57] stressed that either substantially high or sufficiently low temperature would reduce the quantity of leachate. Maximum amount of inorganic leachate has been found from processes operated between 750 to 850 °C. Parker *et al.* [70] found more materials were released when the retorting temperature ranged from 600 to 800 °C. Fox *et al.* [25] indicated that shale retorting at temperature, beyond 1000 °C with a slow retorting rate would minimize the leachability of spent shale. Other retorting parameters such as oxygen concentration and atmosphere in a retort may also affect the quality and quantity of the leachate from spent shale [72, 92].

Table 9. Leachate composition of spent shale from various retorts

Constituent	Simulated in-situ retorts	Surface retorts
General water quality measures		
pH (Standard Units)	7.8 - 12.7	7.8 - 11.2
Total dissolved solids	80 - > 2,100	970 - 10,011
Major inorganics		
Bicarbonate	22 - 40	20 - 38
Carbonate	30 - 215	21
Hydroxide	22 - 40	-
Chloride	5.5	5 - 33
Fluoride	1.2 - 4.2	3.4 - 60
Sulfate	50 - 130	600 - 6,230
Nitrate	0.2 - 2.6	5.1 - 5.6
Calcium	3.6 - 210	42 - 114
Magnesium	0.002 - 8.0	3.5 - 91
Sodium	8.8 - 235	165 - 2,100
Potassium	0.76 - 18	10 - 625
Organics		
Total organic carbon	0.9 - 38	-
Trace elements		
Aluminum	0.095 - 2.8	-
Arsenic	-	0.10
Boron	0.075 - 0.14	2 - 12
Barium	-	4.0
Chromium	0.002 - 1.8	-
Iron	0.0004 - 0.042	-
Lead	0.014 - 0.017	-
Lithium	0.020 - 0.42	-
Molydenum	trace	2 - 8
Selenium	-	0.05
Silica	25 - 88	-
Strontium	0.004 - 8.7	-
Zinc	0.001 - 0.025	-

Unit: mg/L, except as noted.
Source: [89]

Stollenwerk and Runnel [92] reported that elevated level of molydenum, fluorine, and boron were released from TOSCO II spent shales. Kuo *et al.* [57] conducted laboratory batch and column experiments to investigate the leachability of spent shale from MIS processing. They concluded that calcium, potassium, sodium, sulfate and hydroxy ions were constituents predominant in the leachate whereas organic matter in the leachate was negligible. Their conclusion is supported by other researchers' work that high concentrations of calcium, sodium, magnesium, and sulfate were found in the runoff from TOSCO II, USBM, and Union spent shales [77].

Higher concentration of TDS, fluoride, sulfate, nitrate, magnesium, sodium, potassium, boron and molydenum are released from surface retorted shale relative to *in situ* spent shale. On the other hand, *in situ* spent shale leachates have a higher carbonate content [89]. The inorganic constituents leached from *in situ* spent shale can be categorized in accordance with their estimated quantities in the leachate [89]:

Group 1 (< 10 mg/100 g): NO_3, Cl, F, Mg, Al, B, Cr, Fe, Li, Mo, Pb, Sr, Zn.

Group 2 (10 to 100 mg/100 g): HCO_3, OH, K, Si.

Group 3 (>100 mg/100 g): CO_3, SO_4, Ca, Na.

By contrast, few organic compounds have been identified in spent shale leachate. Most organic matter present in shale leachates remains uncharacterized. Leaching of organic carbon is governed by two separate leaching mechanisms [25]:

1. Surface leaching: Rapid release of organic carbon from surface of shale particles.

2. Internal leaching: Slow transfer of organic carbon from internal pores.

Surface leaching is predominant in the initial leaching stage. However, since internal leaching persists much longer than surface leaching, it controls the leaching process after most of the soluble organic carbon on the surface of shale particles has been released.

Schmidt-Collerus and Bonomo [85], in their leaching experiments using benzene and water as leachent, found the presence of azarines and polyaromatic compounds in the leachate. Amy and co-workers [3] conducted thirty-day batch leaching experiments to monitor the organics released from simulated *in situ* retorted shale by measuring total organic carbon (TOC) content in leachates. The experiments were performed at different water temperatures (20 °C to represent room temperature and 80 °C to simulate the temperature within an un-cooled retort) and different water quality (distilled water and synthetic groundwater). Amy *et al.* [3] concluded that the leaching of organic compounds was influenced by retorting conditions, water temperature, and the quality of leach water. The solubility of organic compounds was increased with temperature. The initial quality of leach water affected the leachability of organics at higher temperature. In addition, particle size distribution is another important factor in considering the leaching of organic compounds [89]. Smaller particle size yields more organic matter because of the larger surface area contacting with water.

2.6 Co-disposing Retort Water with Spent Shale

Co-disposal of retort water with spent shale has been proposed by developers because of following advantages:

1. It reduces the huge amount of external water requirement for shale oil production.

2. It eliminates wastewater discharges to receiving water.

3. It reduces process costs by eliminating certain retort water treatment processes which would be necessary if retort water were disposed alone, and thus their costs.

Table 10 shows the major water requirements at oil shale plants. These data indicate that at surface retorts, all the process waters produced could be co-disposed with spent shale for moisturization. In the case of MIS retorts, additional treatments are needed to upgrade the process waters to a higher quality suitable for reuse other than moisturization of spent shale because the quantity of process waters produced are far beyond that needed for spent shale moisturization.

Although the co-disposing option is cost-effective, some uncertainties must be cleared before it can be taken into practice. First, the possible contamination of ground water due to leaching of organic compounds and inorganic elements in retort water from disposal piles must be considered. A second concern is the possibility of increasing the mobility of originally insoluble species in spent shales due to synergistic reactions of retort water and spent shale.

Jackson and Jackson [48] examined the impact of co-disposing spent shale with retort water, and compared it with data obtained by using distilled, deionized water instead of retort water. They found sulfate, chloride, ammonia nitrogen, and total organic carbon (TOC) were not released from spent shale moisturized with retort water. Therefore, they suggested that spent shale should be considered as "an effective scavenger" of ammonia nitrogen and TOC. The authors concluded that co-disposal of retort water had no significant environmental impact in comparison with wetting spent shale with "clean" water. Another study was conducted by using the RCRA extraction procedure (EP) toxicity test to evaluate the potential hazardous effects of moisturizing Lurgi spent shale with treated and untreated retort waters [88]. Results of both cases showed that the mixture was non-hazardous according to the RCRA EP toxicity test. However, further investigations are required to determine whether there are undesirable materials being leached from disposal piles owing to the incorporation of process water.

Table 10. Major water requirements at oil shale plants

		Surface	MIS
Water needs:			
Spent shale,	moistening	600-1,350	370
	revegetation	260-670	250
Dust control,	in situ	380	140
	other	120-280	115
Cooling water make-up		1,600	2,200
Boiler feed water		150-1,600	5,000
Total		3,110-5,880	8,075
Wastewater Produced:			
Gas condensate		400	2,200
Retort water		-	900
Blowdowns		1,000-1,800	3,850
Total		1,400-2,200	6,950

Unit: gpm.
Source: [44]

2.7 Migration of Chemicals in Soil

The soil environment is a complex three-phase system composed of minerals, organic matter and water. The solid phase, occupying roughly 50% of most soils, consists of a number of elements including minerals (Al, Si, Fe, Ca, Mg, Na, and K) and anion-forming elements (C, N, P, and O). Other elements such as Cd, Co, Cr, Cu, Mo, Pb, Se, Ti, and Zn are present in lesser amounts.

Various flow processes occur within the soil matrix. Soil can retain chemicals in percolating flows and, on the other hand, leach chemicals into percolating flows. The migration of chemicals is primarily controlled by soil physical and chemical properties as well as the concentration and nature of the constituents in the percolating flow. Important physical characteristics include texture, structure, and soil depth. The chemical parameters are pH, organic matter content, minerals, and cation exchange capacity (CEC).

The ability of soils to retain organic and inorganic species in the soil solution has great practical significance since the potential pollutants in the soil solution may be filtered by the adsorptive action of the soil colloids and may be prevented from entering the water course. Retention processes involve various reactions such as ion exchange, surface adsorption, precipitation, and complexation. The adsorption capacity of soil denotes "the concentration of a constituent in soil above which an unacceptably high concentration of the constituent will enter leachate generated on-site."[4] Quantitative information concerning adsorption capacity is deficient. Finer textured (high clay content) soils usually have a higher adsorption capacity than coarse textured (low clay content) soils. Since soil is a negatively charged adsorbent at most pH values, soil with high cation exchange capacity will adsorb positively charged compounds, decrease the mobility of cationic and nonionic organic constituents, and increase the mobility of anionic organic constituents [43]. Artiola-Fortuny and Fuller [5] reported that intermediate solution pH favored the adsorption of phenols by soil.

The movement of organic chemicals, especially nonpolar organics, is inversely related to the organic content of the soil. Several studies have noted the predominance of organic matter in soil in controlling the sorption of organic chemicals [39, 52, 98, 102]. Metal ions may be retained by soil organic matter through organic chelation or metal complexation. Mineral content, such as iron oxide, may correlate with anionic adsorption, as well [5, 55].

2.7.1 Exchange Reactions

Soil clays ordinarily carry negative charges which attract the cations in soil solution to the clay surface and give rise to cation exchange reactions. The cations associated with negative sites on soil colloids through electrostatic bonding are subject to interchange with cations in soil solution. These cations are termed exchangeable cations which include Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, and Al (Al^{3+} and $Al[OH]^{2+}$). The extent of the exchange reaction depends on the concentration and the nature of replacing cations. Divalent ions are normally adsorbed more strongly than monovalent ions, and ions with smaller hydrated size are preferably adsorbed. However, not all of these cations in the soil matrix are exchangeable. For example, Keeney [53] cited that most of the calcium (76.9%), magnesium (96.2%), and potassium (99.6%) in the soil are nonexchangeable. Because sorption can take place not only on the outer surfaces but also in the interlayer regions of some soil colloids, under certain conditions, adsorbed cations, e.g., K^+ and NH_4^+, may be entrapped in the intermicellar regions of the the colloids after penetrating into the intermicellar space and cannot be replaced by other cations [13]. In other words, these adsorbed cations are held firmly by the soil and become relatively unexchangeable.

Some soils also carry positive charge at the edges of clay surfaces, which is significant especially at pH values below zero point of charge. Anion exchange is important in acid soils high in hydrous oxide and kaolinite. Many anions, e.g., NO_3^-, Cl^-, and SO_4^{2-}, exhibit this type of exchange. The pH of the soil is a major factor that influences exchange reactions. At neutral condition or pH >6, sorption of SO_4^{2-} and Cl^- was small. In addition, sorption of sulfate usually resulted in an increase in the pH of the system. The sorption preference of some anions commonly found in soils has been reported in the following order [12]:

$$SiO_4^{2-} > PO_4^{3-} >> SO_4^{2-} > NO_3^- \cong Cl^-$$

2.7.2 Retention of Metals

The extent of participation of metals in the cation exchange reaction depends on the concentration and nature of metals, pH, competing cations and organic chelates in the system. In addition to cation exchange, precipitation and organic chelation are also important in controlling the sorption of metal ions. Metal ions can be retained on soil by forming complexes with organic matter on the soil surface. Stable complexes are generally derived from transition metals. The stability of complexes increases with increased charge and decreased metal ion size.

Precipitation of metal ions with anions, e.g., OH^- and CO_3^{2-}, is controlled by solution metal concentrations, pH and the possibility of forming organo-metal complexes. Redissolution of a precipitate may occur due to decrease of the concentrations of metals in solution or due to change in solution pH. Some metals, e.g. Fe, Pb, and Mn, are most likely to be controlled by precipitation reactions.

2.7.3 Adsorption of Organic Compounds

Organic compounds are sorbed by soil through physical, hydrogen, eletrostatic, and coordination bonding. The organic cations may be sorbed on the negatively charged surface of soil colloids, whereas organic anions are likely to be sorbed on the edges of soil surfaces [97]. Uncharged organic compounds can be adsorbed on soil surface, directly or indirectly.

Uncharged organic compounds are directly sorbed on the soil colloids by physical forces (van der Waals forces). The attraction forces increase, to a certain extent, with the size and chain length of the organic molecules. The uncharged organic compounds can, indirectly, sorbed to the soil colloids through linkage, or complexation, to metal ions which are attached to the soil surface. Another type of reaction is that some organic compounds can form hydrogen bonding with the water molecules which are sorbed on the soil surfaces. Interlayer adsorption of organic compounds may also take place in soil clays, especially in 2:1 type layer clays such as montomorillonite and illites [93]. Note that illite is one of the mineral constituents in oil shale.

2.8 Sorption from Solution at the Solid/Liquid Interface

Sorptive behavior, including adsorption and absorption, is a principle factor in the leaching mechanism. Finely divided solids tend to have excess surface energy. This energy level may be lowered by reducing surface area, which is generally accomplished by aggregation of dissolved substances on particle surface. In a sorption process, the adsorptive material is transferred from the solution phase to a surface phase. The driving force for this phase transfer is the concentration gradient of solutes between the two phases, and is related either to the "solvent-disliking" nature of solutes or to a higher sorbent affinity of solutes [103]. The nature of sorbate, sorbent and solvent are, therefore, primary factors that determine the sorptive behavior of a system.

2.8.1 Sorption Interactions

Depending on the nature of forces involved, adsorption may be classified into three types, physical, chemical and exchange adsorption [40, 60, 103]. Physical adsorption is attributed to van der Waals-London interactions between the sorbent surface and sorbate molecules. These forces, primarily resulting from short range instantaneous dipole-dipole interaction, bring about attractions contributing to the sorption of those molecules in closest contact with the surface, or maintaining close contact between adjacent molecules and atoms. Physical adsorption is characterized by its relatively low energy of adsorption, and is predominant at low temperature [103]. The adsorbed molecules are free to migrate about the interface rather than being affixed at specific sites on the surface. Because interactions are reversible, desorption may occur at the same temperature.

The second type of adsorption is chemical adsorption (or chemisorption). Chemical adsorption involves transfer of electrons and formation of chemical bonds between the adsorbate and adsorbent. The interaction is exothermic which exhibits a high energy of adsorption; therefore, it is favored by higher temperature. Generally, this mechanism also includes ligand exchange and hydrogen bonding. In comparison with physical adsorption, chemisorption is much slower, and the adsorbed molecules are localized on adsorptive sites. A distinguishing feature of chemisorption is that it may take place at saturated adsorption sites in low solute concentration. Hence, the sorption isotherm of chemisorption starts along the adsorption axis rather than at the origin [36, 54].

Exchange adsorption is a process in which ions held at functional groups on an adsorbent surface by electrostatic forces are exchanged for ions of different species in solution. The charges on ions and molecular size are considered the determining factors for exchange adsorption [103]. Ions in solution with higher charges are more strongly adsorbed on adsorbents. Smaller ions are favored for closer approaching to the specific site on the adsorbent surface. Hamaker and Thompson [40] indicated that the solvation of adsorbent, adsorbate, and water had a pronounced influence on the extent and rate of adsorption. Temperature affects exchange adsorption little.

Most adsorptive phenomena are combinations of two or more forms of adsorption depending on the nature of the functional groups and the physical and chemical properties of the system. Kipling [54] believed physical adsorption probably occurred on top of the layer adjacent to the adsorbent surface, which was formed by chemisorption.

2.8.2 Factors Affecting the Sorption Process

Since sorption is a surface phenomenon relating to the reduction of surface tension, the area and configuration of sorbent surface are principle factors affecting the adsorption capacity of the sorbent. The adsorption capacity is the limiting amount of adsorptive material that can be adsorbed by the adsorbent when saturation is attained. The extent of adsorption is proportional to the specific area of the adsorbent, i.e. the area which is available for adsorption. The specific area is closely related to particle size and pore structure of the adsorbent [103]. The more finely divided, more porous the solid, the more surface area may be available. Thus, a greater adsorption capacity may be expected.

The chemical characteristics of adsorbate may affect the adsorption capacity to a certain extent. For example, an inverse proportionality is generally expected between solubility and adsorptive capacity [6, 23, 103, 104]. However, Bailey and White [6] emphasized that this relationship could only be applied to adsorptive species which were analogues in chemical character.

Many investigators [2, 87, 103, 104] have indicated that an increase in the molecular weight of organic substances results in a greater adsorption capacity due to the introduction of substitutes on aromatic rings or an increase of chain length on aliphatic compounds. This is in accordance with the Traub's rule which states that for adsorption of organic compounds, the sorption capacity increases as a homologous series ascends [1]. Al-Bahrani and Martin

[2], in their study on the effect of molecular structure on carbon adsorption, found that introduction of methyl groups on aromatic rings would favor the adsorption process. Geissbuhler and co-workers [35] found that addition of a second aromatic ring to phenyl rings showed a positive effect on soil adsorption. Although the sorption of aromatic compounds may be influenced by the number of substitutes on the ring structure, the substitute position on the ring appears to have no effect on adsorption [87, 90]. Branching of straight chains may reduce surface area and therefore reduces adsorptive capacity.

Temperature may markedly affect adsorption through its influence on solubility and on the forces of adsorption. Since adsorption is a spontaneous exothermic process, an increase in temperature would normally reduce adsorption rate and favor desorption [23]. However, greater adsorption at higher temperatures has also been reported [6].

The pH of the solution determines the extent of ionization. In general, for sorption from solution on a negatively-charged sorbent such as soil, the adsorptive interaction is favored at lower pH values due to the neutralization of the negative charges by a higher hydrogen ion concentration [103]. For carbon adsorption , the sorption of organic acids is favored by low pH, whereas the sorption of organic base is preferential a higher pH environment. Myers and Zolandz [65], in their studies of bisolute (phenol and nitrophenol; $pK_a \cong 10$) adsorption on carbon, found a considerable reduction of adsorbed material at high pH ($\cong 12$) relative to that adsorbed at intermediate pH ($6 \sim 7$) or at low pH ($\cong 2$).

The relative polarity of solute, solvent and sorbent is another important factor in controlling the adsorption at the solid-liquid interface. Based on the principle of "like adsorbs like", a polar solute would prefer the more polar phase. Bailey and White [6] indicated that the polarity of molecules determined their interlamellar adsorption on clays.

2.8.3 Sorption Equilibria and Sorption Models

From a kinetic view, sorption equilibrium is a dynamic steady state involving a constant interchange of sorptive material. The transfer of adsorptive material between the bulk solution phase and solid surface is driven by the concentration gradient of diffusion species within two phases. At equilibrium, the net diffusion rate of sorptive species becomes zero, i.e. adsorption and desorption proceed at the same rate. The position of equilibrium depends on characteristics of the system such as temperature, pH, and the nature of the solvent, sorbent, and sorbate. At the point of equilibrium, a defined distribution of solutes exists between the bulk solution and the sorbent. Several models have been developed to describe the relationship between the specific amount of solute adsorbed on adsorbent and the equilibrium concentration of the solute in the bulk solution. Each model has its limitation when applied to experiment data. Nevertheless, all of the models reduce to a linear relationship at low concentrations. Consequently, the choice of an adequate model depends on the intended use of the model parameters under certain circumstances.

2.8.3.1 Langmuir Adsorption Equation

The Langmuir equation was initially developed for the adsorption of gases on solids, based on the following assumptions [23, 98]:

1. The solute is adsorbed as a complete monomolecular layer at the adsorbing surface.

2. The adsorbing surface is energetically homogeneous, i.e. the heat of adsorption is constant over the adsorbing surface.

3. Adsorption occurs on localized sites that there is no lateral interaction between adsorbed molecules and no migration of adsorbed molecules across the surface.

The Langmuir adsorption isotherm is expressed by the equation:

$$X = \frac{X_m b C_E}{1 + bC_E} \qquad [2.1]$$

where X is the amount of solute adsorbed per unit weight of adsorbent; X_m is the monolayer sorption capacity representing the monolayer coverage per unit weight of adsorbent; C_E is the equilibrium concentration of solute; and b is the reciprocal of the concentration at which half coverage is achieved.

In order to linearize sorption data, the Langmuir equation can be rearranged to:

$$\frac{1}{X} = \frac{1}{X_m} + \left(\frac{1}{bX_m}\right) \frac{1}{C_E} \qquad [2.2]$$

Plotting $\frac{1}{X}$ versus $\frac{1}{C_E}$ yields a straight line having a slope of $\frac{1}{bX_m}$ and an intercept $\frac{1}{X_m}$ from which the value of X_m and b can be determined.

2.8.3.2 *Freundlich Adsorption Equation*

The Freundlich equation is an empirical expression used to describe sorption behavior in dilute solutions based on the assumption that the decrease of surface energy with accumulation of solutes on surface is due to surface heterogeneity [6]. The Freundlich adsorption equation is expressed as:

$$X = KC_E^{\frac{1}{n}} \qquad [2.3]$$

X and C_E have the same meaning in the Langmuir equation, K is a measure of the efficiency and capacity of sorption, and $\frac{1}{n}$ may be taken as indicative of the degree of non-linearity between surface concentration, X, and solution concentration, C_E, of the adsorptive molecules [17, 23, 98]. Hamaker and Thompson [40] summarized the available data for the Freundlich isotherm of chemicals in soil, and found the value of $\frac{1}{n}$ varied from 0.7 to 1.0.

Although lacking theoretical basis, the Freundlich equation often adequately describes sorption data which can not be fitted by the Langmuir model. Kipling [54] indicated that a distinguishing feature between these two isotherms was that the Langmuir isotherm had an asymptote determined by the slope at the origin, whereas the Freundlich isotherm had no asymptote, and the slope at the origin was infinite.

2.8.3.3 *The BET Adsorption Equation*

The Brunauer, Emmett, Teller (BET) adsorption model may be used to consider the multilayer adsorption on homogeneous surface. It assumes that layers of molecules are adsorbed on top of the previously adsorbed molecules, and each layer adsorbs in the same way described in the Langmuir adsorption model [54, 98]. The BET isotherm can be expressed as:

$$X = \frac{B X_m C_E}{(C_s - C_E)[1 + (B - 1)(\frac{C_E}{C_s})]} \qquad [2.4]$$

where X, X_m, and C_E have the same meaning as defined in the Langmuir equation ; C_s is the saturation concentration of solute; and B is a constant related to the energy of adsorption.

The linear form of the BET equation is:

$$\frac{C_E}{(C_s - C_E)X} = \frac{1}{KB} + \frac{K - 1}{KB}(\frac{C_E}{C_s}) \qquad [2.5]$$

which, by plotting $\frac{1}{X}$ verses $\frac{C_E}{C_s}$, is a straight line with a slope of $\frac{(K - 1)}{K B}$ and a y-intercept at $\frac{1}{K B}$.

2.8.4 Adsorption Kinetics

2.8.4.1 Theoretical Consideration

Kinetic relationships can be developed based on the assumptions [66]: (1) the adsorption rate is proportional to the concentration of the solute in dissolving phase, C, and the differences between the sorption capacity of sorbent and the amount of solute adsorbed per unit weight of adsorbent, X_m ; and (2) the rate of desorption is proportional to the amount adsorbed on the sorbent, X. The kinetic equation may be expressed as:

$$\frac{dC}{dt} = -K_a C(X_m - X) + K_d X \qquad [2.6]$$

where K_a is the adsorption rate constant; and K_d is the desorption rate constant.

At equilibrium, the concentration gradient reduces to zero. Therefore, the kinetic equation becomes:

$$X = \frac{bCX_m}{1 + bC} \qquad [2.7]$$

where $b = \frac{K_a}{K_d}$, which is the Langmuir adsorption equation. Previous studies [51] on the sorption of hydrophobic compounds onto natural sediments have revealed that sorption isotherms are linear if the equilibrium concentration of solute in the liquid phase is less than 1 ppm or below one half of the solute solubility. In very dilute systems, e.g., natural environments, where the sorption capacity, X_m, is generally much greater than the solid phase concentration, X., the relationship between the concentration of solute in solid, X, and aqueous phase, C, becomes:

$$X = bCX_m \qquad [2.8]$$

or

$$\frac{X}{C} = bX_m \qquad [2.9]$$

which implies that the ratio of the amount of the solute in the solid phase to the dissolved concentration, or the sorption partition coefficient (X/C) may be obtained from the linear portion of the Langmuir isotherm at low concentrations.

2.8.4.2 Adsorption Rate

Sorption is an instantaneous reaction normally considered as rapid and reversible [98]. Sorption from solution by porous adsorbents may be described by three consecutive steps: (1) film diffusion; (2) intraparticle diffusion; and (3) surface sorption [61, 98, 103, 106]. Film diffusion is the first step that the solutes are transported from the bulk solution through the boundary layer to the external surface of the adsorbent by molecular diffusion. The driving force in film diffusion, as mentioned earlier, is the concentration gradient. The second step, termed intraparticle diffusion or pore diffusion, involves the transport of the adsorptive material from an external surface into interior sorption sites through capillary pores. Finally, the adsorption of solutes occurs at active sites on the interior surfaces of the adsorbent. Normally, surface adsorption itself is not considered the rate-determining step [66, 103]. Either film diffusion or pore transport determines the over-all uptake rate of adsorbates.

In batch systems, the rate-limiting step may be determined by plotting the amount of solute adsorbed per unit weight of adsorbent, X, versus the square root of reaction time, $\sqrt{t}$. A linear relationship indicates that intraparticle diffusion is the controlling step [106]. A strict proportionality between the sorption rate and concentration is expected if the adsorption is controlled by film diffusion [23].

Several investigators have found that the sorption process is initially controlled by film diffusion in batch and column systems [1, 30]. As more adsorbate aggregates on the sorbing surface, the rate-limiting step shifts to intraparticle diffusion. Other researchers [61, 106] reported that intraparticle diffusion was the rate-determining step in batch reactors, and film diffusion controlled the sorption rate in column systems.

2.8.4.3 The Reversibility of Adsorption

Usually it is assumed that the same isotherm may be applied to describe desorption as well as adsorption, based on the hypothesis of the reversibility of adsorption reactions. However, recent studies [21, 51, 72] showed that only partial reversal was achieved in experiments with the sorption of aromatic hydrocarbons on sediments and clays. The degree of nonsingularity has been proven to be proportional to the quantity adsorbed before initiation of desorption, the adsorption rate, and the adsorption energy [76]. Di Toro and Horzempa [21] considered the nonsingularity was probably due to the adsorbed constituents which were resistant to desorption.

2.8.5 Competitive Adsorption

Since natural waters and wastewaters contain various constituents, adsorption involving multisolute competition is most likely to occur. Competition between different solutes for the available sites on sorbing surfaces may contribute a significant influence on the extent of adsorption [62, 105]. In addition, competitive adsorption has been considered as one of the major factors affecting desorption of weakly adsorbed molecules due to chromatographic effects [30, 62]. However, there is a very limited theoretical background for the analytical description of multicomponent adsorption.

Several models have been developed to predict the behavior of multicomponent adsorption [14, 49, 74, 81]. Of these models, the Langmuir competitive model and the Ideal

Absorbed Solution (IAS) model are most widely used to describe the sorptive behavior of compounds in systems containing two or three components [16, 66, 110].

The Langmuir competitive equation developed by Butler and Ockrent [14] is formulated:

$$X_i = \frac{X_{m,i} b_i C_{n,i}}{1 + \sum_{n=1}^{j} b_j C_{n,j}} \qquad [2.10]$$

where X_i is the amount of solute, i, adsorbed per unit weight of adsorbent at concentration C_i ; X_m is the monolayer sorption capacity; C_i is the equilibrium concentration of solute, i, in bulk solution; and b_i is a constant related to the adsorption energy of solute, i.

The IAS model is based on the thermodynamic equivalence of the spreading pressure of a solute, which is the difference between the interfacial tension of the pure solvent-solid interface and that of the solution-solid interface for specific solutes at equilibrium. Parameters may be predicted from single-solute isotherms [74]. Detailed calculations for the IAS model have been cited elsewhere [110]. If the Freundlich equation is used in IAS calculations, the behavior of each solute in a system containing N components may be described by:

$$X_i = \frac{C_i}{\sum_{j=1}^{N} n_j C_j} \left(\frac{\sum_{j=1}^{N} n_j C_j}{n_i K_i} \right)^{n_i} \qquad \text{for } i = 1 \text{ to } N \qquad [2.11]$$

Crittenden and co-workers [16] conducted sorption experiments with mixed volatile organic compounds in different combinations such as two, three, and six components. The IAS model was satisfactorily applied to describe competitive adsorption of mixtures containing similar volatile organic compounds. In a series of studies on adsorption of phenolic compounds from solutions, Yen and Singer [87, 110] have demonstrated that the IAS model is superior to the Langmuir competitive model. On the other hand, Thacker and Snoeyink [94] reported that IAS model overestimated solution concentration in their experiments concerning the adsorption of phenol compounds on carbon.

Mutual inhibition of the adsorptive capacity of individual solutes in mixed solution due to the presence of other solutes is usually encountered in aqueous systems. The extent of interference is dependent on relative concentrations, molecular sizes, and adsorptive affinity of solutes. Weber and Morris [105] investigated competitive adsorption from bisolute solutions. Compared to the adsorption rates and the adsorption capacity of each solute in its pure solution, the breakthrough of each solute in multicomponent solution was more rapid, but the overall capacity was greater. The overall enhancement of adsorption capacity was probably due to increase in concentration and due to the selectivity of sorbent for certain solutes. The authors suggested that the adsorption capacity of sorbent determined from single-solute adsorption experiments be used as indicative of the minimum accumulative adsorption capacity for multicomponent systems.

Martin and Al-Bahrani [62], in their studies of competitive adsorption on carbon of aromatic organic compounds, summarized that the total capacity of multicomponent adsorption was not necessarily increased with the number of solutes in the solution. They reported that the accumulative capacity of a tertiary system was higher than the individual capacities of two components, but lower than that of the third component. Similar results were also found in a system containing five components. Other characteristics of solutes such as its compatibility with a given sorbent, molecular size, etc. need to be taken into account. When the total amount of adsorbed material per unit mass of sorbent was measured, the results showed that a multicomponent system could be treated as a "pseudo-single" component system, and the adsorption data could be adequately fitted by the Langmuir adsorption equation.

Chapter III

MATERIALS AND METHODS

Two types of laboratory experiments, (1) preliminary batch experiments and (2) continuous-flow column experiments, were conducted to assess the sorption capacity of four different types of oil shale and a western soil. The preliminary batch experiments involved mechanical shaking of a unit volume of distilled water or an alternative solution with a unit mass of shale or soil. The column experiments involved the continuous flow of solution through a fixed shale or soil bed. Both of these experiments were carried out with single- and multi-component solutions. The analytical parameters selected to monitor the quality of leachate were pH, conductivity, redox potential, alkalinity, and residual solution concentrations of sorbates.

3.1 Characteristics of Shales and Soil

Shale and soil samples examined in this study were received from the Department of Energy's (DOE) Laramie Project Office in Laramie, Wyoming. The soil was sampled in an area referred to as the North Site by DOE. The shales included a raw shale and three spent shales. The raw shale, Anvil Points shale, was obtained from the Anvil Points area in Colorado. The spent shales, Antrim, Oxy 6, and Run 16 shale, were produced by different modified *in situ* processes. The retorting conditions employed during the production of the spent shales are summarized in Table 11.

Two particle sizes of shales were chosen for batch and column experiments. Shales passing an 8-mesh sieve and being retained on a 30-mesh sieve were selected for column system. In batch experiments, finer shales passing through the 30-mesh sieve were used because of their larger surface area. The physical characteristics, including bulk density, solid density, and porosity, of the shale samples were determined previously, and are listed in Table 12.

The soil samples were prepared by air-drying and then sieving through a 2-mm mesh screen. Among the soil properties measured were moisture content, pH, organic matter content, cation exchange capacity, porosity, bulk density, particle density, and field capacity. These properties were determined in accordance with the procedures described in *Methods of Soil Analysis* [10, 11, 69].

3.2 Reagents and Chemicals

The organic compounds selected in the shale/soil sorption experiments were 2,6-dimethylpyridine (DMP), 2-hydroxynaphthalene (HN), 1,2,3,4-tetrahydroquinoline (THQ),

Table 11. The retorting conditions of spent shales

	Shale Type		
	Oxy 6	Antrim	Run 16
Type of Retort	MIS[1]	Simulated MIS[2]	Simulated MIS[3]
Retort Gas	air/steam	air (recycle)	air (recycle)
Maximum Oprating Temperature, °C	800-1,000	793	660
Length of Run, days	330	5.54	22.56

[1] Modified *In Situ* retort.
[2] 10 Ton.
[3] 150 Ton.
Source: [11]

Table 12. Characteristics of the oil shales

Physical Property	Type of Shale							
	Anvil Points[1]		Antrim[2]		Oxy 6[2]		Run 16[2]	
	fine[3]	coarse[4]	fine[3]	coarse[4]	fine[3]	coarse[4]	fine[3]	coarse[4]
Bulk Density, g/cm^3:								
Minimum	0.966	1.043	1.022	1.010	0.891	0.940	0.867	0.906
Maximum	1.238	1.215	1.365	1.202	1.078	1.111	1.078	1.104
Solid Density, g/cm^3:	2.25	2.24.	2.56	2.52	2.08	1.90	2.64	2.66
Porosity, %:								
Minimum	0.450	0.458	0.467	0.523	0.482	0.415	0.582	0.594
Maximum	0.571	0.534	0.601	0.599	0.572	0.505	0.672	0.659

[1] Raw shale.

[2] Modified *in situ* retorted shale.

[3] Particles passed through no. 30 mesh.

[4] Particles passed through no. 8 mesh but retained on no. 30 mesh.

and 2,3,5-trimethylphenol (TMP). These reagents were purchased from Aldrich at a purity level of 97~99%. The characteristics of each compound are listed in Table 13.

The inorganic ions considered in soil sorption studies were arsenic (As), cadmium (Cd), calcium (Ca), iron (Fe), potassium (K), ammonium (NH_4), fluoride (F), and sulfate (SO_4). Atomic absorption standards of arsenic, cadmium, iron and potassium were used. Ammonium, fluoride, calcium and sulfate solution were prepared by dissolving reagent grade ammonium chloride (NH_4Cl), sodium fluoride (NaF), calcium chloride ($CaCl_2$), and sodium sulfate (Na_2SO_4) in distilled deionized water. The pH of solution used in each trial was adjusted, if necessary, with HNO_3, HCl or NaOH.

3.3 Experimental Procedure

3.3.1 Preliminary Batch Experiments

The batch experiments consisted of placing a certain mass of shale or soil (3 g shale or 7.5 g soil) and a certain volume of solution (100 ml with shale or 150 ml with soil) into a series of 250 ml Erlenmeyer flasks. The flasks were sealed with Parafilm and placed on a shaking water bath (Fisher, Model 129) which was kept at 25 ± 3 °C and set at a rate of 120 strokes/min. Approximately 5 ml sample was removed from each flask at 4, 8, 12, 24, 48, 72, and 96 hours, and filtered through a 0.45 μm membrane filter (Gelman, GA-6 Metrical) to remove suspended matter. Among the parameters of each organic sample measured were pH, alkalinity, conductivity, and concentrations of organic compounds.

The sorption of organic compounds on shales/soil was studied with different combinations of organic compounds. Six flasks with added organic agents were used in each trial. Four of the flasks contained each organic compound alone in solution; a fifth flask contained

Table 13. Selected properties of organic compounds

Compound	Mol. Wt. (g/mole)	Solubility (> 10%)	Acid/base
2,6-dimethylpyridine, $(CH_3)_2C_5H_3N$	107.16	ethanol, ether	base
2-hydroxynaphthalene, $C_{10}H_7(OH)$	144.19	ethanol, ether benzene	acid
1,2,3,4-tetrahydroquinoline, $C_9H_{10}NH$	133.2	ethanol, ether	base
2,3,5-trimethylphenol, $(CH_3)_3C_6H_2(OH)$	136.19	—	acid

Source: [99-101]

three compounds (HN, THQ, and TMP); and the last flask contained all four compounds (DMP, HN, THQ, and TMP). An additional control flask, containing only shale-water/soil-water but no added chemicals, was also prepared. The initial concentration of each compound in the solution was approximately 25 mg/L, prepared by diluting stock solution (~ 1000 mg/L) with distilled deionized water. The concentration of organic compounds in the filtrate samples were analyzed by means of reverse-phase, high performance liquid chromatography.

The HPLC system employed consisted of an isocratic liquid chromatograph (Beckman, Model 341) equipped with a sample injector (Beckman, Model 210A with 5 μL injection loop), a fixed wavelength detector (Beckman, Model 160), and an integrator manufactured by Spectra-Physics (Model SP-4270). Analysis of HN, THQ, and TMP in samples was performed through the isocratic elution (flow rate = 1.0 ml/min) of a C-18 reverse phase column (Fisher, Resolvex; 4.6 mm i.d. x 25 cm) with a 50:50 mixture of acetonitrile (HPLC grade, Fisher) and distilled water. The distilled water was generated by a Milli-Q reagent water purifying system (Millipore). After the eluent mixture was prepared, it was filtered through a 0.2 μm filter (Gelman, Alpha-200) and then degassed with helium. The residual solution concentrations of the organic compounds were determined by comparing the area of the detected peaks of collected samples with those determined from a series of standard solutions of known concentration. The standards were prepared by dissolving HN (99% pure, Aldrich), THQ (97% pure, Aldrich), and TMP (99% pure, Aldrich) in methanol to provide for a 1000 mg/L stock solution and then diluting to the specific concentrations with distilled water.

The sorption of inorganic ions on soil was studied with different combinations of ions. Initial concentration of each ion was approximately 66.7 mg/L. Ten flasks were used in each trial. Eight of the flasks contained each ion alone in solution. A ninth flask contained the metal ions, As, Ca, Cd, Fe, and K, in the solution. The last flask contained only a soil-water suspension.

For each type of trial, an accompanying control test was accomplished by using soil-water leachate, instead of using distilled water, as the solvent. The soil-water leachate was generated by shaking 1:20 soil/water mixture for 96 hours, and then the mixture was filtered through a 0.45 μm membrane filter. The filtrate was collected and used as the solvent in the control tests.

Among the properties of each inorganic sample measured were pH, alkalinity, conductivity (YSI conductance meter, Model 32) , redox potential (Fisher; platinum combination electrode), and ion concentrations. Analysis of As, Cd, Ca, Fe, and K were performed on an atomic adsorption (AA) Spectrophotometer (Perkin-Elmer, Model 703) with acidified filtrate samples (pH ~ 1.8). Alkalinity and sulfate concentration were measured in accordance with *Standard Methods for the Examination of Water and Wastewater* [91]. Ammonium concentration was analyzed by using an Orion ammonia electrode. Fluoride concentration was determined by means of a Dionex 2010i ion chromatograph equipped with a conductivity detector (flow rate = 2.5 ml/min). A mixture composed of 0.0028 mg/L $NaHCO_3$ and 0.0022 mg/L Na_2CO_3 was used as the anion eluent. Dilute H_2SO_4 (0.025 mg/L) was used as the regenerant solution.

3.3.2 Column Experiment

In column experiments, sorption of organic compounds on shale or soil was conducted with feed solutions containing four organic compounds (DMP, HN, THQ, and TMP). The initial concentration of each compound in the feed solution was approximately 25 mg/L, the same as that used in batch trials. Sorption of inorganic agents on soil was carried out with different combinations of ions. Three types of solutions with each constituent at a concentration of 10 mg/L were pumped up through the soil columns:

1. a mixture of eight ions (As, Ca, Cd, K, Fe, NH_4, SO_4, and F);
2. a mixture of four cations (As, Ca, Cd, K); and
3. a mixture of the NH_4, SO_4, and F.

Each type of experiment was conducted in triplicate.

Configuration of the column experimental system is shown in Figure 2. A glass chromatography column (LKB, No. 2137) with an internal diameter of 2.6 cm was used. The column was fitted with a water-jacket to regulate temperature. The bottom of the column was fitted with an adjustable plunger with a removable polyester/polypropylene mesh filter disk on it to support the shale/soil bed. The shale column was constructed by placing approximately 100 g of 8 - 30 mesh shale in the glass column. The configuration of the soil columns was quite different from that of shale columns. Due to the excessive headloss across the soil columns, soil alone could not be used in the column trials. Therefore, a 50/50 blend of soil and sand was prepared for the experiments. The soil columns were constructed by placing 25 g of acid-washed sand (30 - 60 mesh size) on the bottom column plunger which had a filter disk on it. Approximately 100 g of the 50/50 soil-sand mixture was layered over the sand and then an additional 25 g of acid-washed sand was placed on top. After shale/soil was tapped along the column, another filter disk and plunger were fitted to prevent shale/soil escaping along with eluents.

All of the experiments were carried out at 25 ± 3 °C by using a circulating water bath (Lauda, K-2/R) to regulate the temperature of the shale/soil bed and the feed solution. Two glass carboys were used for preparing the feed solution. Eight liters of solution in each carboy were prepared at a time. The solution was pumped through Teflon tubing to the shale/soil column at a flow rate of 1 ml/min. The column system was designed in an upflow mode so that optimum contact between shale/soil and feed solutions would be ensured.

Each trial was conducted for a period of 96 hours. The effluent from the top of the shale/soil bed was directed into glass, screw-capped, test tubes held by an ISCO fraction collector. Approximately 13 ml of effluent was collected in each tube. The flow rate of the effluent was measured by the number of pore volumes replaced. One pore volume represented a volume of fluid equivalent to the total volume of pores in the shale/soil bed. Effluent samples of selected pore volumes were analyzed in the same way as the previously described batch experiments.

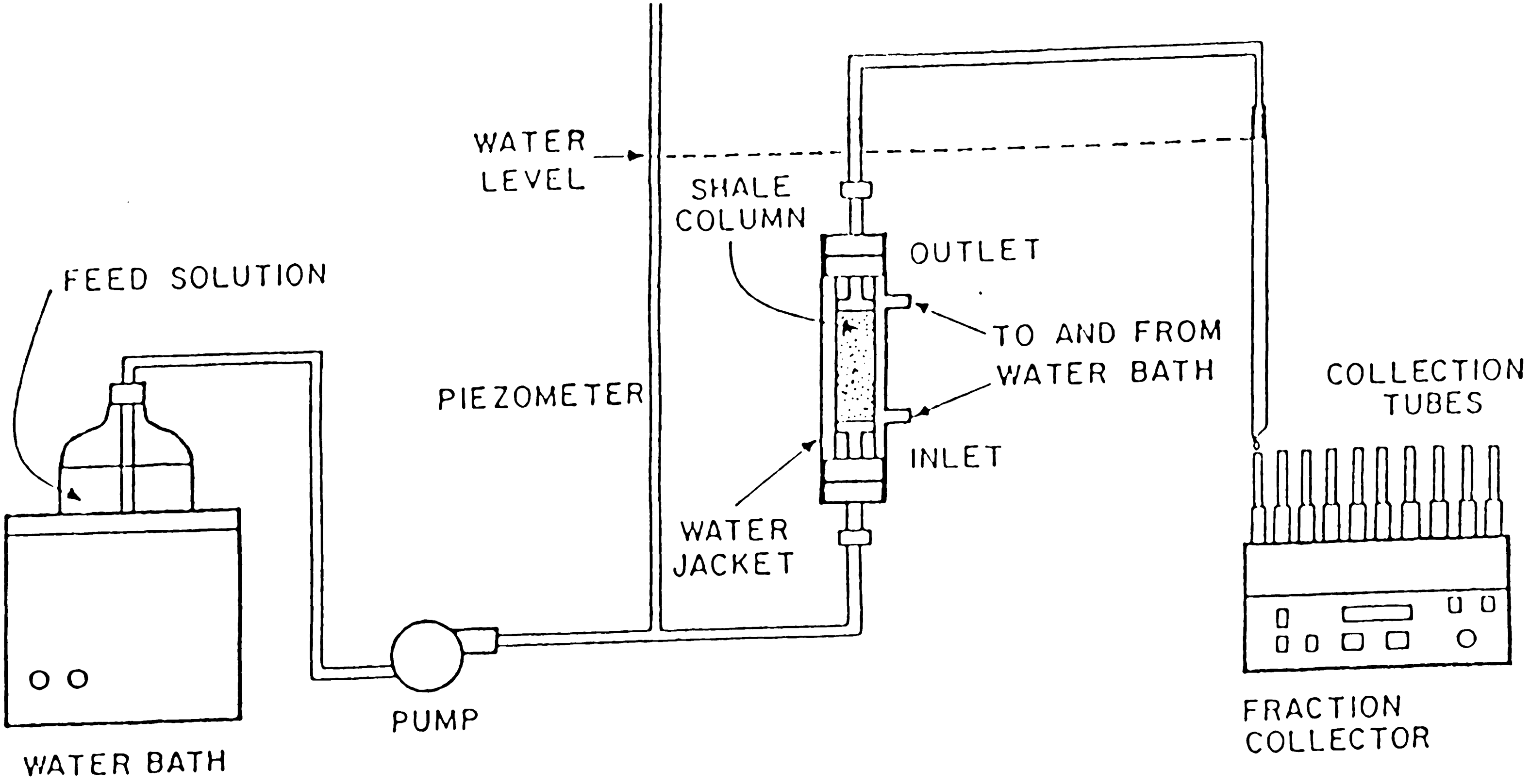

Figure 2. The column experimental system

Chapter IV

RESULTS

Laboratory data concerning the sorption of chemical agents on four types of shale and a western soil are presented in this chapter. These include properties of the western soil, sorption data of batch type experiments, and sorption data of column type experiments. The latter two categories are subdivided into sorption of organic compounds on shales/soil and sorption of inorganic agents on soil.

4.1 Soil Properties

Table 13 presents selected properties of the western soil considered in the experiments. As received, the pH and moisture content of the soil were approximately 7.7 and 11%. Field capacity was in the area of 16%. The particle density was in the area of 2.6 g/cm^3, and bulk densities varied from 0.9 to 1.9 g/cm^3. Organic matter and cation exchange capacity were in the area of 0.5% and 9.9 meq per 100 g of soil, respectively. Porosities ranged from 25 to 64%. The porosity of soil is defined as:

$$n = \frac{V_v}{V_T} x\, 100$$

where n represents porosity, V_v is the volume of air and water in soil pores, and V_T is the total volume of soil mass.

In comparison with the shales' properties, the minimum bulk density and particle density were comparable to those of the shales. However, the maximum bulk density of soil was below those of the shales. The soil's maximum porosity was greater than that of all but the Run-16 shale.

4.2 Batch Sorption Experiments

4.2.1 Elution of Organic Compounds

The elution experiments were conducted by shaking the shale-water/soil-water suspensions without chemical added in a constant temperature water bath for a period of 96 hrs. No organic compounds considered were found in the shale and soil eluents. This suggested that either none of the organic compounds were leached from the shales and soil, or these compounds were present at levels below detection on the HPLC.

Table A2 in Appendix-A presents the pH data obtained during the elution experiments. Variations in the pH of elution trials are shown in Figure 3. The eluents from Antrim, Anvil Points, Oxy-6, and Run-16 shale were basic in nature, and the variation of pH, in most cases, was less than one pH unit.

Table 14. Selected properties of the western soil

pH	7.7
Moisture, %	11.37
Density, g/cm^3:	
Partical	2.55
Bulk:	
Maximum	1.91
Minimum	0.92
Porosity, %:	
Maximum	63.92
Minimum	25.10
Organic Matter, %	0.5
Cation Exchange Capacity, meq/100 mg	9.9
Field Capacity, %	15.68

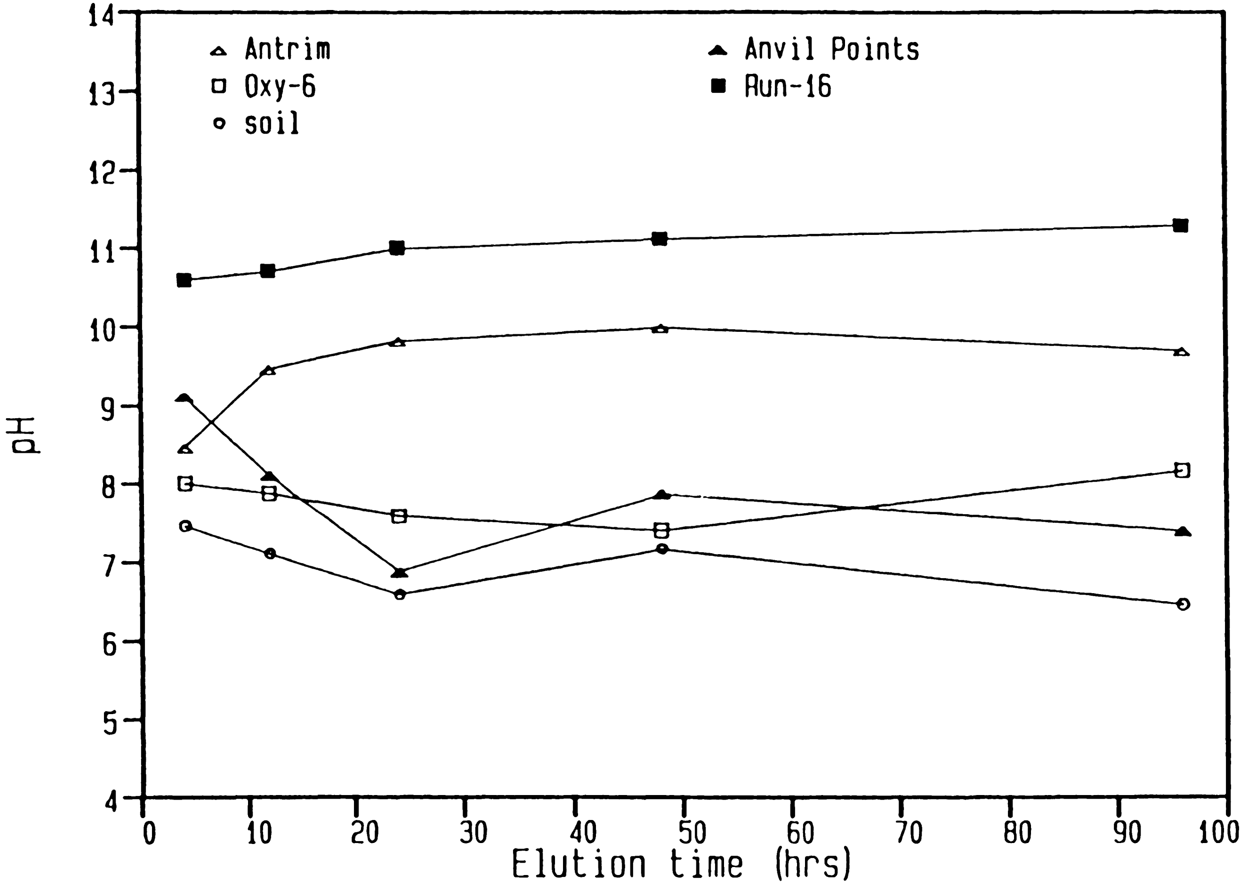

Figure 3. Variation of pH in batch elution from the shales and soil

Run-16 shale exhibited the highest pH (greater than 11.0) of all the shales, and its pH tended to continue increasing after 96 hrs. Antrim shale generated an alkaline eluent with pH in the range between 8.5-9.5. The other two shales, Anvil Points and Oxy-6, produced eluents with pH ranging from 6.9 to 9.1. The soil reacted quite different from the shales. It was the only sorbent that produced acidic eluents after 96 hrs. The soil eluent was slightly basic (pH = 7.5) in the beginning, and then became slightly acidic (pH = 6.5) at the end of the trial.

4.2.2 Sorption/desorption of Organic Compounds

This section presents the sorption results of organic compounds (DMP, HN, THQ, TMP) on the oil shales and the western soil. The change in concentration of organic agents in the solutions was measured as a function of time. Results are summarized in Appendix-A Table A2. As mentioned in the previous chapter, three types of solutions were used. However, it was found that the DMP in both the prepared standards and the collected samples could not be detected by the HPLC method used. Although concentrations of DMP were not determined, for some multi-sorbate trials in which DMP was present in the soil solution, the influence of DMP on sorption/desorption behavior of the systems could be considered.

4.2.2.1 Sorption/desorption in Single Sorbate Solution

Sorption of individual compounds on oil shales and soil was illustrated in Figures 4-8 according to the data summarized in Appendix-A Table A2. These figures indicate that equilibrium of each single sorbate trial was reached within 24 to 48 hrs. As shown in Appendix-B Figures B1 through B5, in most cases, the adsorption processes occurred in either alkaline or near neutral solutions. However, exceptions were found in the sorption trials of DMP and TMP on Anvil Points shale during the period between 30 and 90 hrs (see Appendix-B Figure

B2) where reactions proceeded in an acidic environment. Figure 4 indicates that nearly all of the HN, THQ, and TMP adsorbed on Antrim shale in 24 hrs. Other adsorbents were less efficient, and Run-16 shale appeared to be the poorest sorbent of all. Greatest sorption of HN, THQ, and TMP generally occurred within 24 to 48 hrs. Thereafter, desorption of organic agents on some sorbents, e.g. Anvil Points and Oxy 6, occurred for some period of time. In all cases, HN, relative to THQ and TMP, was well adsorbed. The amount of organic compounds sorbed on shales and soil ranged from 5 mg/L to 25 mg/L.

The sorption of HN, THQ, and TMP on different sorbents is illustrated in Figures 9-11. Figure 9 shows that HN was nearly totally adsorbed by soil and Antrim shale, and well adsorbed by other shales. The affinity of HN for shales and soil can be ranked as:

Antrim > Soil > Oxy-6 > Anvil Points > Run-16

Figure 10 indicates that sorption of THQ on various sorbents followed the typical sorption curves. Compared to HN, THQ was sorbed to a lesser extent. The preference of sorption of THQ may be ordered as follows:

Antrim > Soil > Oxy-6 > Anvil Points > Run-16

The variations in concentration of TMP are presented in Figure 11. Sorptive capacity of Anvil Points shale for TMP was comparable to that of Oxy-6 shale. Significant desorption of TMP from soil occurred after 48 hrs, and the final concentration of TMP was greater than the initial concentration of TMP in the soil flask. Run-16 shale also appeared to be a poor sorbent for TMP. Sorptive affinity for TMP may be ranked as:

Antrim > Anvil Points > Oxy-6 > Soil > Run-16

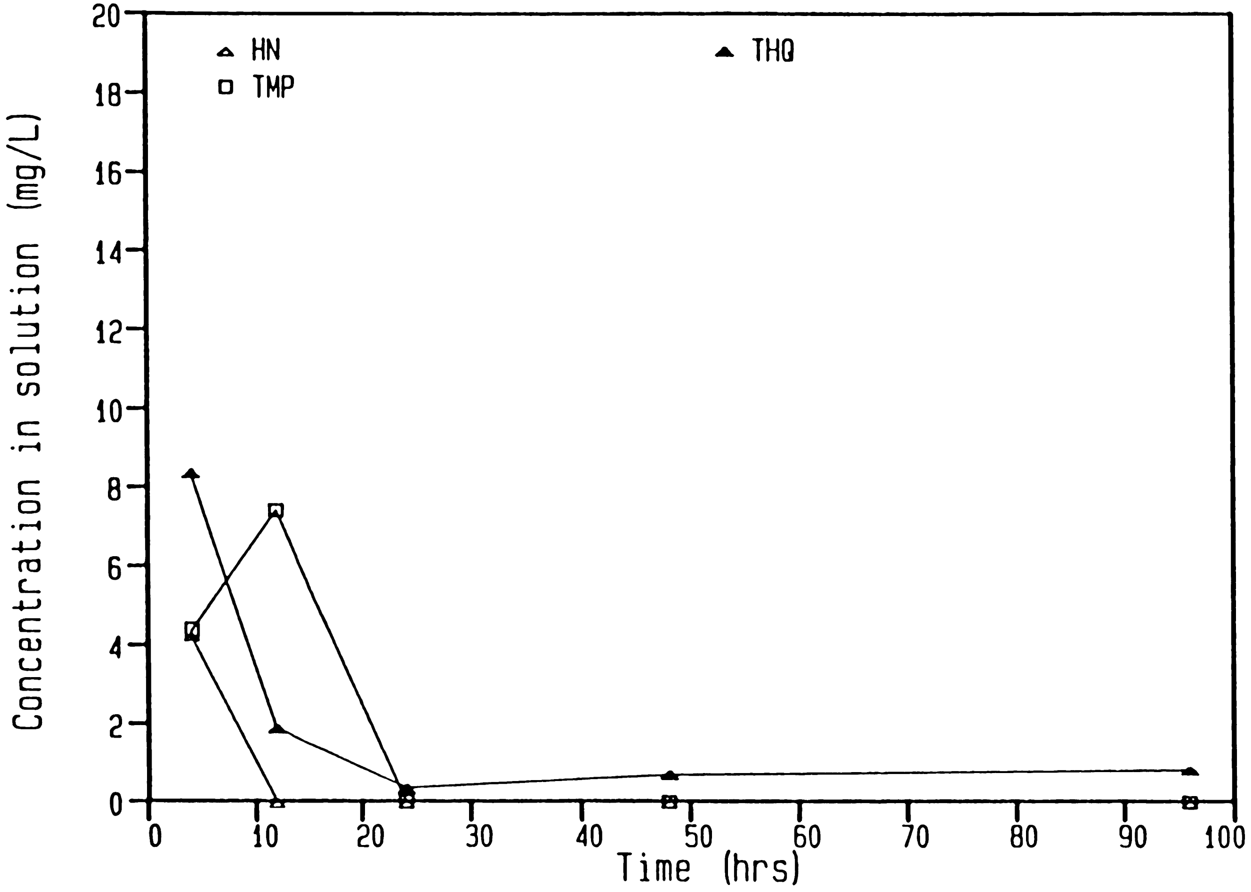

Figure 4. Sorption of HN, THQ, and TMP on Antrim shale: (C_0 = 25 mg/L)

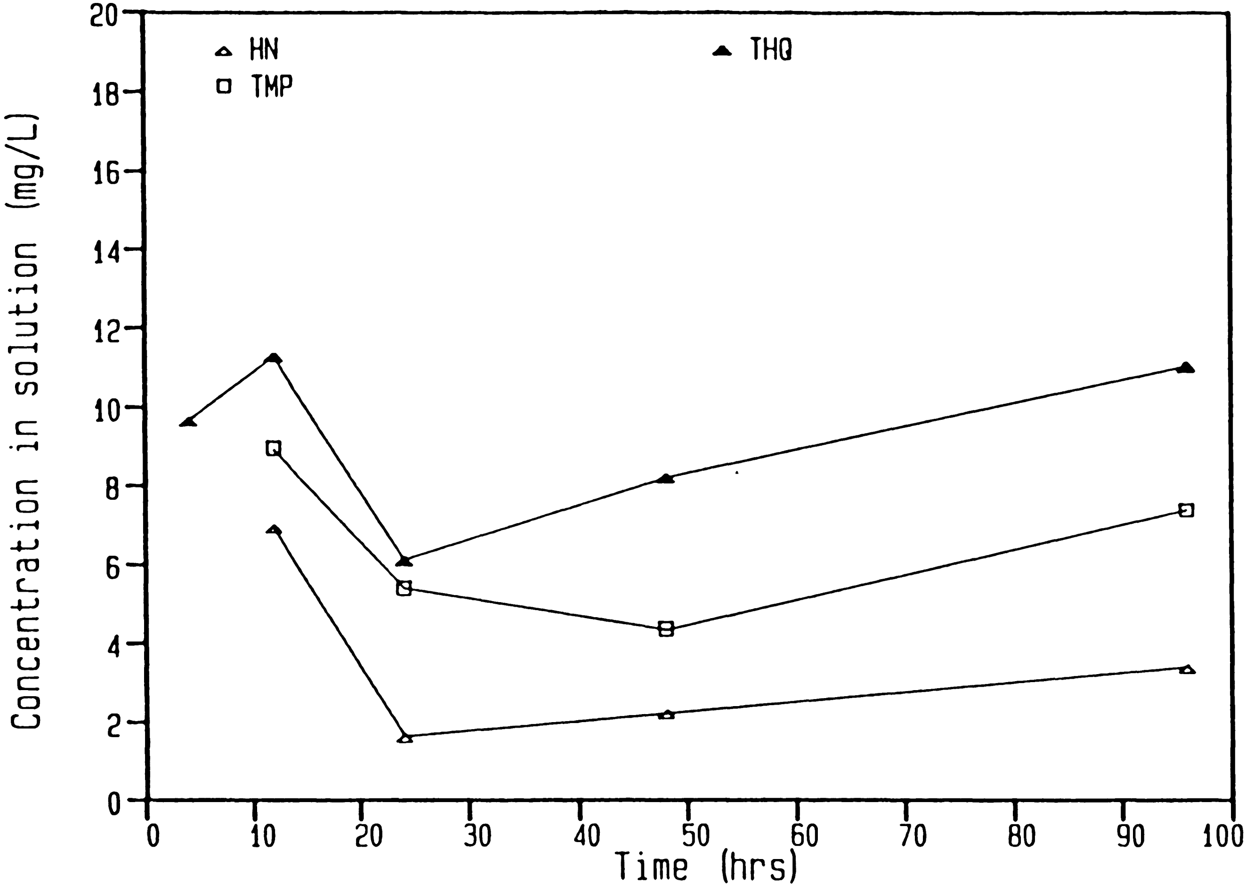

Figure 5. Sorption of HN, THQ, and TMP on Anvil Points shale: (C_0 = 25 mg/L)

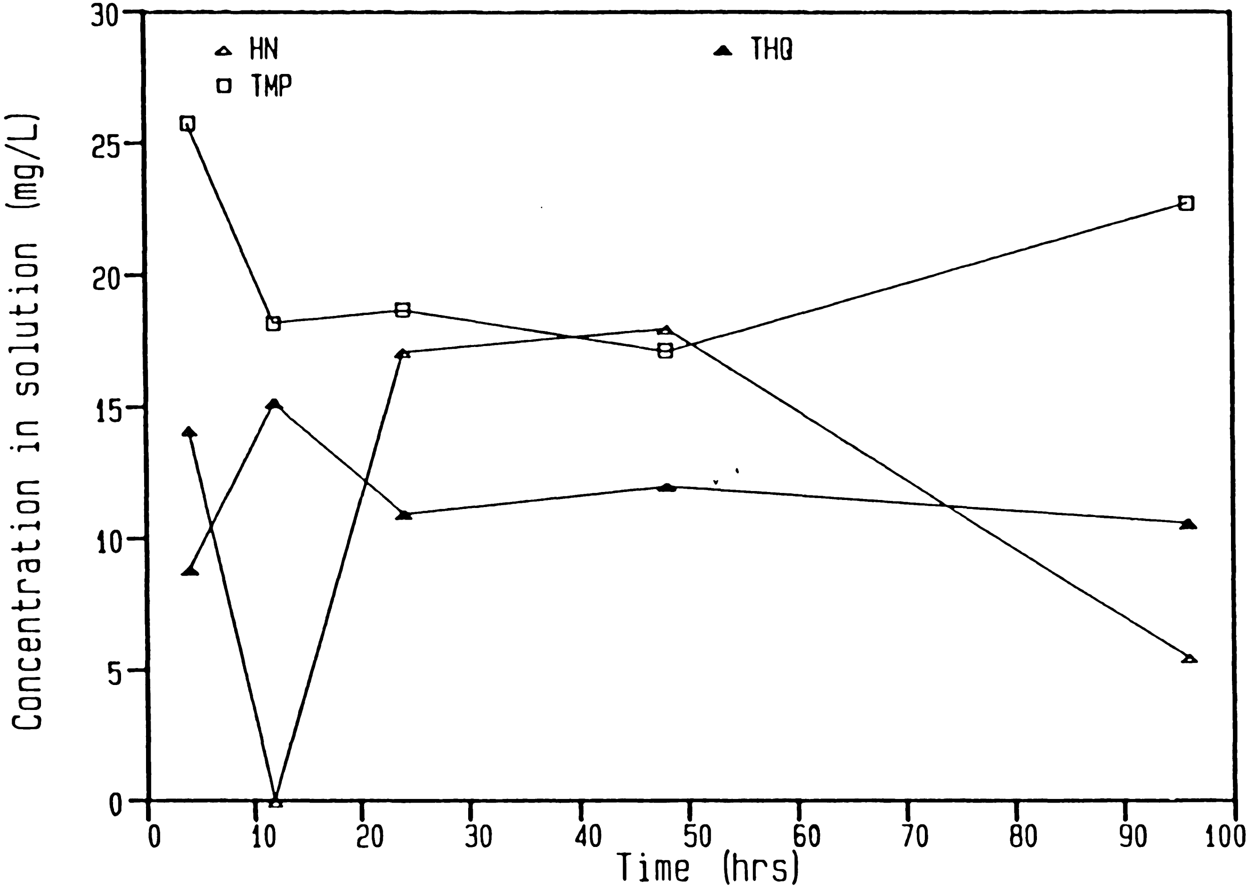

Figure 6. Sorption of HN, THQ, and TMP on Run-16 shale: (C_0 = 25 mg/L)

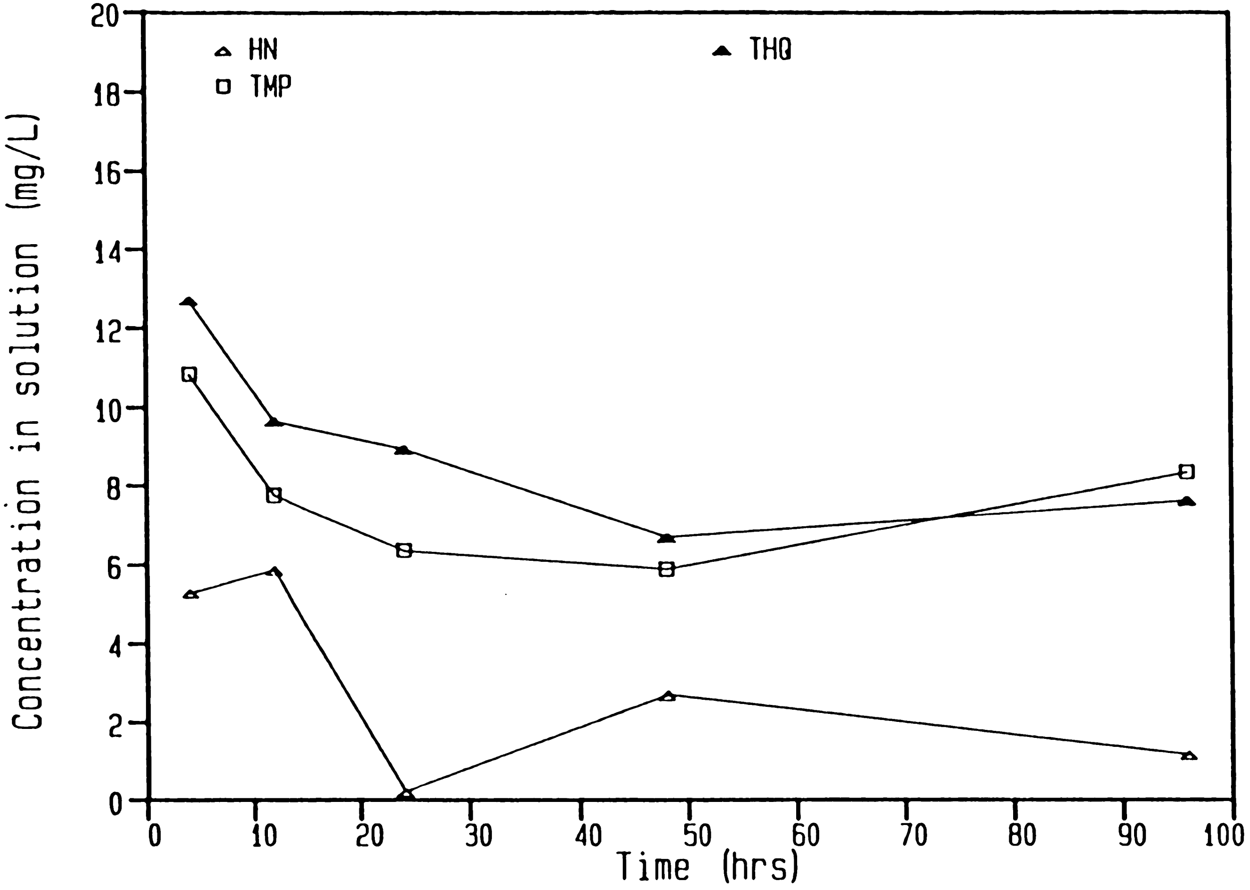

Figure 7. Sorption of HN, THQ, and TMP on Oxy-6 shale: (C_0 = 25 mg/L)

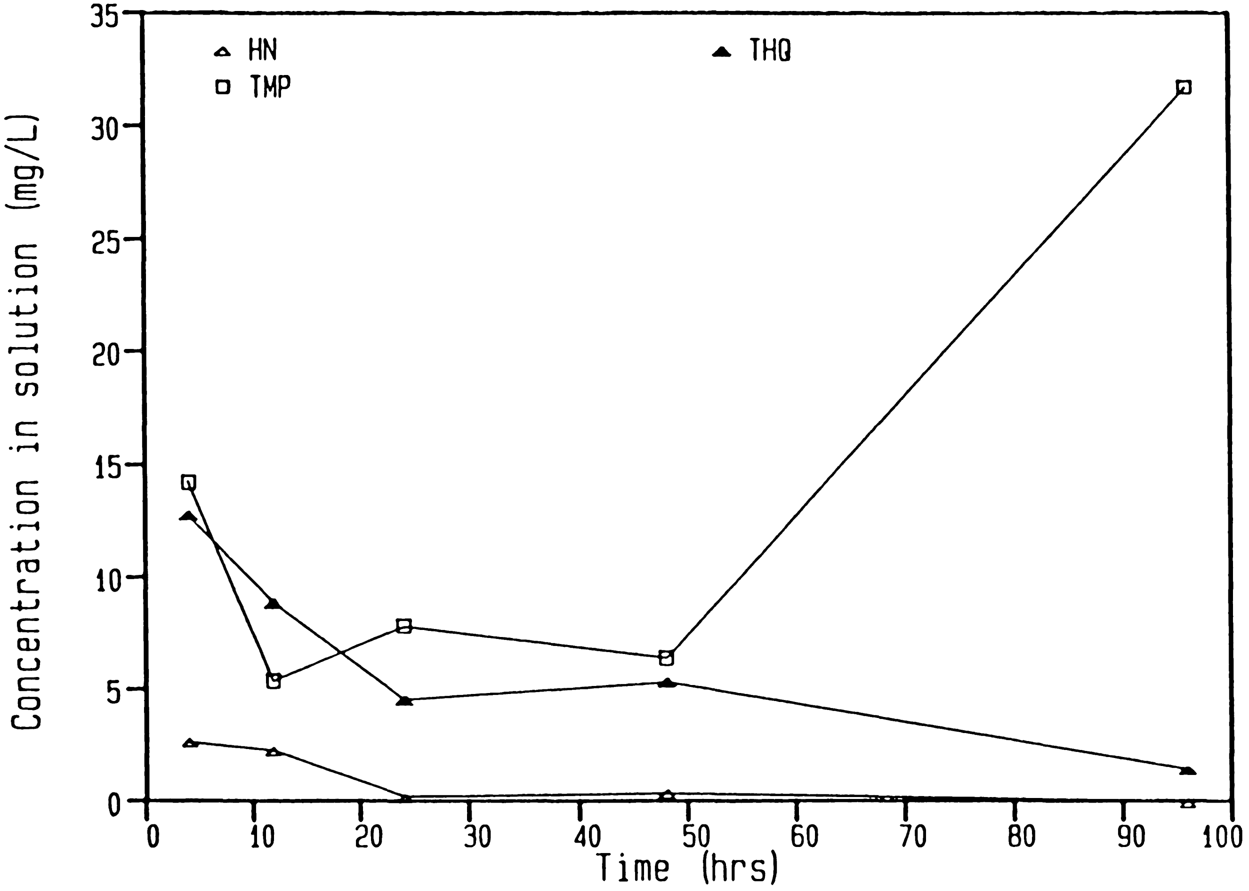

Figure 8. Sorption of HN, THQ, and TMP on the western soil: (C_0= 25 mg/L)

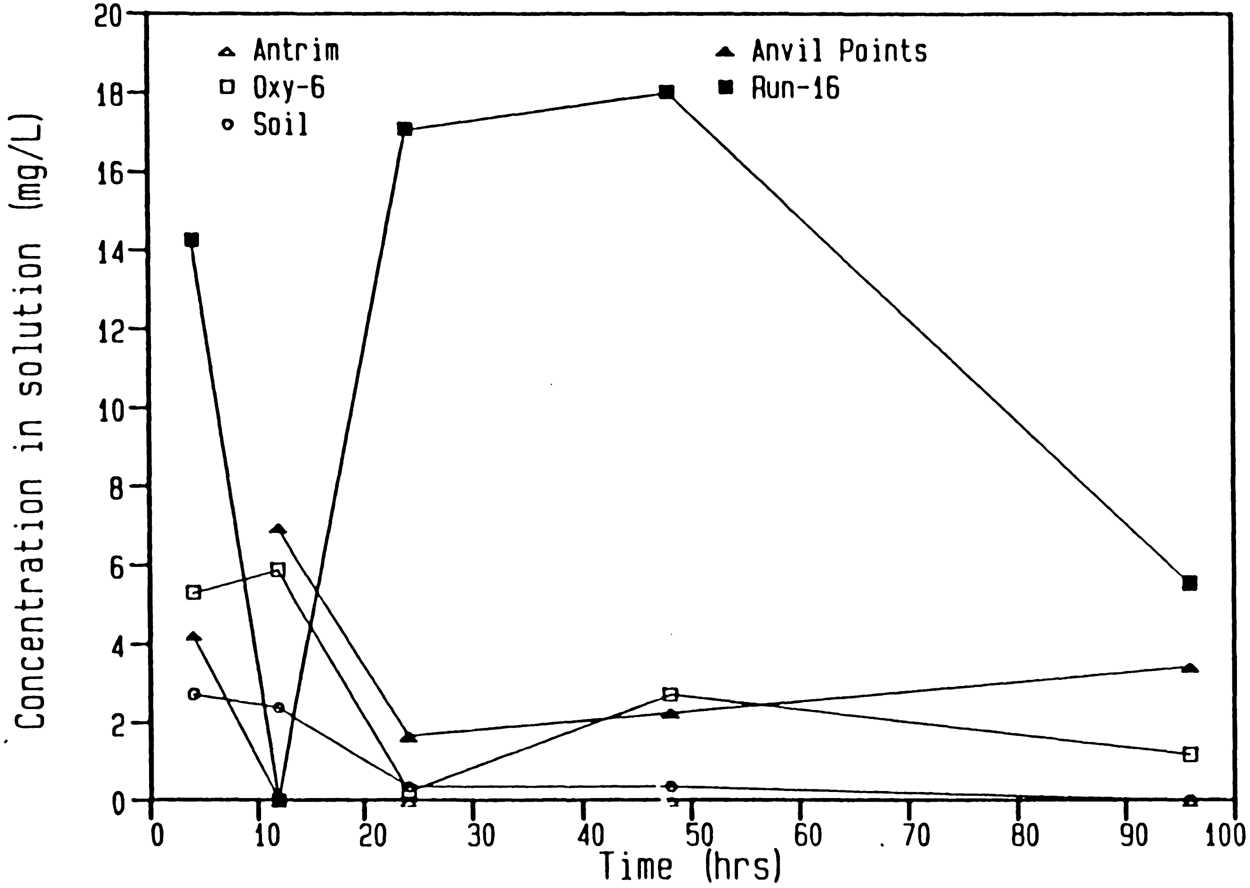

Figure 9. Sorption of HN in single-sorbate systems: (C_0 = 25 mg/L)

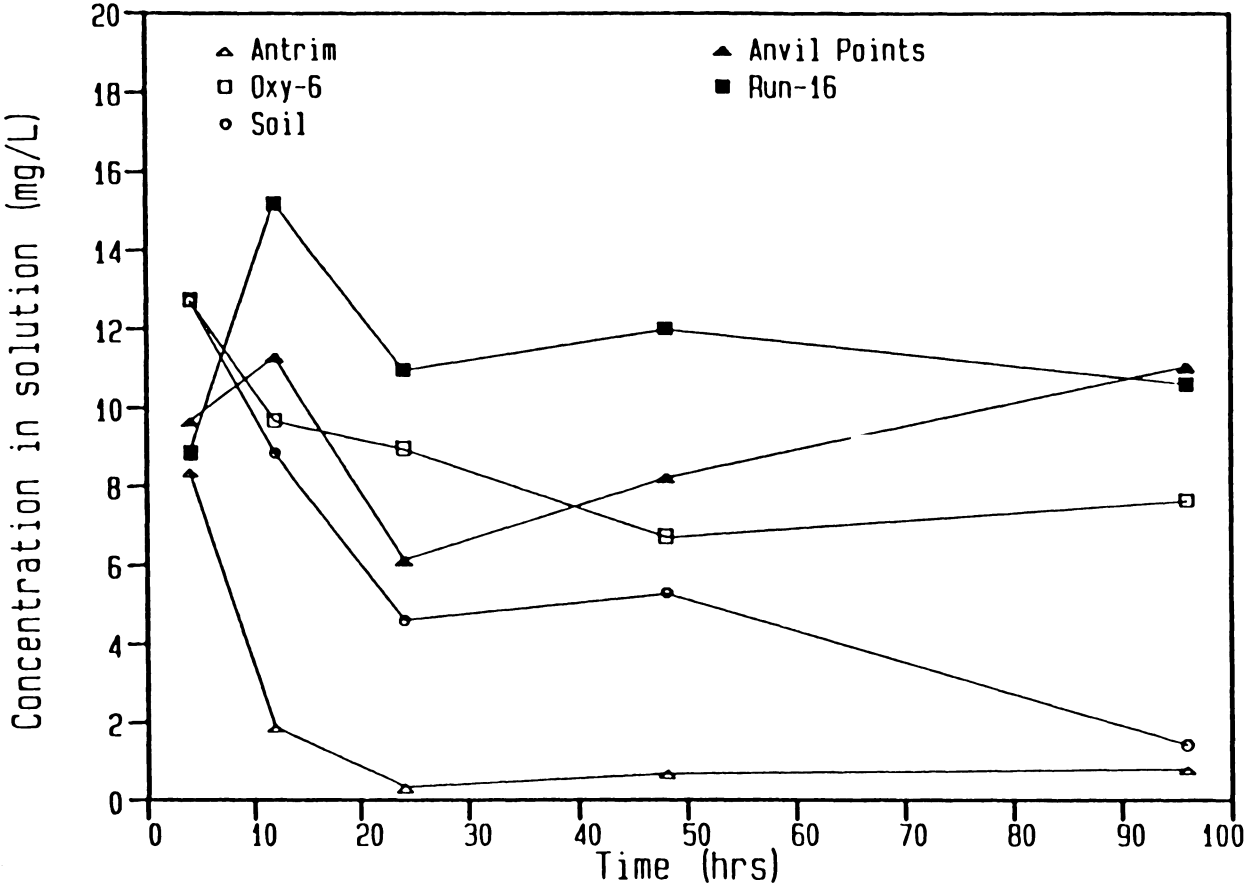

Figure 10. Sorption of THQ in single-sorbate systems: (C_0 = 25 mg/L)

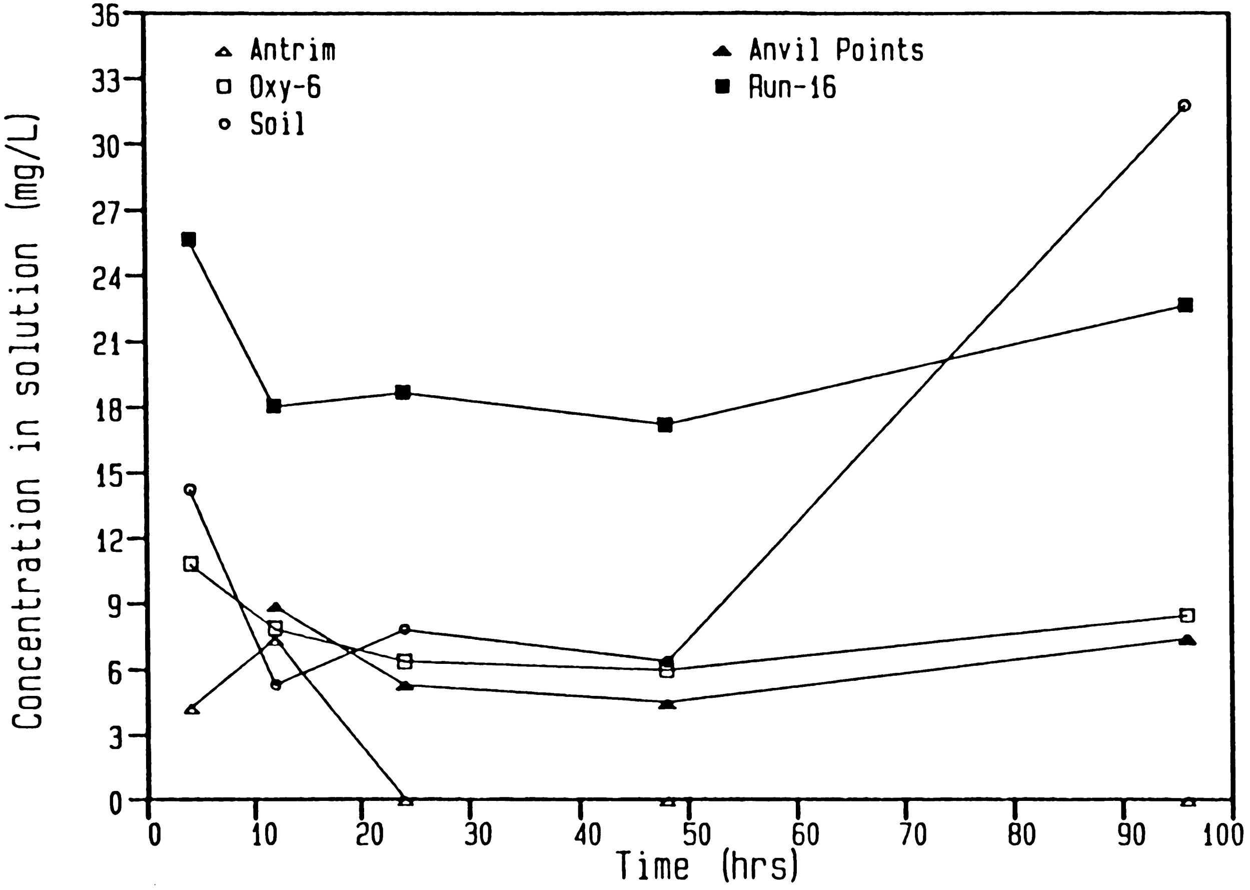

Figure 11. Sorption of TMP in single-sorbate systems: (C_0 = 25 mg/L)

4.2.2.2 Sorption/desorption in Multicomponent Solution

Multicomponent sorption experiments were conducted with two types of solution, solutions with three components (HN, THQ, TMP) and solutions with four components (HN, DMP,THQ, TMP). Figures 12 and 13 present sorption data of HN, THQ, and TMP onto Antrim shale in the three- and four-component solution. The amount of HN sorbed on Antrim shale was in the area of 23 mg/L. Lower quantities of THQ (17 ~ 22 mg/L) and TMP (8 ~ 13 mg/L) were sorbed on Antrim shale.

Sorption of HN, THQ, TMP on Anvil Points shale was illustrated in Figures 14 and 15. The trend of sorption for each organic agents was relatively similar in both types of multicomponent solution. Again, sorption of HN was quite extensive (≅ 21 mg/L), followed by sorption of THQ and TMP. In both systems, desorption happened after 48 hrs.

Figures 16 and 17 show the results of multisolute sorption on Oxy-6 shale. HN was sorbed best, followed by THQ and TMP. It is interesting to note that in the three-component sorption trial, large quantities (16 ~ 21 mg/L) of organic compounds were taken up by the Oxy-6 shale in the initial 4 to 12 hrs. Then, significant desorption of organic compounds from the sorbent took place in the next 20 hrs, especially in the case of TMP desorption where approximately 30 mg/L of TMP was found in the solution, which exceeded the initial concentration (25 mg/L) of TMP added to the flask. However, later adsorption reduced the residual solution concentrations of solutes, and equilibrium was attained at approximately 48 hrs. In the four solute solution, no significant desorption occurred in the earlier stage of the sorption process.

Results of multisolute sorption on Run-16 shale were shown in Figures 18 and 19. The sorption trend of organic compounds was similar in both systems. Greatest sorption of organic compounds occurred within 24 hrs, and then desorption took place for a certain period. The highest amount of TMP (30 ~ 35 mg/L) found in both systems was also greater than the initial concentration of TMP in the solutions. Subsequent adsorption of organic compounds began at approximately 48 hrs.

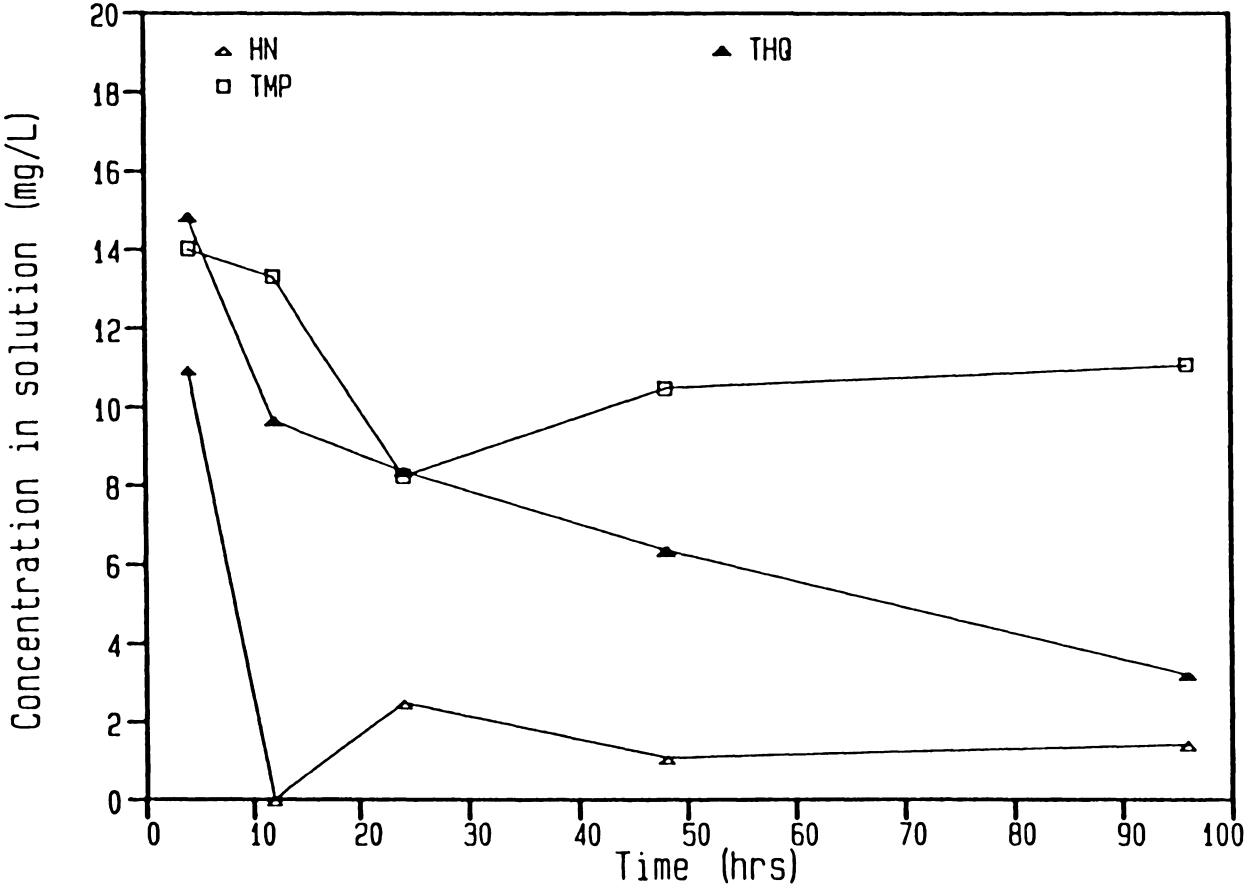

Figure 12. Sorption on Antrim shale in three-component solution: (C_0= 25 mg/L)

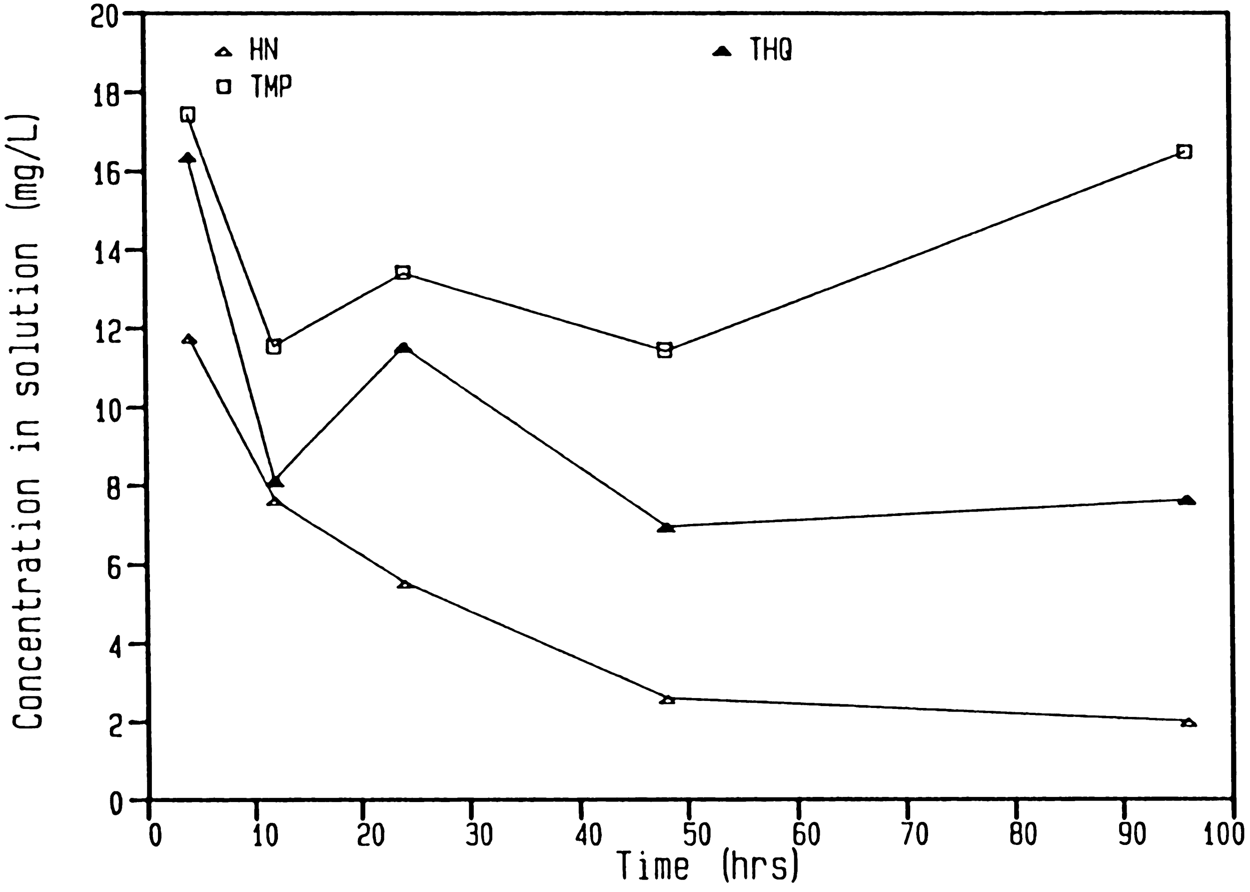

Figure 13. Sorption on Antrim shale in four-component solution: (C_0 = 25 mg/L)

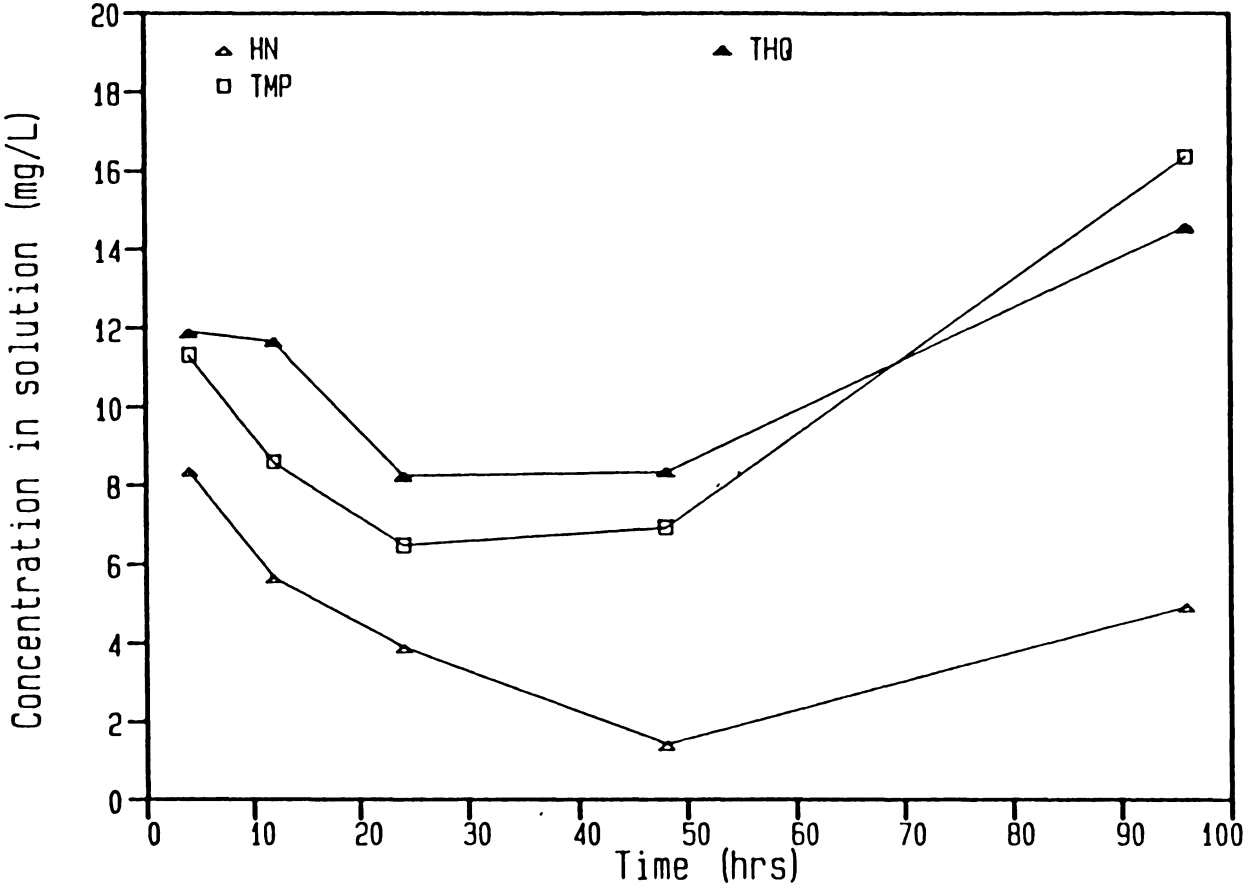

Figure 14. Sorption on Anvil Points shale in three-component solution: (C_0 = 25 mg/L)

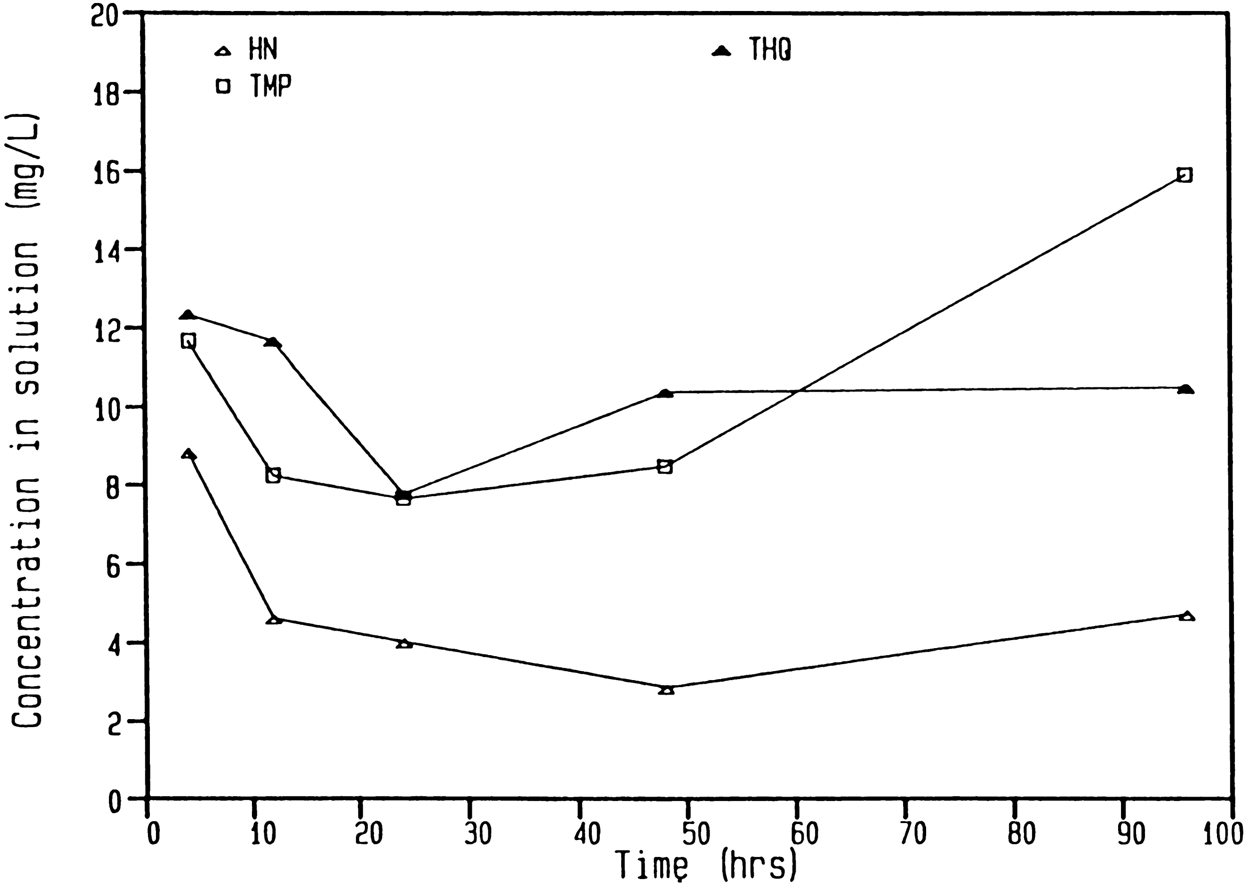

Figure 15. Sorption on Anvil Points shale in four-component solution: (C_0 = 25 mg/L)

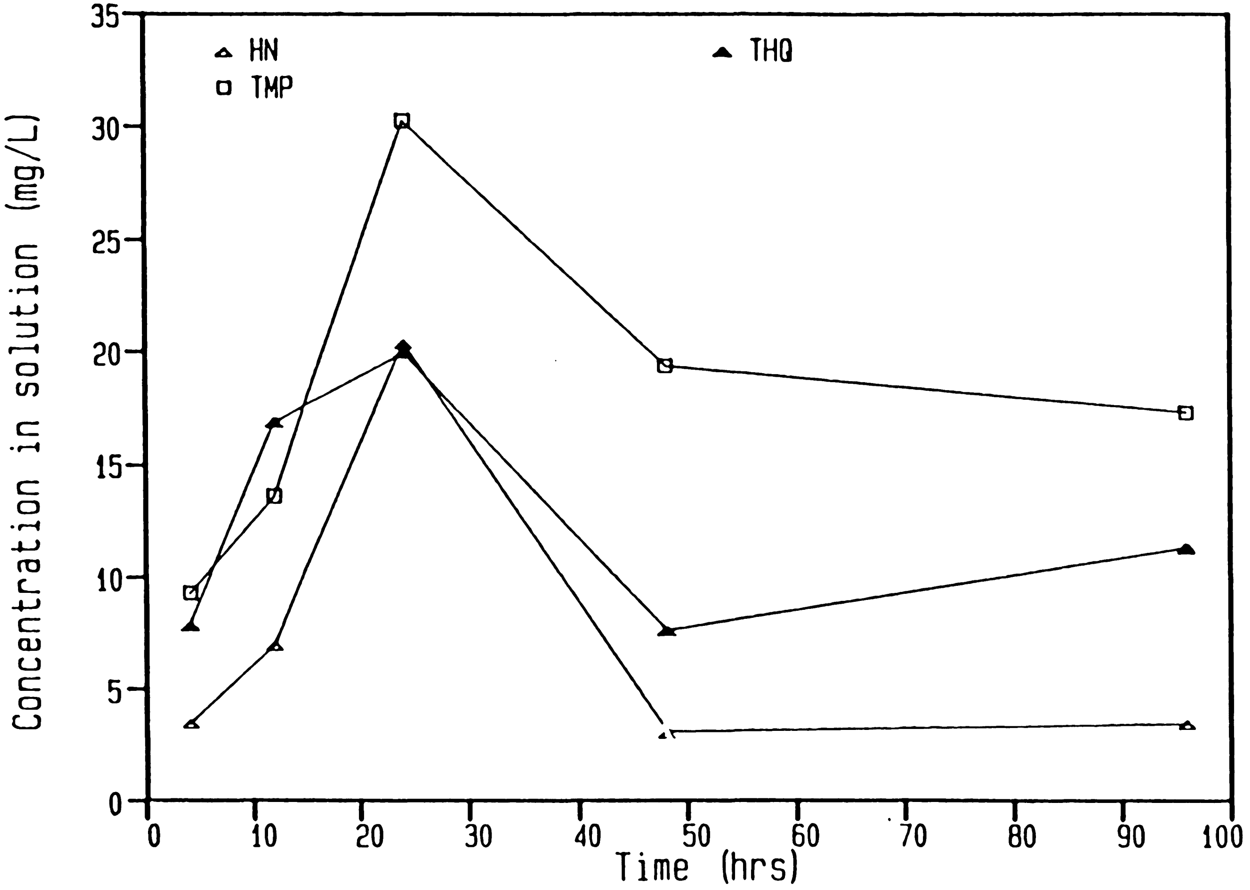

Figure 16. Sorption on Oxy-6 shale in three-component solution: (C_0= 25 mg/L)

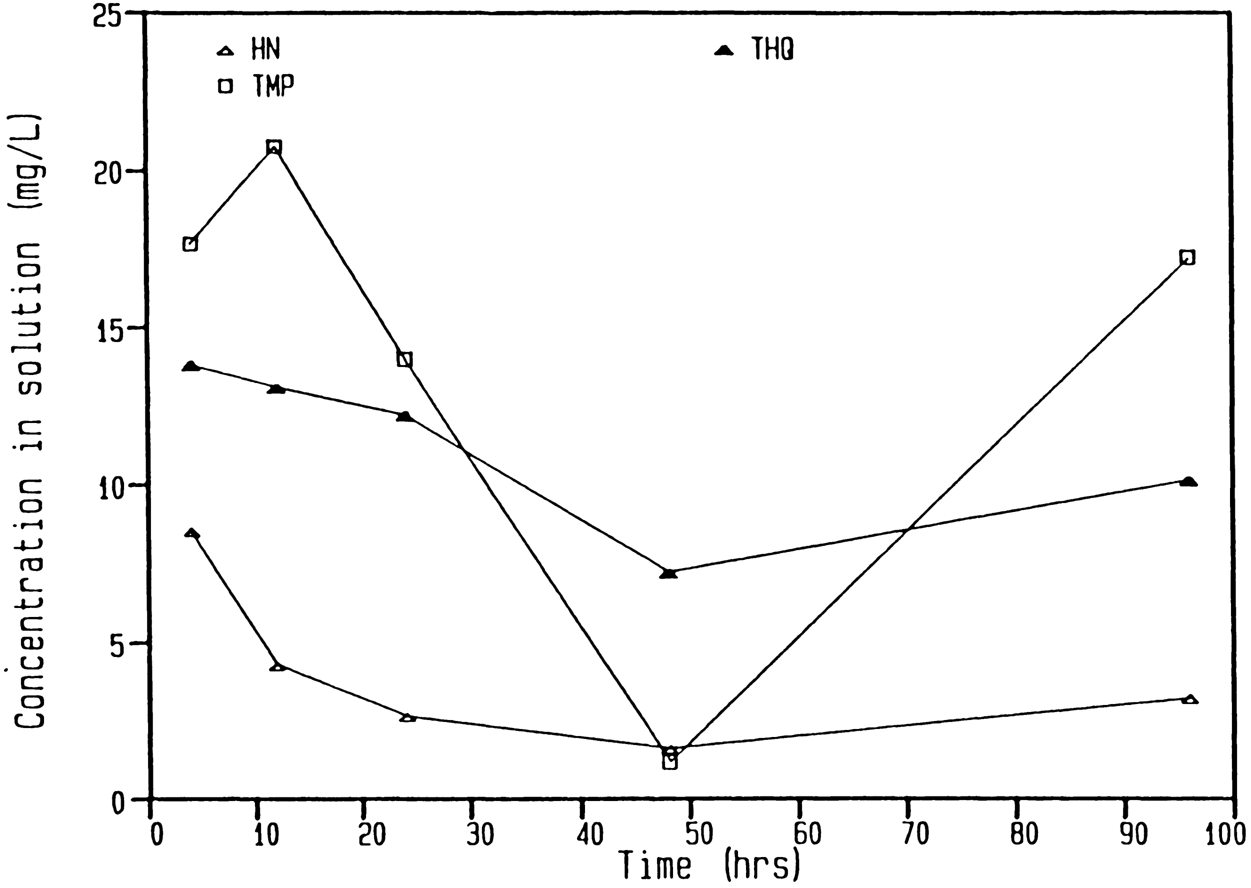

Figure 17. Sorption on Oxy-6 shale in four-component solution: (C_0 = 25 mg/L)

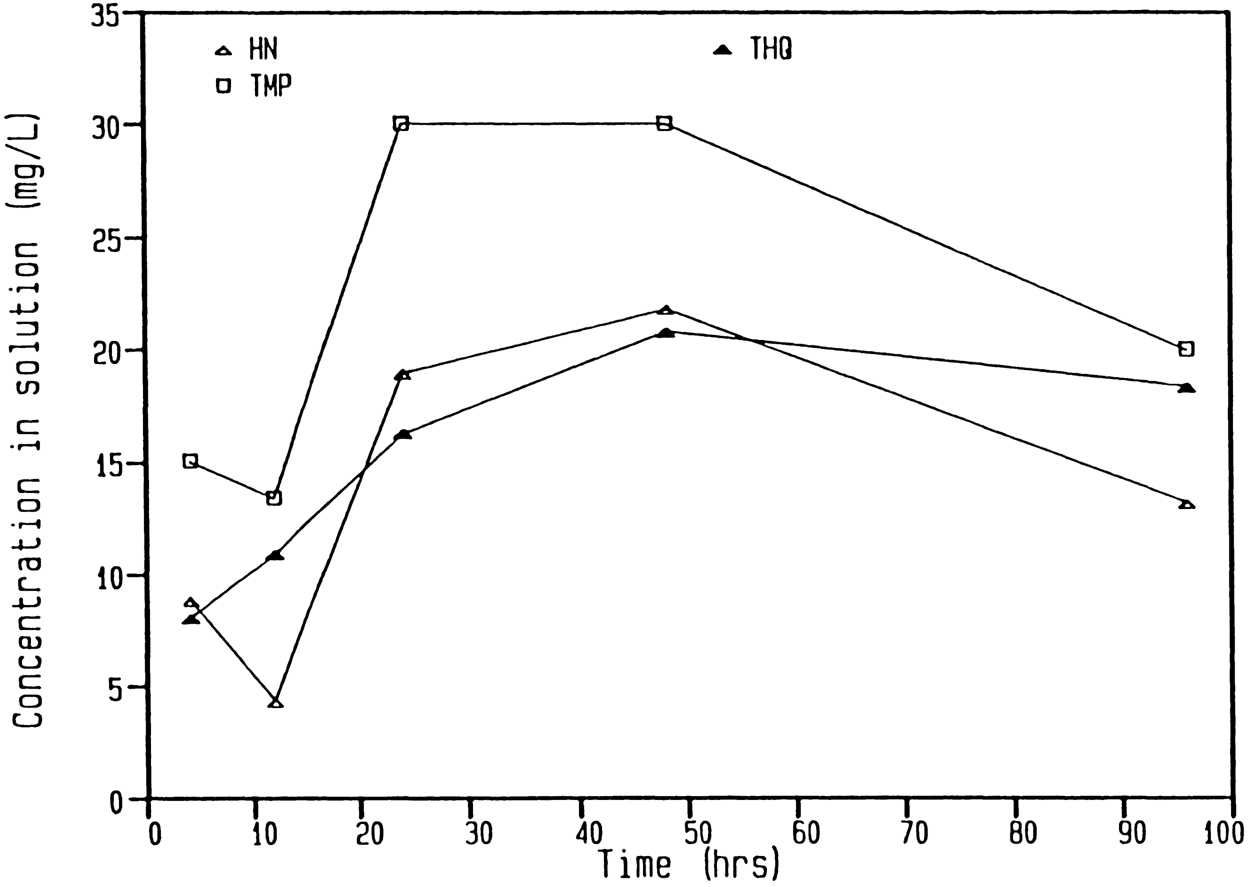

Figure 18. Sorption on Run-16 shale in three-component solution: (C_0 = 25 mg/L)

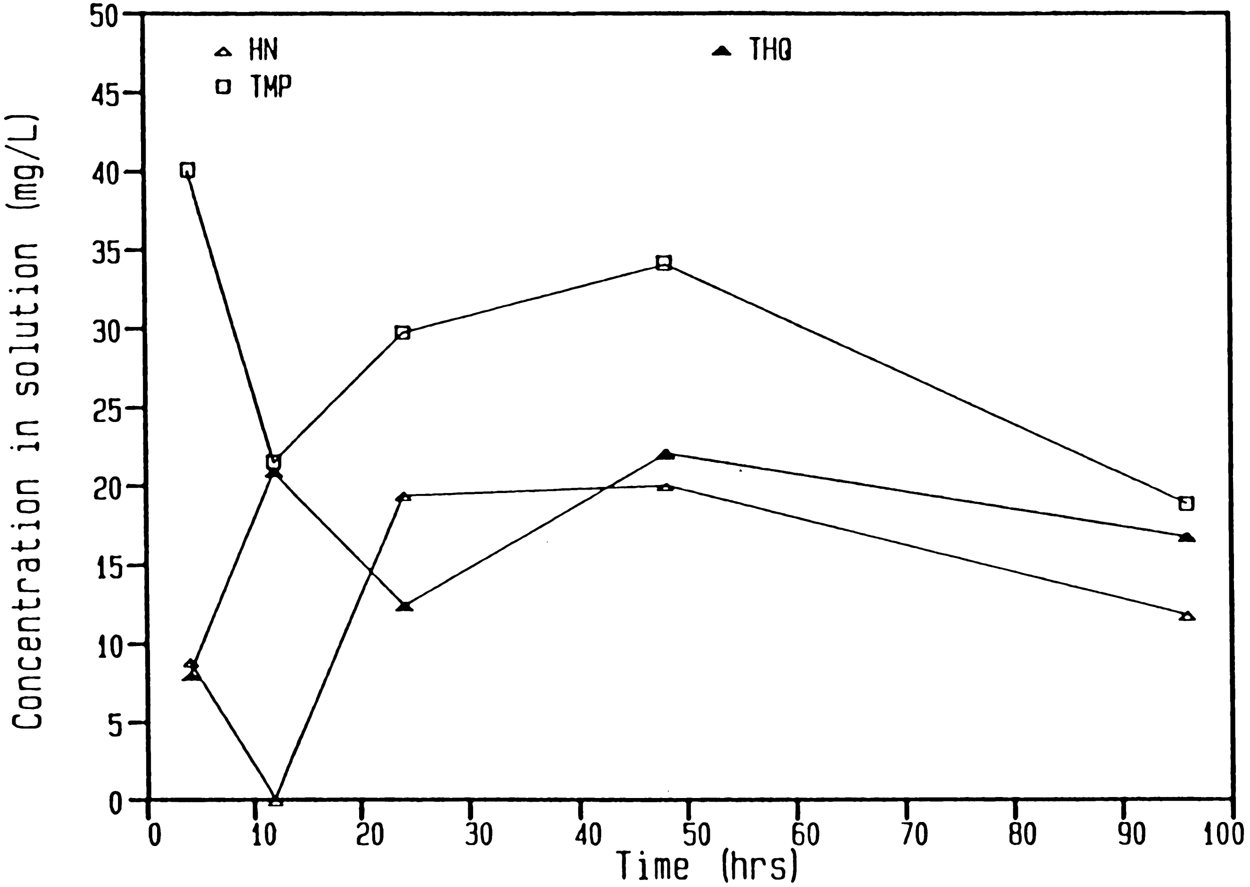

Figure 19. Sorption on Run-16 shale in four-component solution: (C_0 = 25 mg/L)

Sorption data for soil are presented in Figures 20 and 21. Sorption equilibrium was attained in 24 hrs. HN was again sorbed best. THQ was sorbed better than TMP in the four-solute solution, whereas TMP was sorbed better in the three-solute solution.

To better assess the competition effects on the adsorption of HN, THQ, and TMP in multicomponent solutions, variations in the concentration of organic compounds in single-sorbate, three-component, and four-component solutions in the presence of different shales and soil were compared in Appendix-C, Figures C1-C15. It can be seen that adsorption of HN appeared to be the least affected by the presence of other species in the solution. Mutual inhibition of adsorption capacity was evident in every case. Each solute affected adversely both the rate and capacity for adsorption of other compounds present. Generally, three-component solutions and four-component solutions exhibited similarly shaped sorption curves, whereas different sorptive behavior was observed in single-sorbate trials. In most cases, adsorption of organic compounds on the four shales and the western soil in either single-, three-, or four-component solutions followed the order of: HN > THQ > TMP.

4.2.3 Sorption of Inorganic Ions by the Western Soil

Data obtained from sorption of inorganic ions on the western soil are presented in Appendix-A, Tables A3-A5. The overall pH values in this phase of study ranged from 6.2 to 8.2. Generally, the variation of pH in each trial was less than one pH unit (see Appendix-D, Figures D1-D3). Higher pH values were associated with solutions containing NH_4 (7.3-8.1) and F(6.4-8.2). The lower pH values were observed in the solutions containing Cd (6.3-6.4), K (6.2-7.4), and Ca (6.4-7.5).

The multicomponent trials which contained a mixture of five cations (As, Ca, Cd, Fe, and K) resulted in pH values ranging between 6.5-7.1. Soil eluent pHs were in the range of 6.5-7.1. The overall pH range (6.2-8.0) of control tests was relatively comparable to that of sorption trials performed with distilled water.

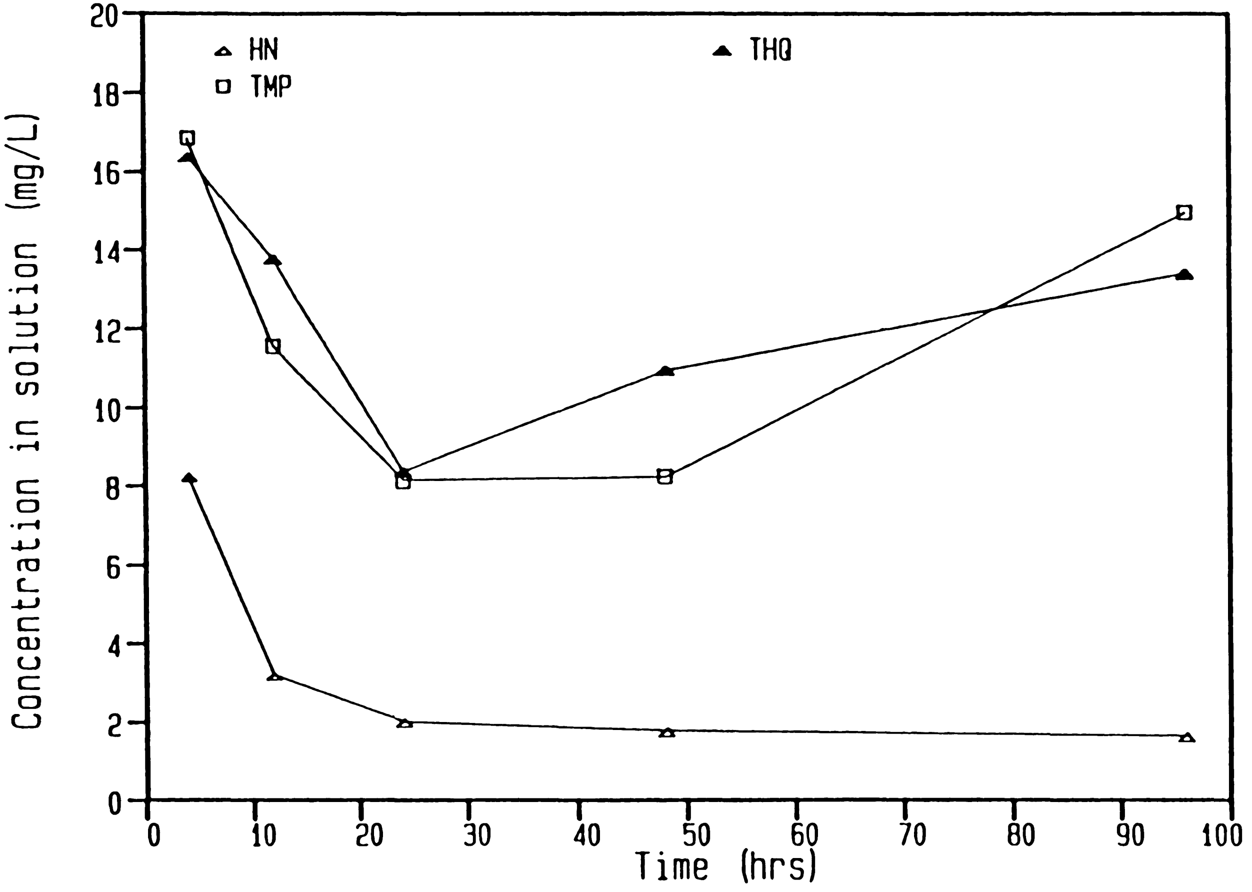

Figure 20. Sorption on the western soil in three-component solution: (C_0 = 25 mg/L)

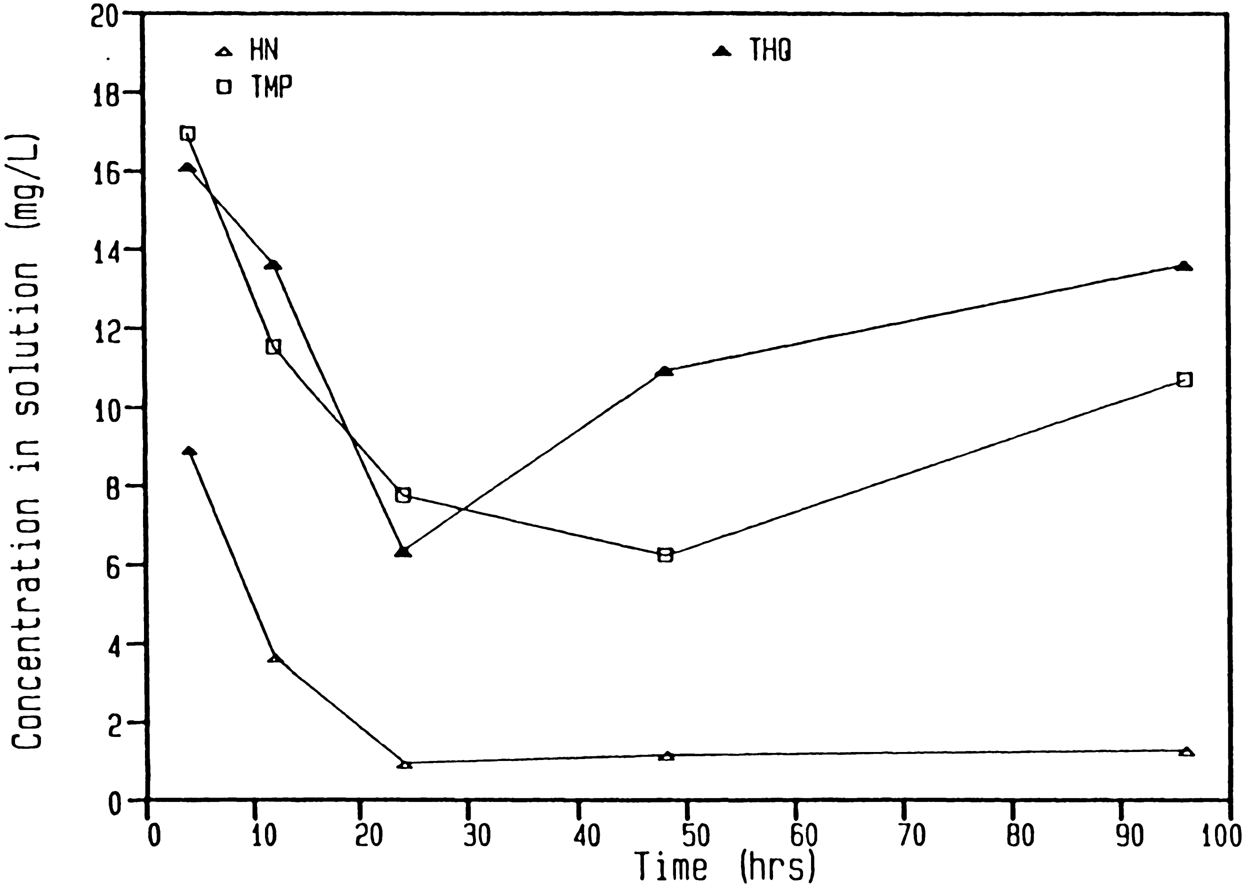

Figure 21. Sorption on the western soil in four-component solution: (C_0 = 25 mg/L)

In most cases, the values of conductivity, measured in mmho/cm, remained relatively constant throughout the course of experiments. The soil eluent exhibited a tendency for very low conductivity (0.19-0.22). Low conductivities were also found in solutions containing NH_4 (0.63-0.72), F (0.34-0.42), and SO_4 (0.28-0.34). The conductivities measured in cation (As, Ca, Cd, K, Fe) containing solutions were approximately an order of magnitude greater than those of NH_4, SO_4, and F containing solutions. The mixture of cations showed higher conductivities (11.6-12.9) than other types of trial, yet the iron containing solution exhibited the highest conductivity (5.5-17.3).

Large variations of conductivity only occurred in the solutions containing Fe and K. In the solution containing Fe, the conductivity increased from 5.5 mmho/cm to 17.3 mmho/cm. The conductivity of K containing solution was relatively stable in the initial 72 hrs (ranging between 5.3 and 6.6); however, it increased to 11.9 mmho/cm after 96 hrs.

Table A5 in Appendix-A presents the data obtained from six different types of batch trial. By comparing the composition of distilled water (type 6) with soil eluent (type 5), it can be seen that large quantities of Ca ($\cong$ 12.65 mg/L), K ($\cong$ 7.3 mg/L), and SO_4 ($\cong$ 33 mg/L) were leached out from the soil, whereas the amount of Fe, F, and NH_4 in the leachate were very low. The amount of As and Cd were below detection levels.

The results of the single-sorbate and multicomponent trials are illustrated in Figures 22-29. In the case of single-sorbate trials, the soil adsorbed approximately 6-8 mg/L As, 12-15 mg/L Ca, 50 mg/L Cd, 10-13 mg/L K, 7-10 mg/L F, 7-10 mg/L NH_4, and nearly all of the Fe added. Nearly 40 mg/L of SO_4 were leached from the soil. Noted that, however, the amount of Ca, K and, especially, SO_4 leached from soil in the elution trial must be considered.

The sorption of each ion in multicomponent trials are compared with data obtained from single-sorbate trials in Figures 22-26. It can be seen that sorption of As (40-45 mg/L) was enhanced greatly by the presence of other ions in the solution. On the other hand, competition for sorption sites greatly depressed the adsorbed amount of Cd and Fe. It appeared that the final concentrations of K and Ca in the residual solution after 96 hrs were greater than their inoculum concentration ($\cong$66.7 mg/L).

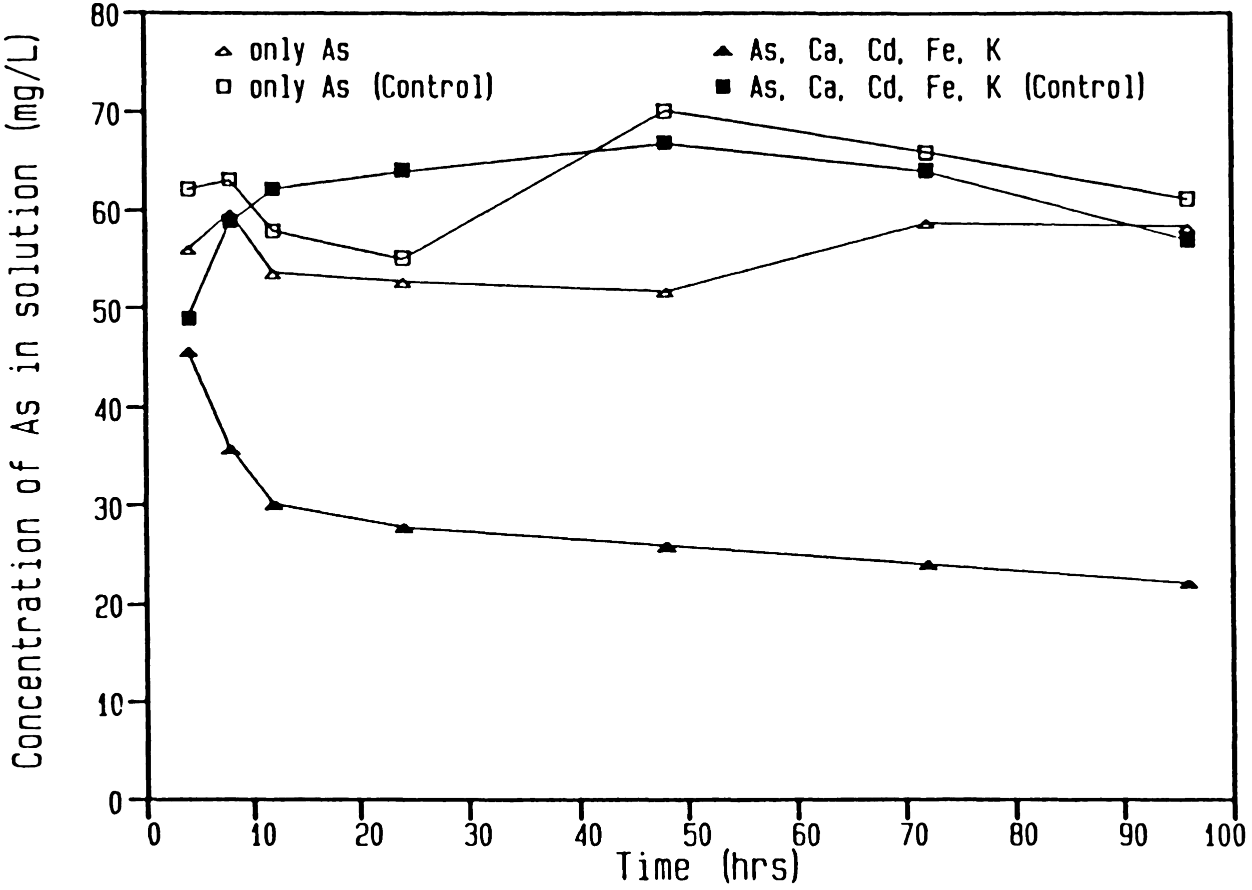

Figure 22. Sorption of As on the western soil: (C_0 = 67 mg/L)

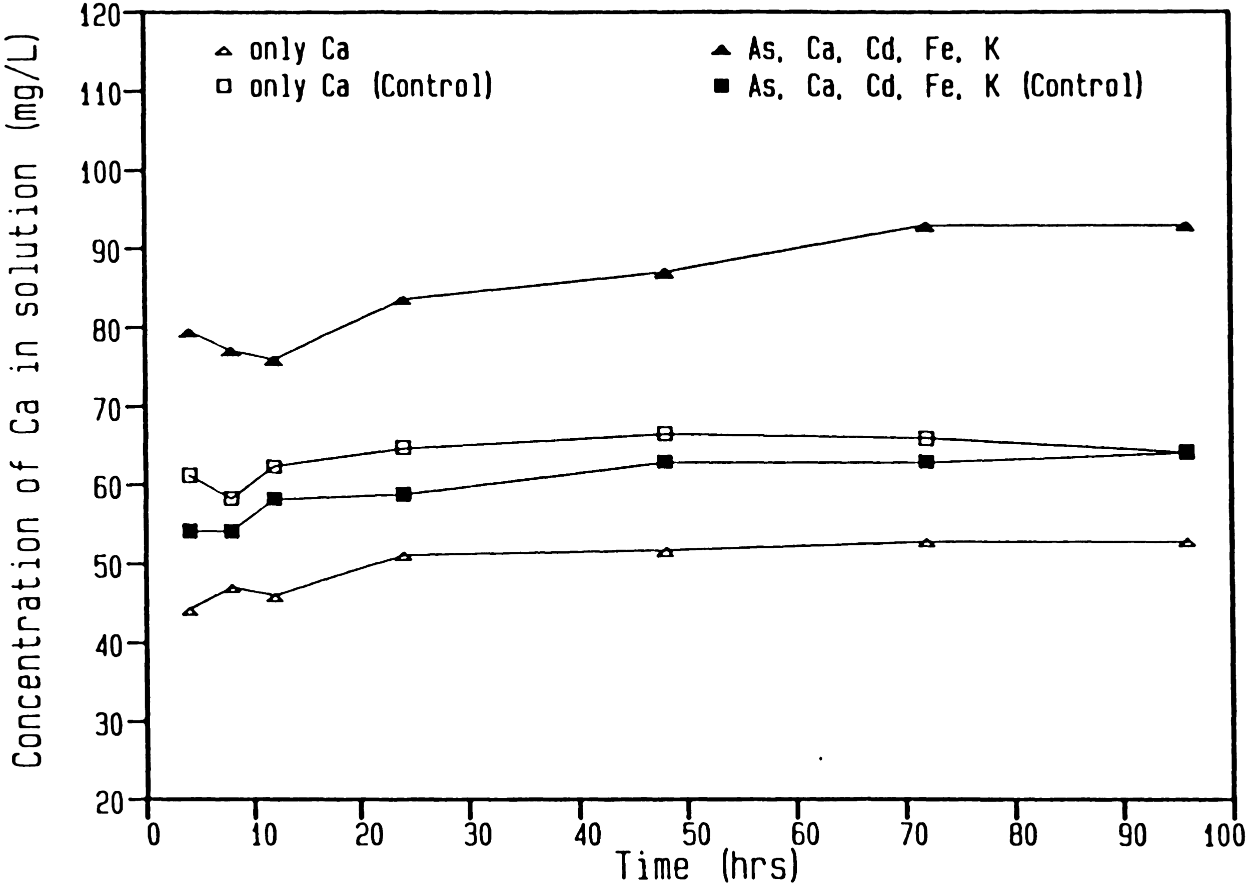

Figure 23. sorption of Ca on the western soil: (C_0 = 67 mg/L)

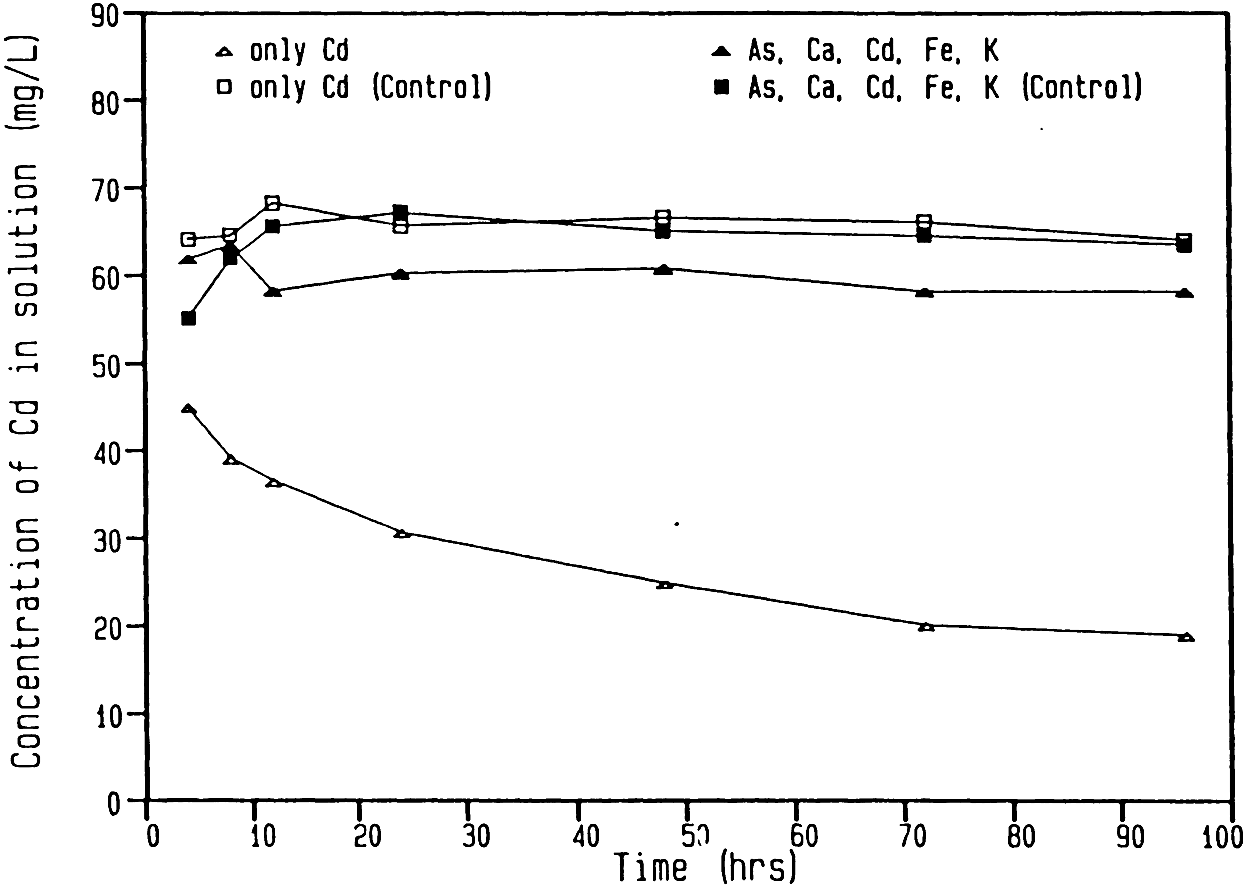

Figure 24. Sorption of Cd on the western soil: (C_0 = 67 mg/L)

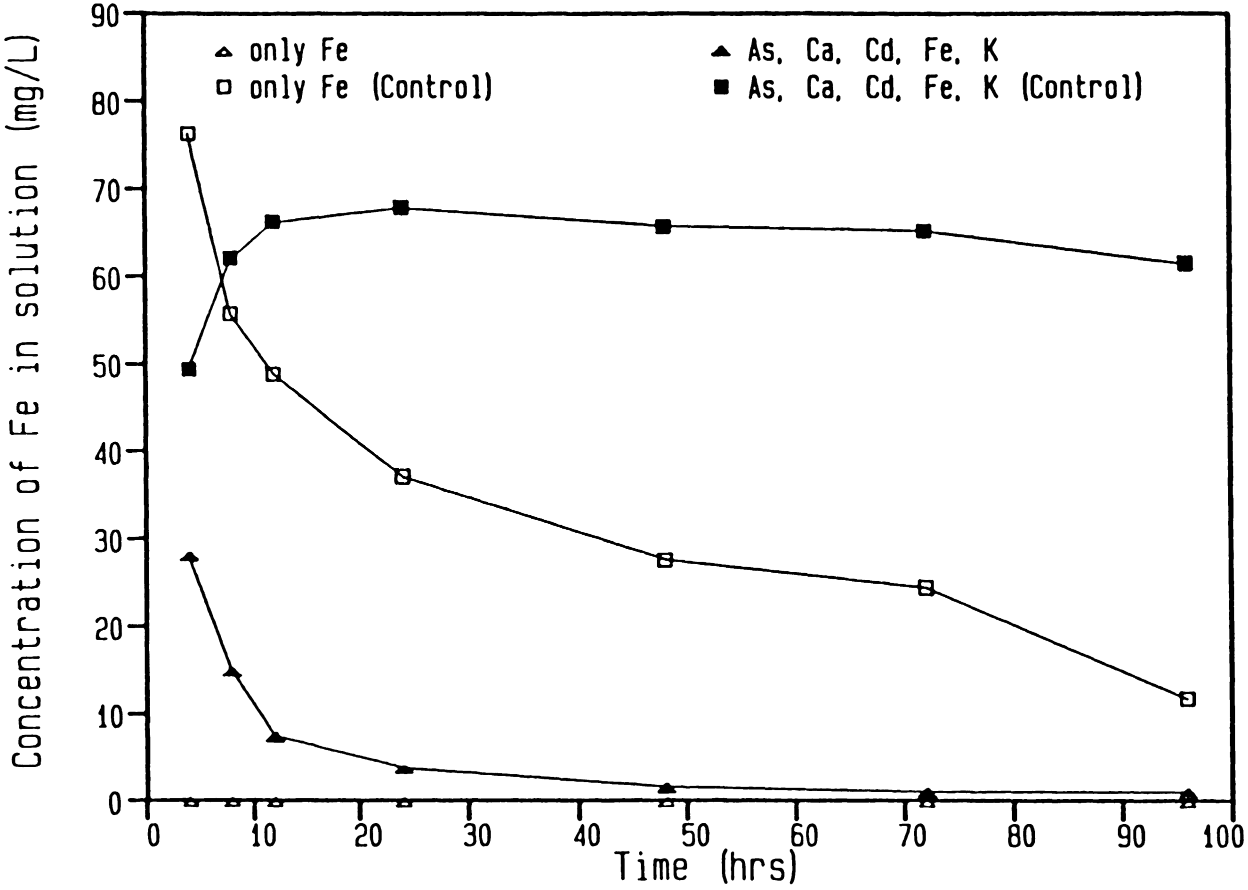

Figure 25. Sorption of Fe on the western soil: (C_0 = 67 mg/L)

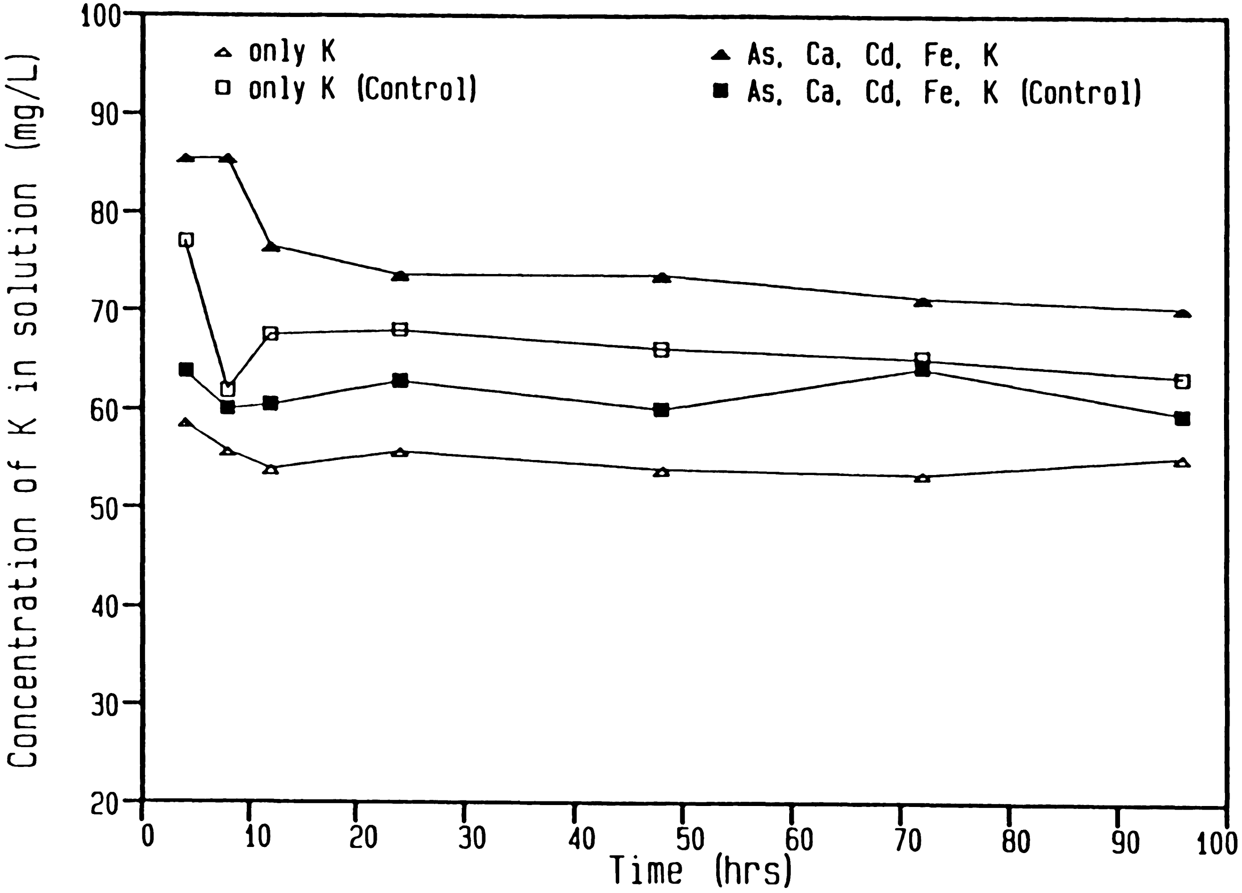

Figure 26. Sorption of K on the western soil: (C_0 = 67 mg/L)

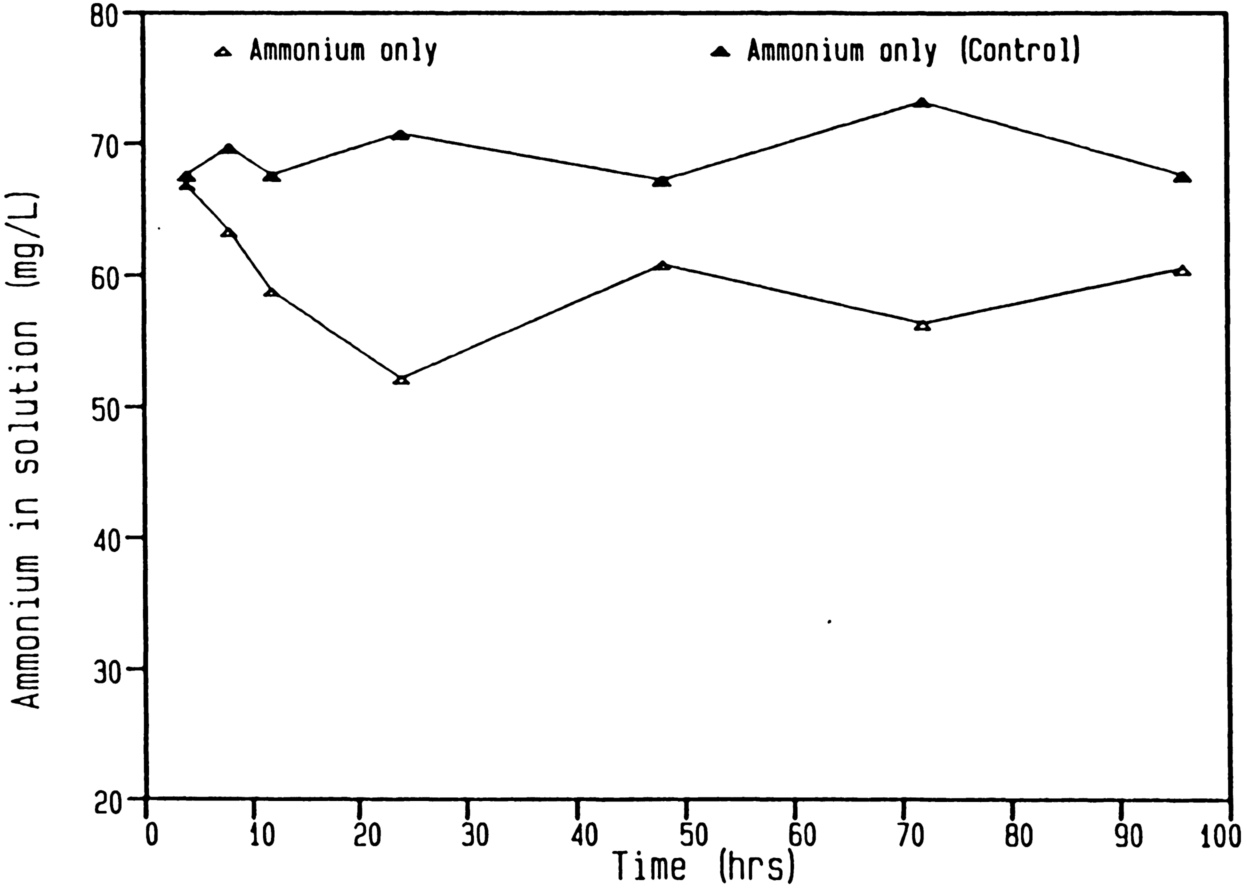

Figure 27. Sorption of ammonium on the western soil: (C_0 = 67 mg/L)

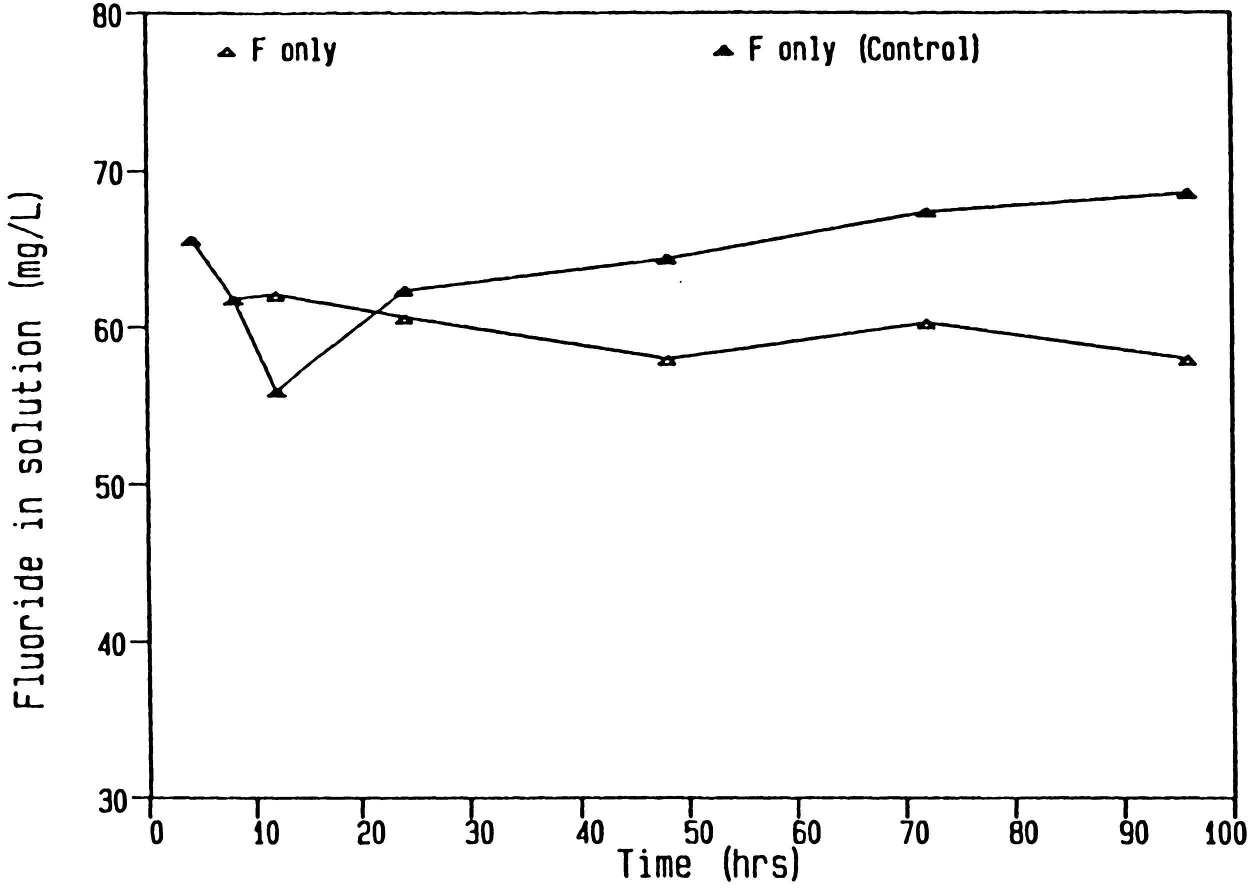

Figure 28. Sorption of fluoride on the western soil: (C_0 = 67 mg/L)

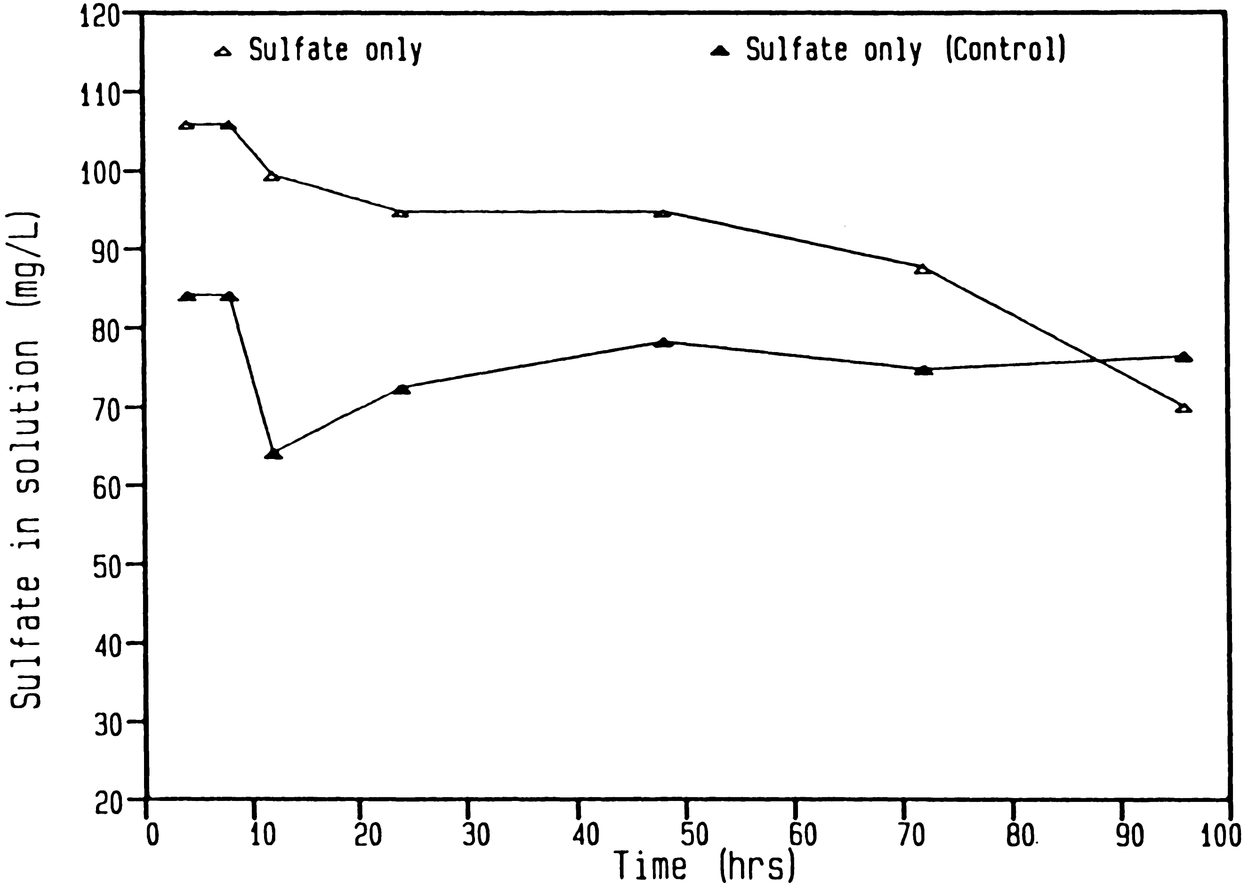

Figure 29. Sorption of sulfate on the western soil: (C_0= 67 mg/L)

4.3 Column Sorption Experiment

4.3.1 Sorption/desorption of Organic Compounds

The experiments in this phase were conducted on a continuous-flow basis in a fixed shale/soil bed. Each type of the experiments was performed in triplicate, except in the case of Oxy 6 shale with which only one column trial was performed. The feed solutions contained either a mixture of HN, DMP, THQ, and TMP (first trial of each type) or a mixture of HN, THQ, and TMP (second and third trials of each type). The concentration of each organic compound in the feed solution was approximately 25 mg/L.

The variations of pH in column trails were in the range between 6.7 and 8.5, except in the case of Run 16 shale where the pHs of the effluent were as high as 11.0. These are illustrated in Appendix-F. Generally, the pH of the effluents approached its equilibrium value after 30-40 pore volumes.

As mentioned previously, due to the high headloss experienced in preliminary column trials, the soil columns actually were constructed with a 50:50 soil/sand mixture to ensure smooth flow of effluent. Nevertheless, this soil/sand column will be referred to as soil column in later sections.

Sorption data in this phase of study are presented by summarizing the data collected from triplicate trials and then plotting the concentration of organic compounds in the effluents against pore volume replacement. For each shale or soil column, the value of pore volume was calculated by multiplying the shale or soil porosity by the column volume, and is used as the basic unit for expressing volume of the effluent. Figures 30-32 display the results of sorption of HN, THQ, and TMP on Antrim shale. It can be seen that HN and THQ were well sorbed on Antrim shale. HN and TMP did not appear in the effluents until approximately 10 pore volumes of effluents had been pumped out of the soil columns, and THQ was totally adsorbed until 6-7 pore volumes of effluents were leached out of the bed. The point of exhaustion cannot be defined in the case of HN and THQ since approximately 12-18 of 25 mg/L HN and 10-14 of 25 mg/L THQ was steadily sorbed on the Antrim shale after 100 and 80 pore volumes, respectively. On the other hand, exhaustion of shale capacity for TMP (i.e., $C_E \cong 95\% C_0$) was reached after approximately 90 pore volumes. Note that the increase in uptake of HN and THQ in replicate trials 2 and 3 occurred in the case where DMP was absent in the feed solution. The affinity of three organic agents for Antrim shale can be ranked in the order of:

HN > THQ > TMP (See Appendix-G, Figures G1-G3).

Figure 33 shows that HN sorbed quite well ($\cong$ 9 of 25 mg/L) on Anvil raw shale after 80 pore volumes with no indication of exhaustion of capacity at the end of the trials. Figure 34 shows that the first trial in which DMP was in the feed solution, the point of exhaustion for THQ was readily reached at approximately 30 pore volumes. However, in the latter two trials for which the feed solution contained only HN, THQ, and TMP, the Anvil raw shale showed a sorption capacity of 6-8 of 25 mg/L THQ after 70 pore volumes. The presence of DMP obviously had a pronounced effect on the uptake of THQ on Anvil raw shale. Exhaustion of TMP on Anvil raw shale appeared after 20-40 pore volumes in three columns (see figure 35), and then a phenomenon generally referred to as "overshoot" was observed in the next 30 pore volumes. This effect was even greater in the case where feed solution contained DMP (first column trial). The magnitude of sorption of organic compounds on Anvil raw shale was in the order of:

HN > THQ >TMP (see Appendix-G, Figures G4-G6).

The sorptive behavior of HN, THQ, and TMP in the presence of Oxy 6 shale is shown in Figure 36. HN again sorbed best. Approximately 10-11 of 25 mg/L HN was sorbed steadily after 30 pore volumes. Although exhaustion of capacity for THQ and TMP did not occurred through the course of the experiments. only little THQ and TMP (2-3 of 25 mg/L) were retained on Oxy 6 shale after 40 pore volumes.

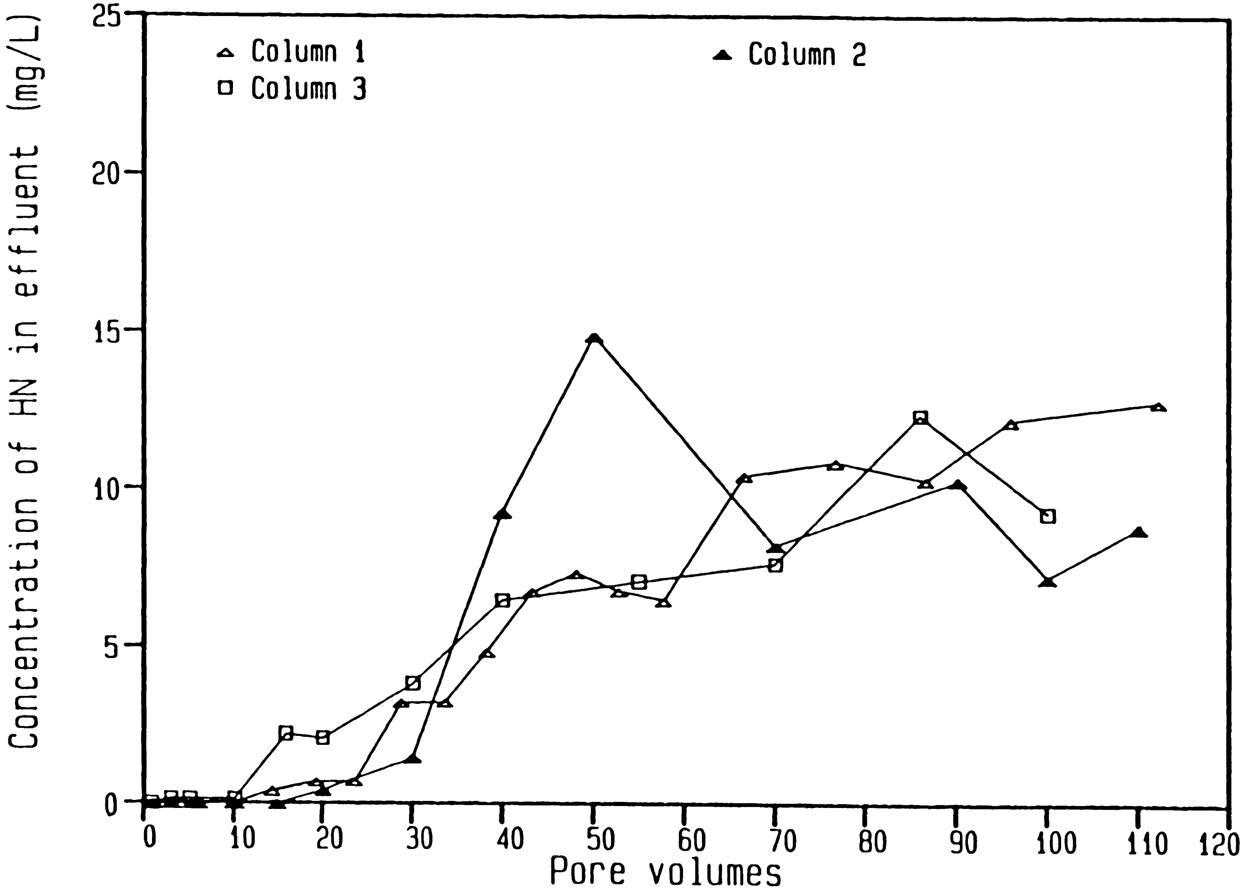

Figure 30. Sorption of HN on Antrim shale: (C_0 = 25 mg/L)

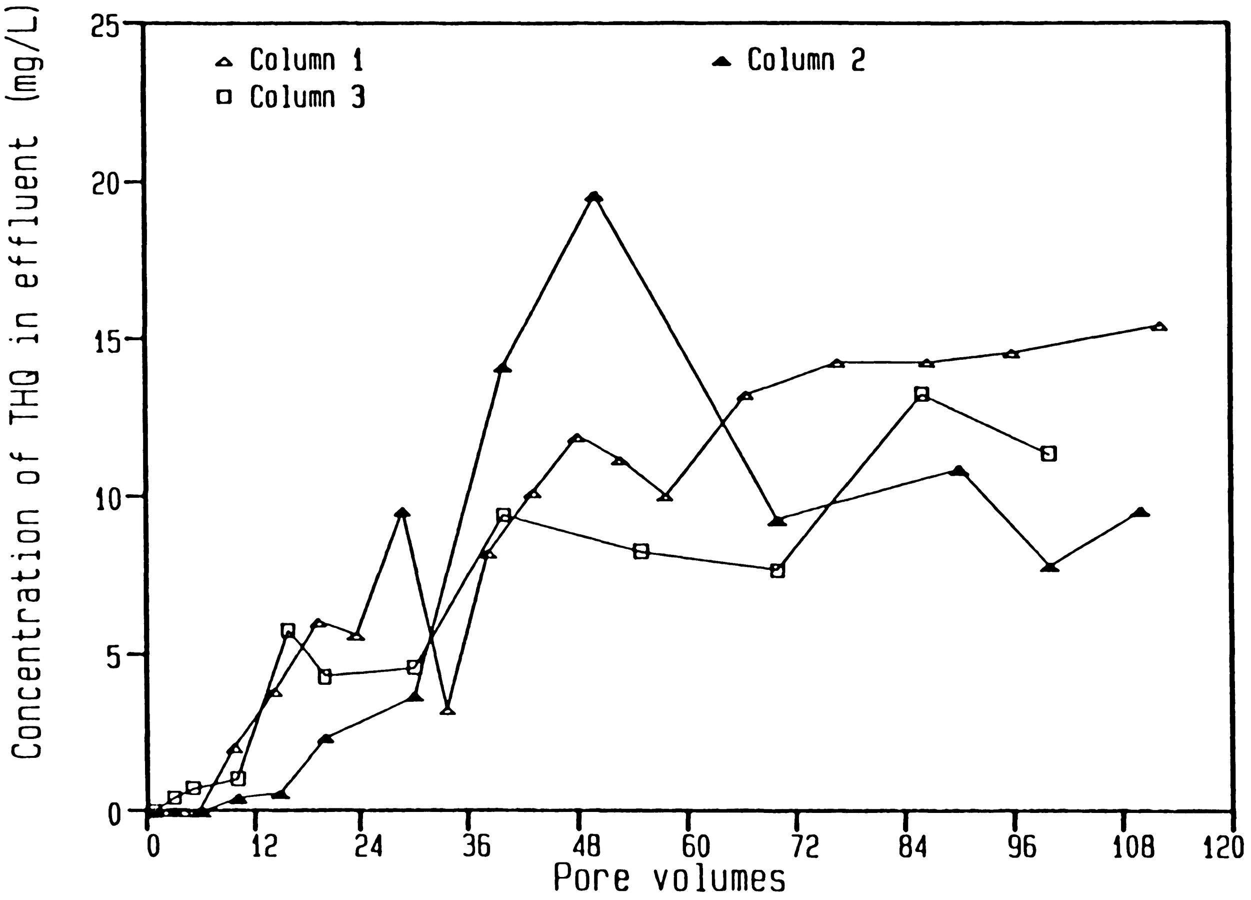

Figure 31. Sorption of THQ on Antrim shale: (C_0 = 25 mg/L)

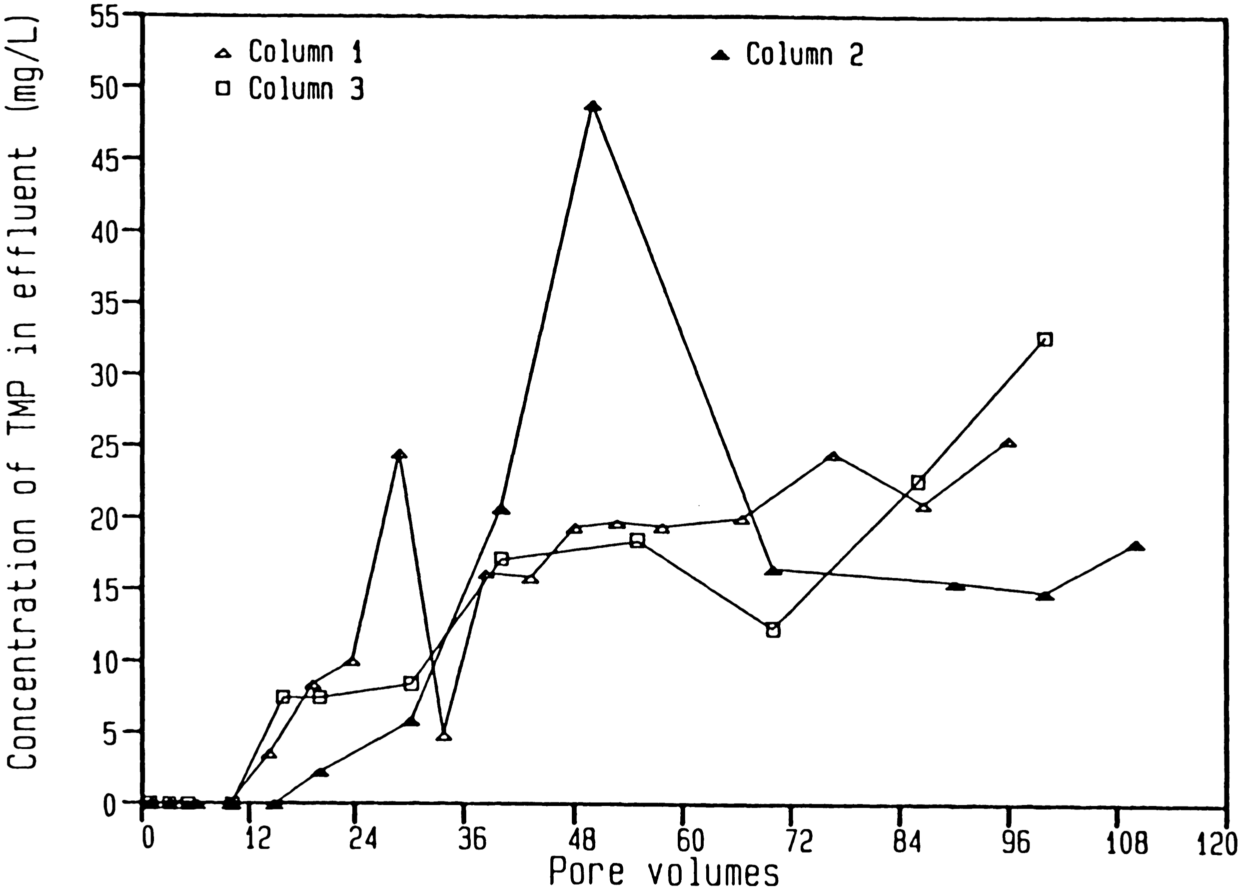

Figure 32. Sorption of TMP on Antrim shale: (C_0 = 25 mg/L)

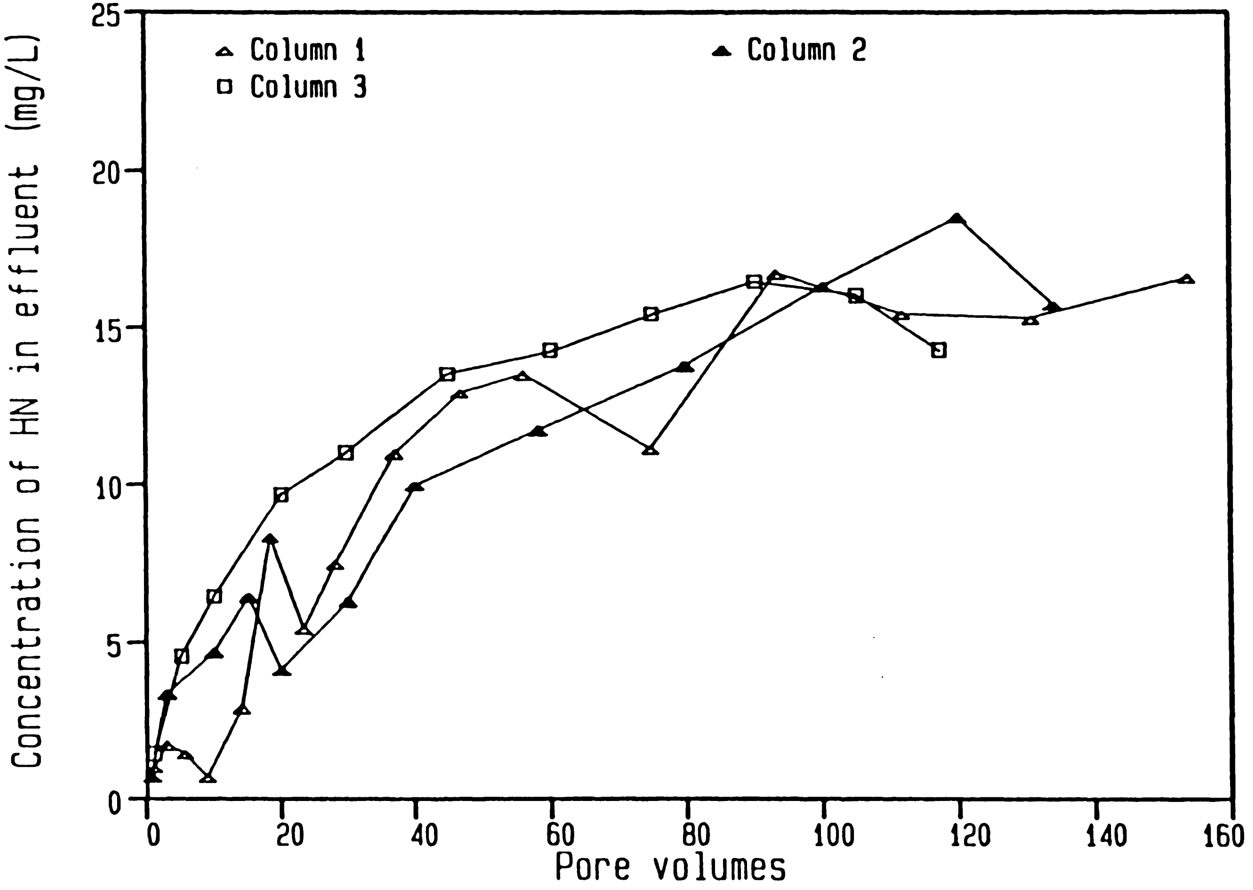

Figure 33. Sorption of HN on Anvil raw shale: (C_0 = 25 mg/L)

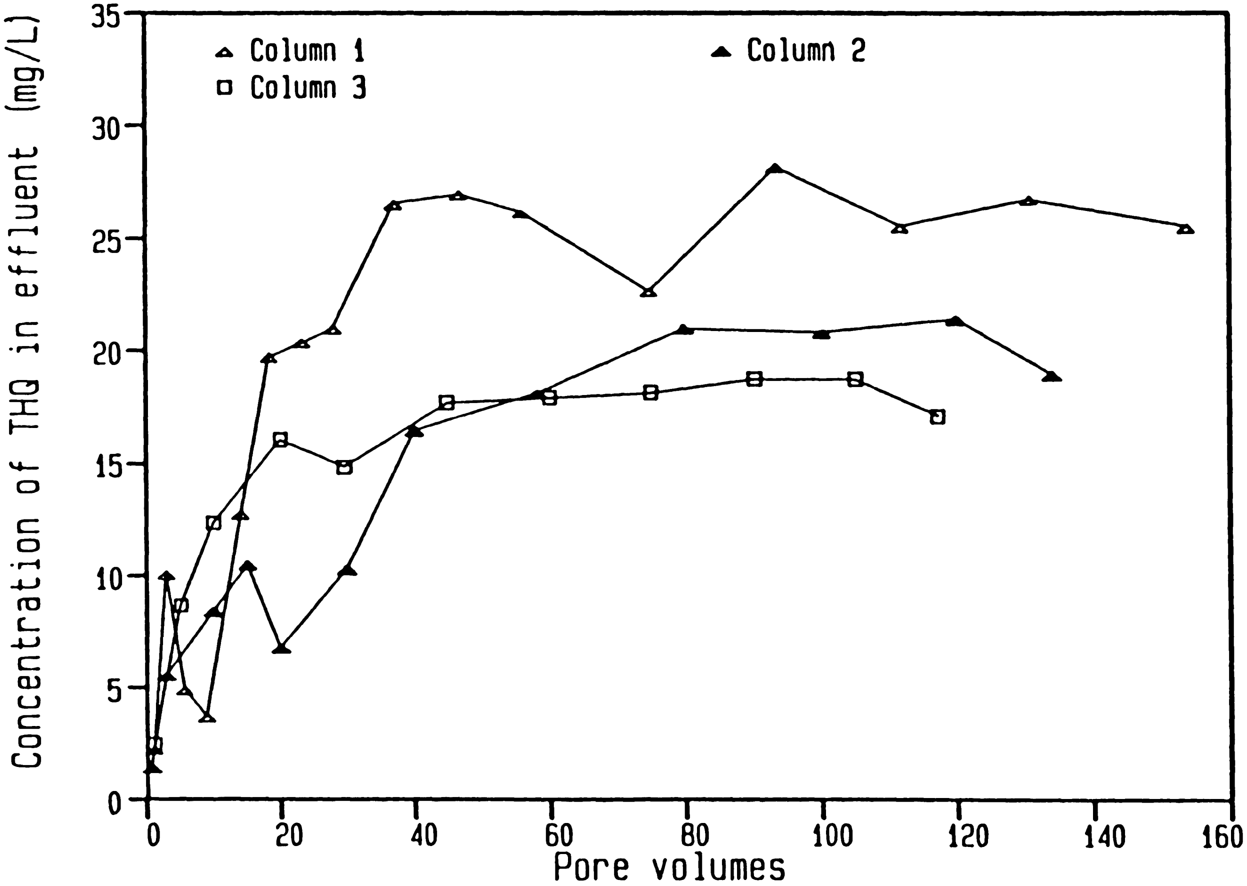

Figure 34. Sorption of THQ on Anvil raw shale: (C_0 = 25 mg/L)

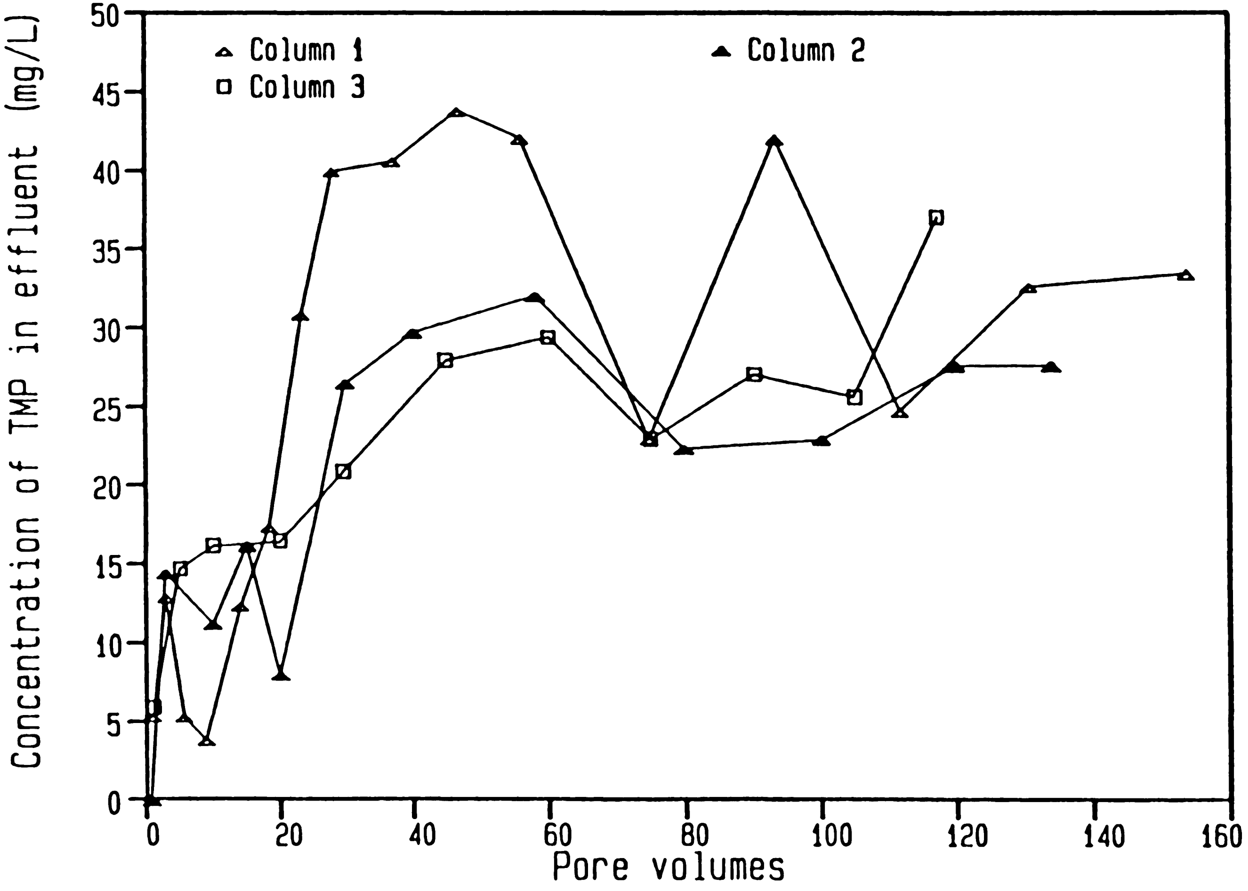

Figure 35. Sorption of TMP on Anvil raw shale: (C_0 = 25 mg/L)

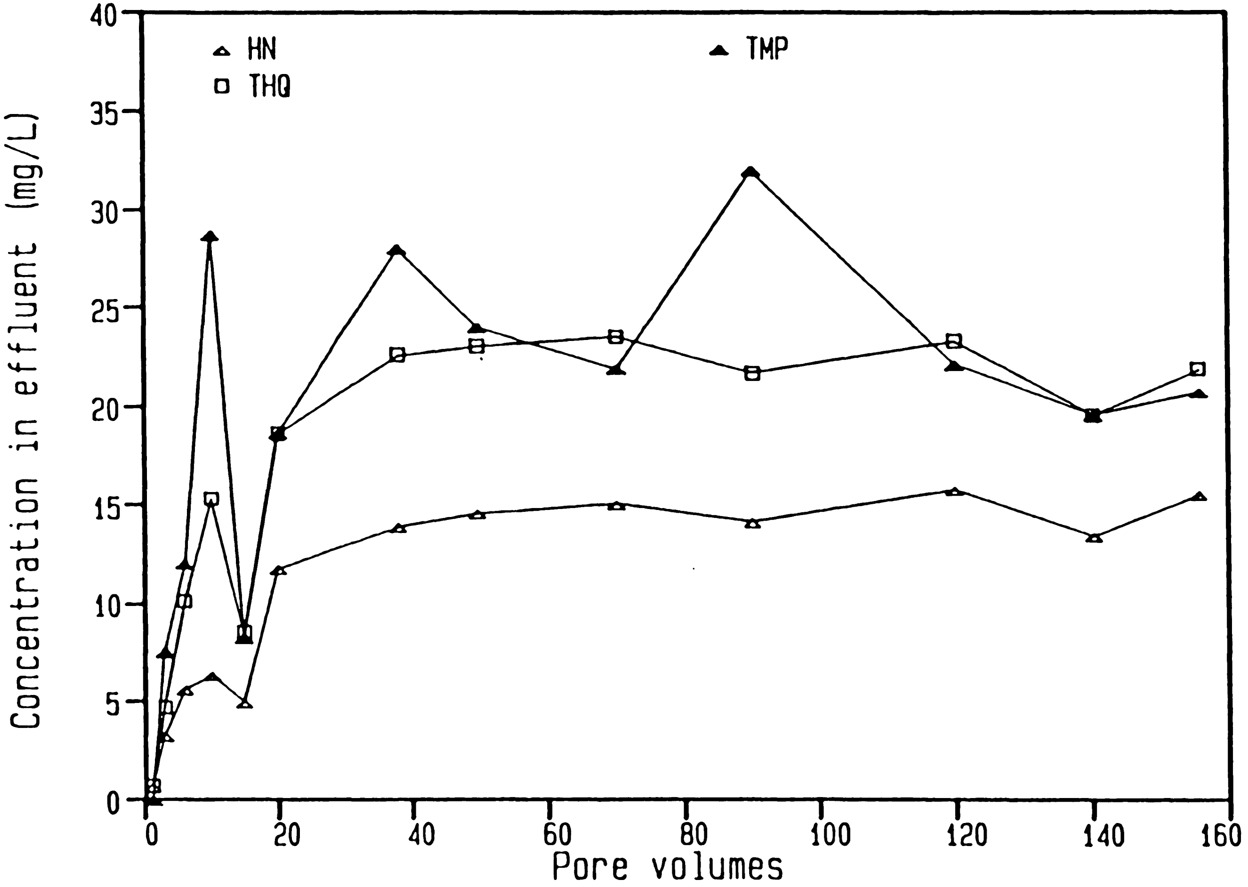

Figure 36. Sorption of HN, THQ, and TMP on Oxy 6 shale: (C_0 = 25 mg/L)

Exhaustion of the sorption capacity of Run 16 shale for HN and THQ was not defined over the course of this experiment. Figure 37 illustrates how HN behaved in the Run 16 shale column. It is interesting to note that the sorption of HN seemed to be increased by the presence of DMP in the feed solution. Figure 38 indicates that 9-10 of 25 mg/L THQ was steadily adsorbed on Run 16 shale. In the presence of DMP, this sorbed quantity reduced to 4-8 of 25 mg/L THQ. Figure 39 shows that the sorption capacity of Run 16 shale for TMP was readily exhausted within a few pore volumes, and large quantities of TMP were released from Run 16 shale over the course of the experiment.

It is interesting to compare the sorptive behavior of HN and THQ on Run 16 shale with DMP in the feed solution (Figure G1) and without DMP in the feed solution (Figures G2 and G3). HN and THQ shared quite similar sorption trends when DMP was not in the feed solution. However, the presence of DMP in feed solutions appeared to enhance the sorption of HN and depress the sorption of THQ which made HN sorb better than THQ, as indicated in Figure G1.

Figures 40-42 illustrate how HN, THQ, and TMP behaved in soil columns. Sorption of HN, THQ, and TMP on the western soil was characterized by their rapid breakthrough (≅ one pore volume). Sorption of HN (7-8 of 25 mg/L) and THQ (7-9 of 25 mg/L) was quite steady over the course of the experiments. The presence of DMP in feed solutions did not show any significant influence on the sorption of HN and THQ. As shown in Figure 42, even with the exclusion of some questionable data points, TMP in the effluents was still routinely greater than the inoculum concentration (25 mg/L). This suggests that some TMP contained in the soil was flushed out from the soil. The affinities of three organic agents for the western soil may be ranked as:

$$\text{HN} \cong \text{THQ} >> \text{TMP}.$$

4.3.2 Sorption/desorption of Inorganic Ions by the Soil

As mentioned in the previous chapter, three different types of multicomponent solution were pumped through soil columns. These included: (1)A mixture of eight ions (As, Ca, Cd, K, Fe, NH_4, F, SO_4); (2) a mixture of four cations (As, Ca, Cd, K); and (3) a mixture of three ions (NH_4, F, SO_4). In addition, an elution test was performed by pumping distilled, deionized water through soil column for 96 hours.

4.3.2.1 Column Elution of Inorganic Ions from the Soil

The eluents from soil columns were analyzed for the ions given in Tables 15 and 16. It is evident that most of the inorganic ions considered in the soil eluents were not released from the soil. The ions in this category included NH_4, SO_4, As, Cd, and Fe.

As much as 50 mg/L calcium was flushed out of the soil in the beginning of the experiment (Figure 43). The concentration of calcium rapidly decreased to its equilibrium value of 5.6-6.7 mg/L within 30 pore volumes. Figure 44 indicates that a similar type of reaction occurred in the case of potassium. Potassium in the soil eluent was at concentrations of 40-46 mg/L in the beginning. As elution proceeded, the amount of potassium in the eluent decreased uniformly to levels below 0.6 mg/L.

In comparison with other ions, elution of fluoride was quite unusual. This is illustrated in Figure 45. The concentration of fluoride in eluents increased initially to a peak concentration of 1.8 mg/L and then decreased rapidly. After approximately 20 pore volumes, no fluoride was detected in the soil eluent.

Table 17 presents some properties of the soil eluents measured during the elution trials. The initial pHs were very closed to that of soil itself which was 7.7. As more water flowed through the soil, the pH of the weakly alkaline soil eluent decreased uniformly to its equilibrium level of 6.9 (Figure 46). The overall pHs were in the range between 6.9 and 7.7.

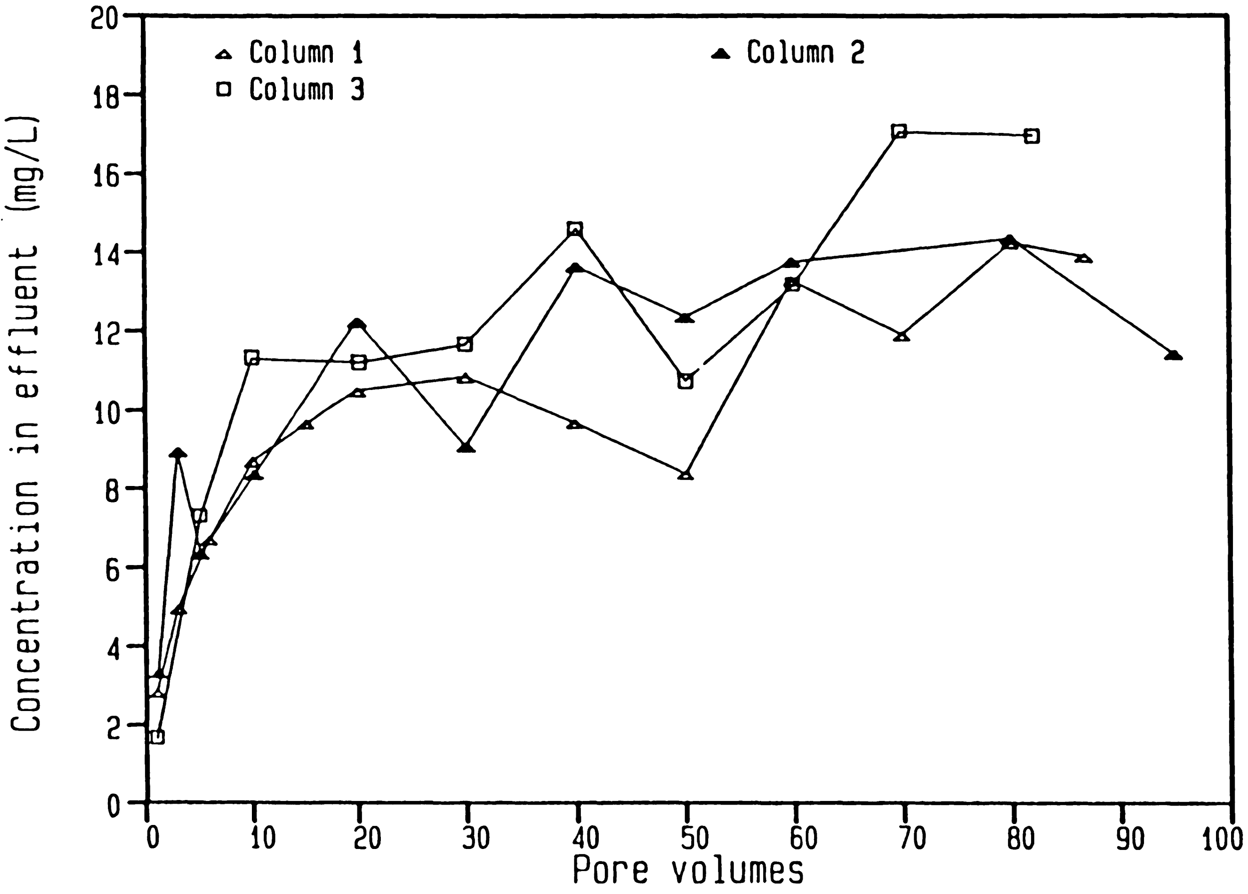

Figure 37. Sorption of HN on Run 16 shale: (C_0 = 25 mg/L)

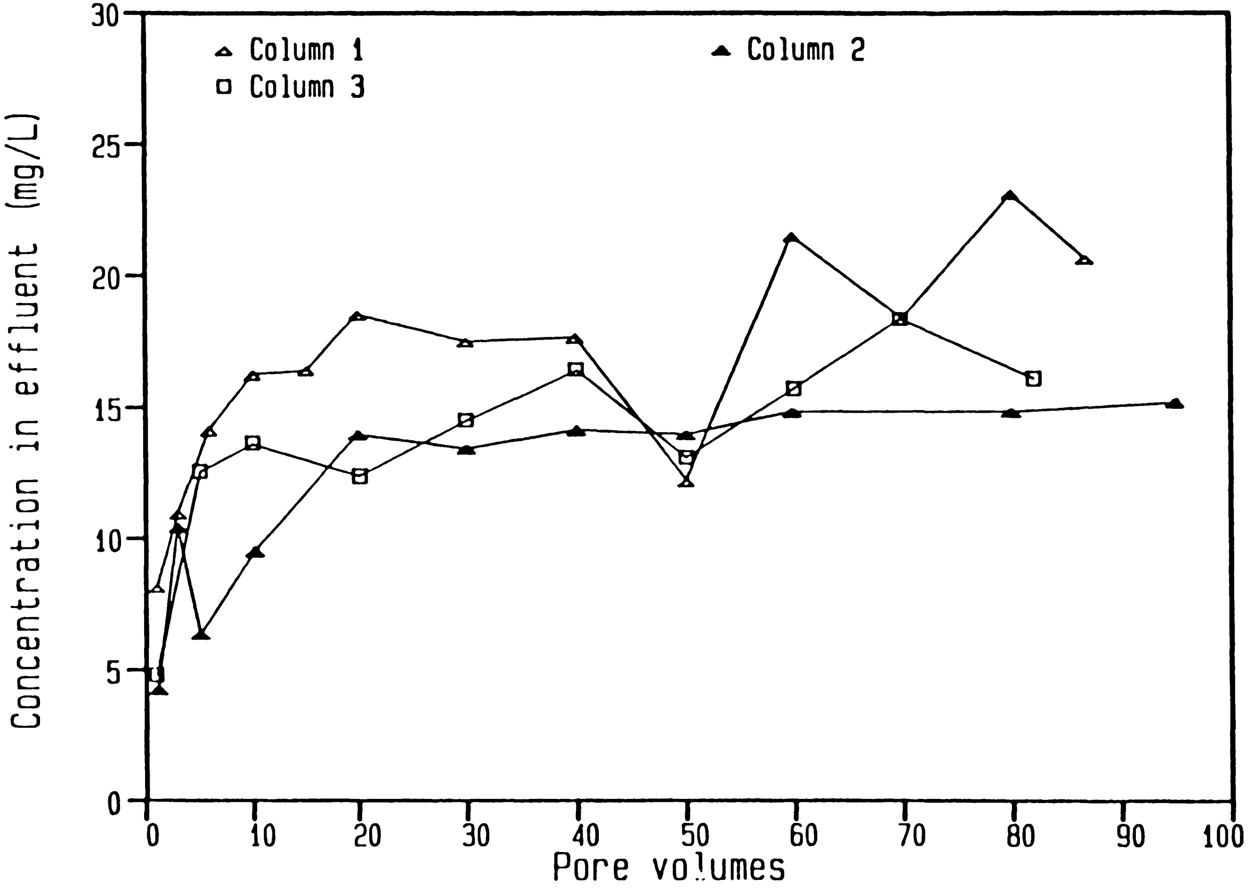

Figure 38. Sorption of THQ on Run 16 shale: (C_0 = 25 mg/L)

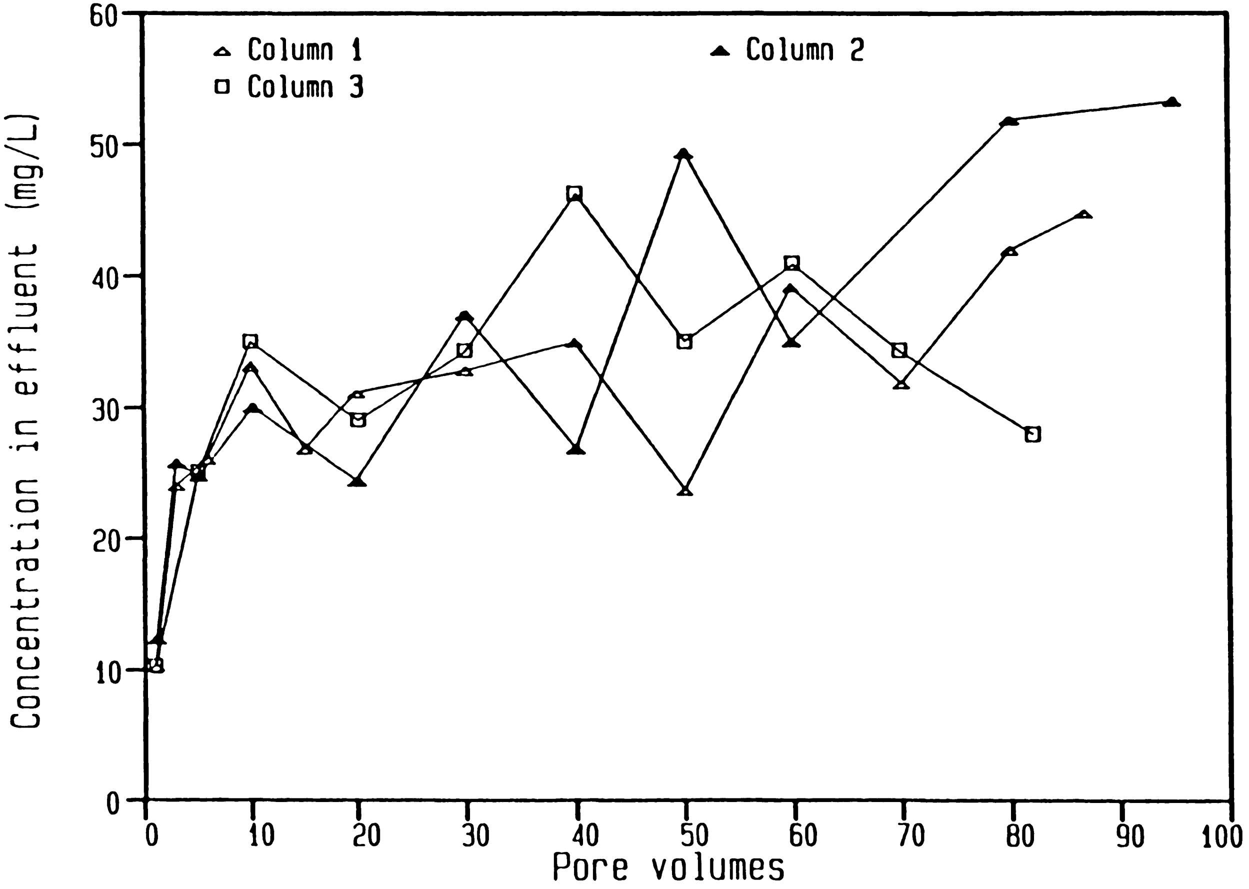

Figure 39. Sorption of TMP on Run 16 shale: (C_0 = 25 mg/L)

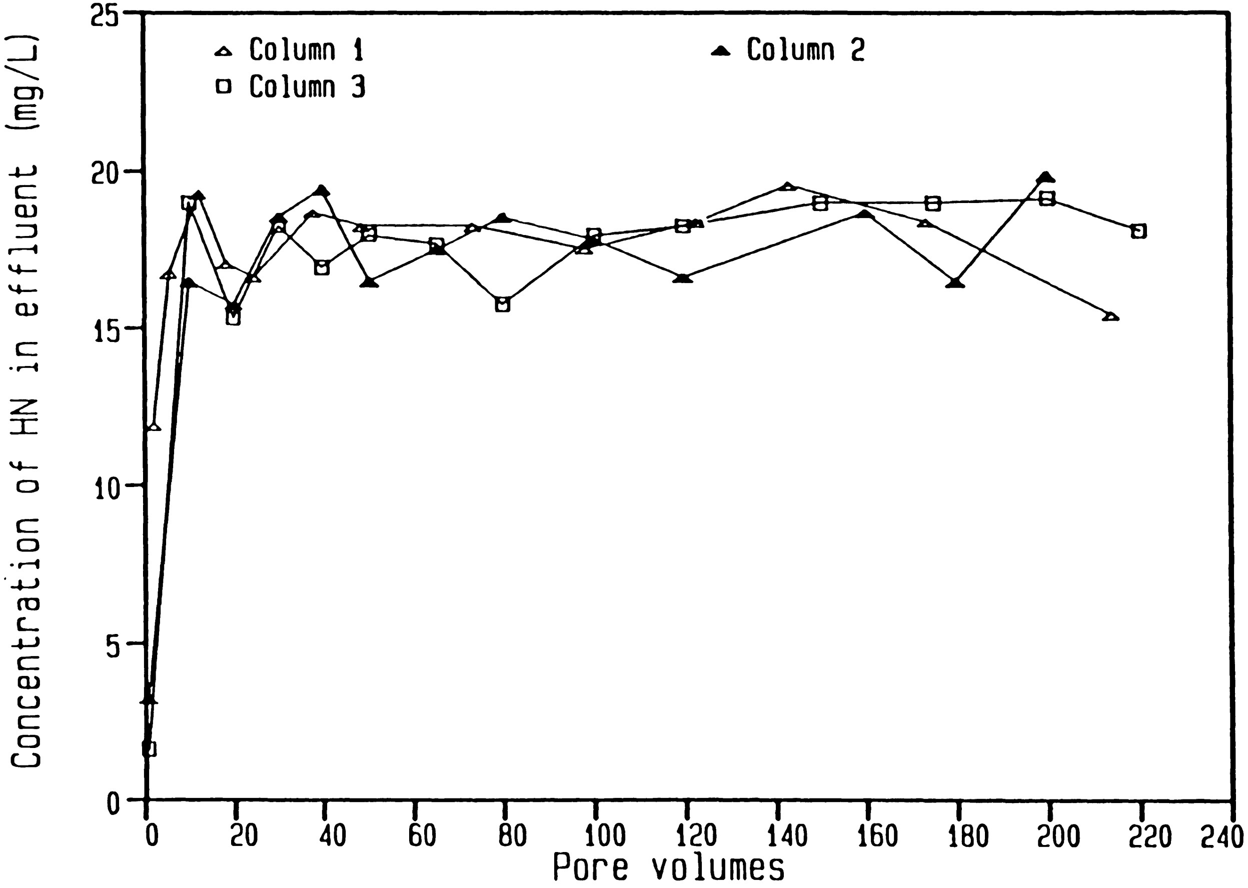

Figure 40. Sorption of HN on the western soil: (C_0 = 25 mg/L)

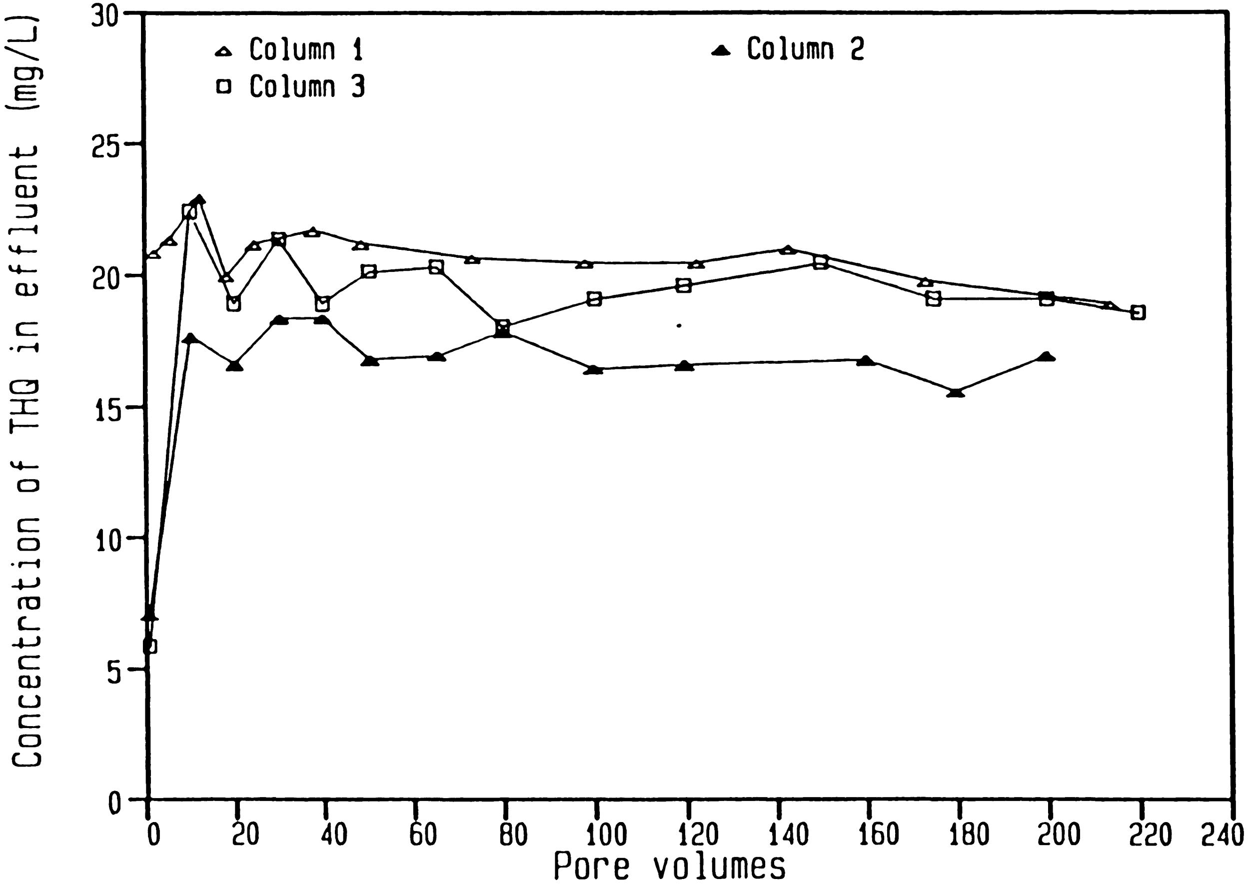

Figure 41. Sorption of THQ on the western soil: (C_0 = 25 mg/L)

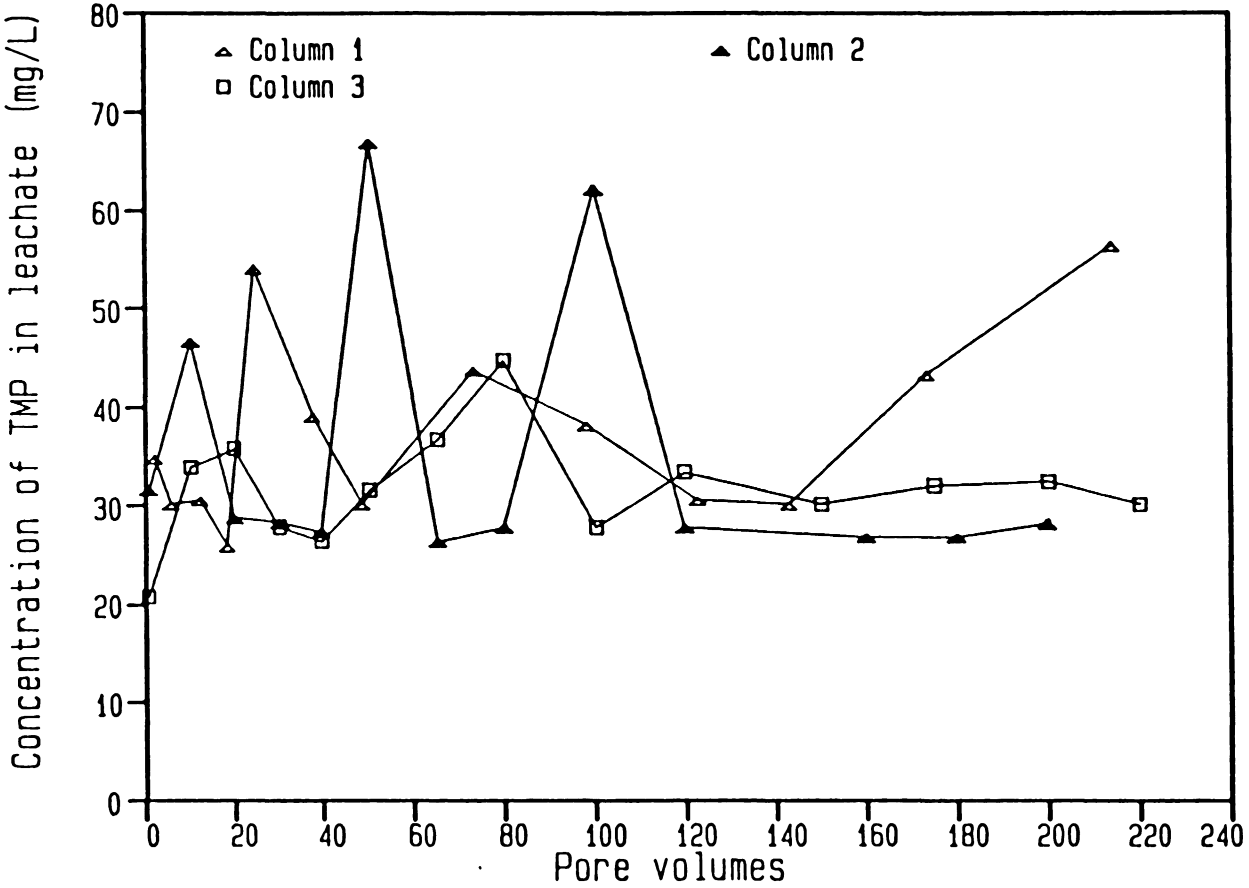

Figure 42. Sorption of TMP on the western soil: (C_0 = 25 mg/L)

Conductivity of the soil eluent is a property attributable to the ions in the solution. The conductivity is proportional to the ion strength of the solution. The high conductivity found in the early stage of the elution trials, as seen in figure 47, reflected the flush of Ca and K from the soil. It is interesting to note that the reduction in conductivity reflected the concentration reduction of Ca and K in the soil eluents illustrated in Figures 43 and 44.

The reduction in alkalinity indicates that some acidic species were released from the soil and were neutralized by the consumption of eluent alkalinity. The alkalinity of soil eluent remained at 29.4 mg/L as $CaCO_3$ when equilibrium was reached. Figure 48 shows the variation of redox potential during the course of elution trials. The overall variations of redox potential were in the range of 194-230 millivolts (mV).

4.3.2.2 Sorption of Inorganic Ions on the Western Soil

The inorganic ions considered in this phase of work are categorized into cations (As, Ca, Cd, Fe, and K) and nonmetals (F, NH_4, and SO_4). Study of cation sorption was performed in two types of feed solutions, a solution composed of a mixture of all of the eight ions, and a solution containing a mixture of four cations (As, Ca, Cd, K). Study of nonmetal sorption was also performed in two types of feed solutions, a mixture of eight ions and a mixture of NH_4, SO_4, and F.

Chemical properties of the effluent from soil columns are presented in Appendix H. In sorption trials with the three different types of feed solution pH generally ranged between 6 and 8 (Figures H1-H3). Reduction in the alkalinity level (100-150 mg/L as $CaCO_3$) of the effluent over the course of experiments was evident (Figures H4-H6). Variance in redox potential was in the range between 170 to 230 mV. Conductivity was slightly higher than that observed in elution trials, yet it remained relatively constant through the trials. Data concerning the sorption by soil of each ion specie in different types of feed solutions are presented in the following section.

Table 15. Elution of caions from the western soil

Pore Volume	Concentration in effluent, mg/L[1]				
	As	Ca	Cd	Fe	K
0.8	0.003	50.8	0.005	0.14	45.80
10.0	0.042	17.0	0.032	0.04	11.50
19.8	0.006	6.6	0.005	0.05	6.36
30.1	0.003	5.6	0.005	0.04	4.47
39.8	0.004	6.5	0.005	0.02	3.16
50.1	0.003	5.4	0.006	0.06	2.36
59.9	0.002	5.3	0.005	0.05	1.88
70.2	0.003	5.5	0.007	0.02	1.64
90.2	0.002	5.4	0.005	0.02	1.22
110.2	0.002	5.5	0.020	0.03	0.88
140.0	0.001	5.9	0.005	0.05	0.62
169.8	0.001	6.2	0.013	0.02	0.54
200.2	0.001	5.6	0.017	0.30	0.54

[1] feed solution: distilled, deionized water.

Table 16. Elution of NH_4, SO_4, and F from the western soil

Pore volume	Concentration in effluent, mg/L[1]		
	NH_4	SO_4	F
2.39	0.03	0.9	0.75
6.21	0.03	1.3	1.80
10.99	0.16	—	0.51
16.25	0.09	—	—
21.02	0.07	1.3	0.00
30.10	0.06	0.4	—
40.61	0.05	0.0	0.00
50.65	—	0.9	—
71.19	0.05	0.4	0.00
91.26	—	0.0	—
116.10	0.05	0.0	0.00
180.84	0.04	0.0	0.00

[1] Feed solution: distilled deionized water.

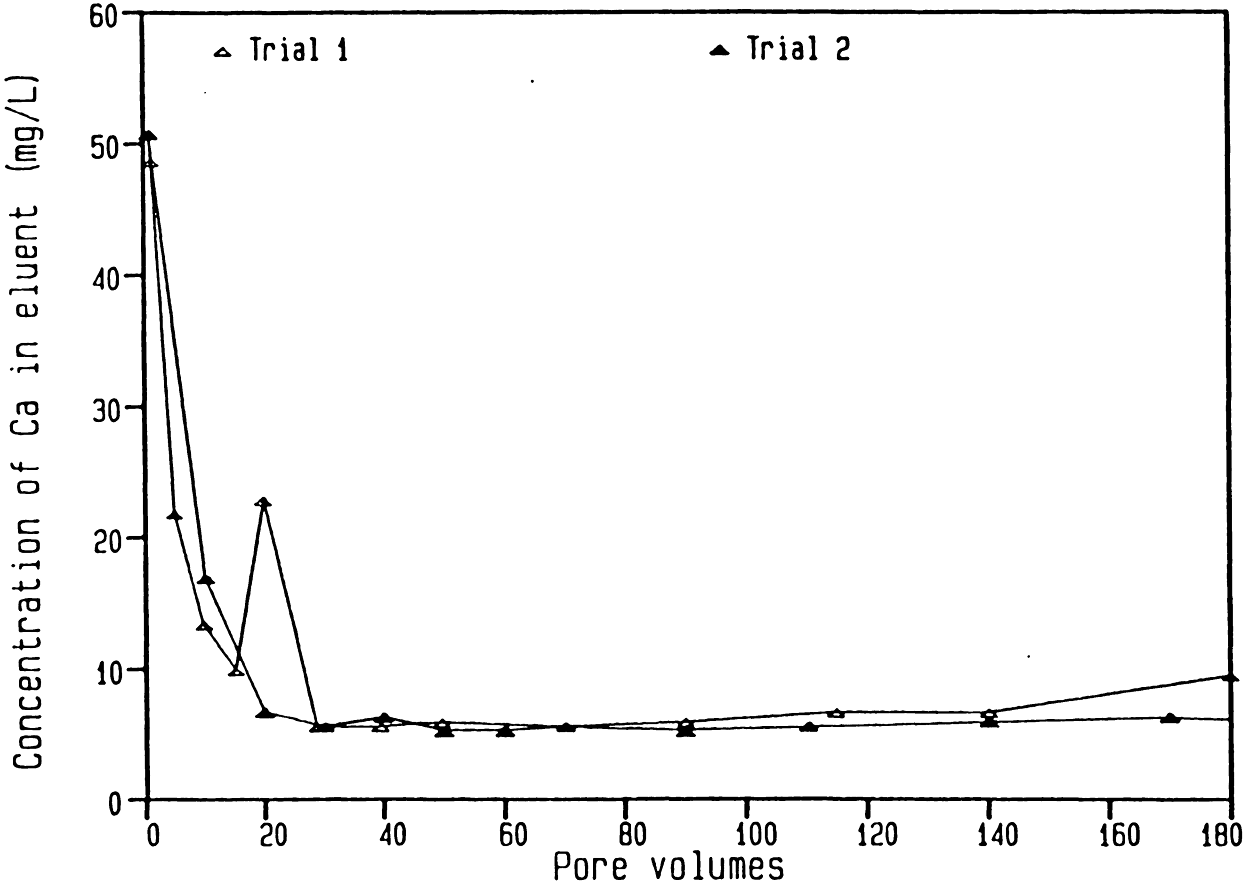

Figure 43. Variation in concentration of Ca in soil eluent

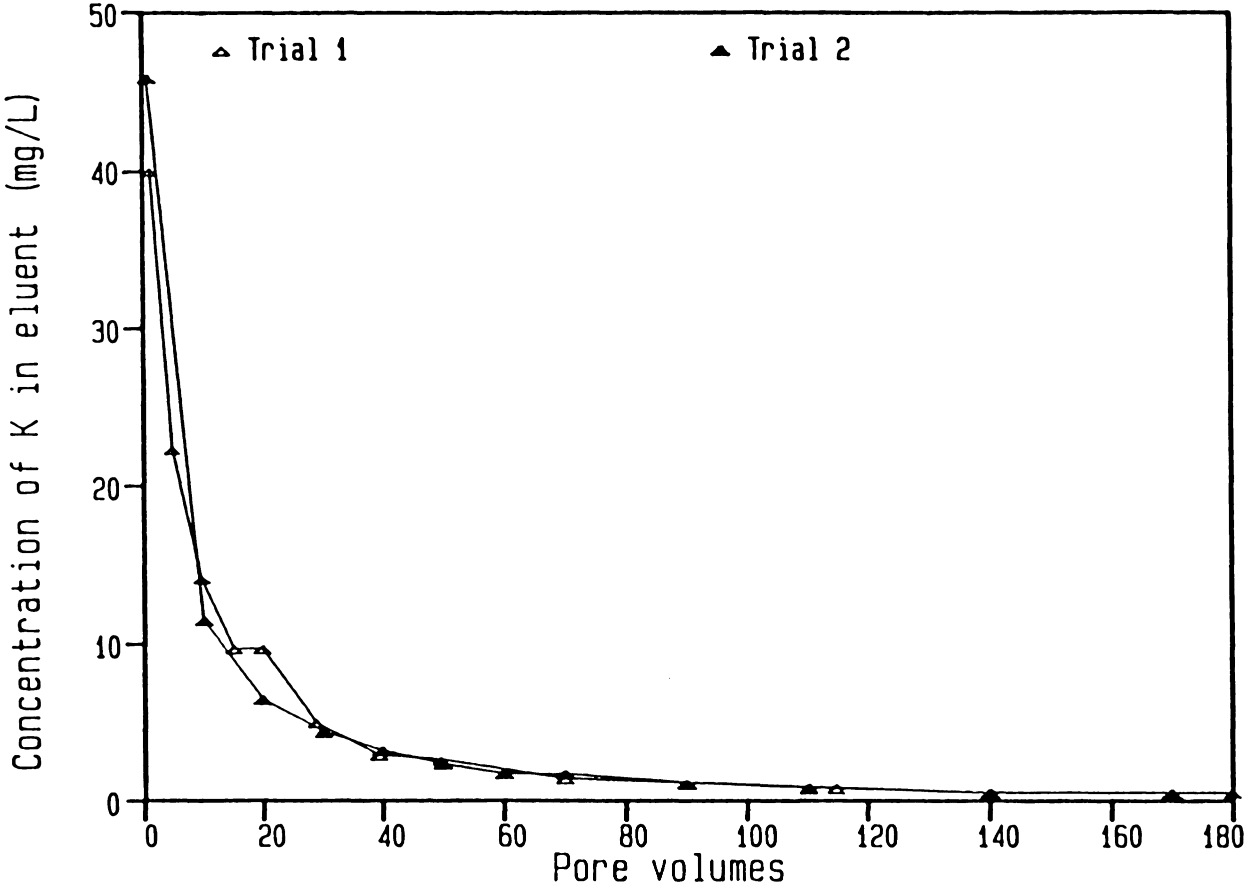

Figure 44. Variation in concentration of K in soil eluent

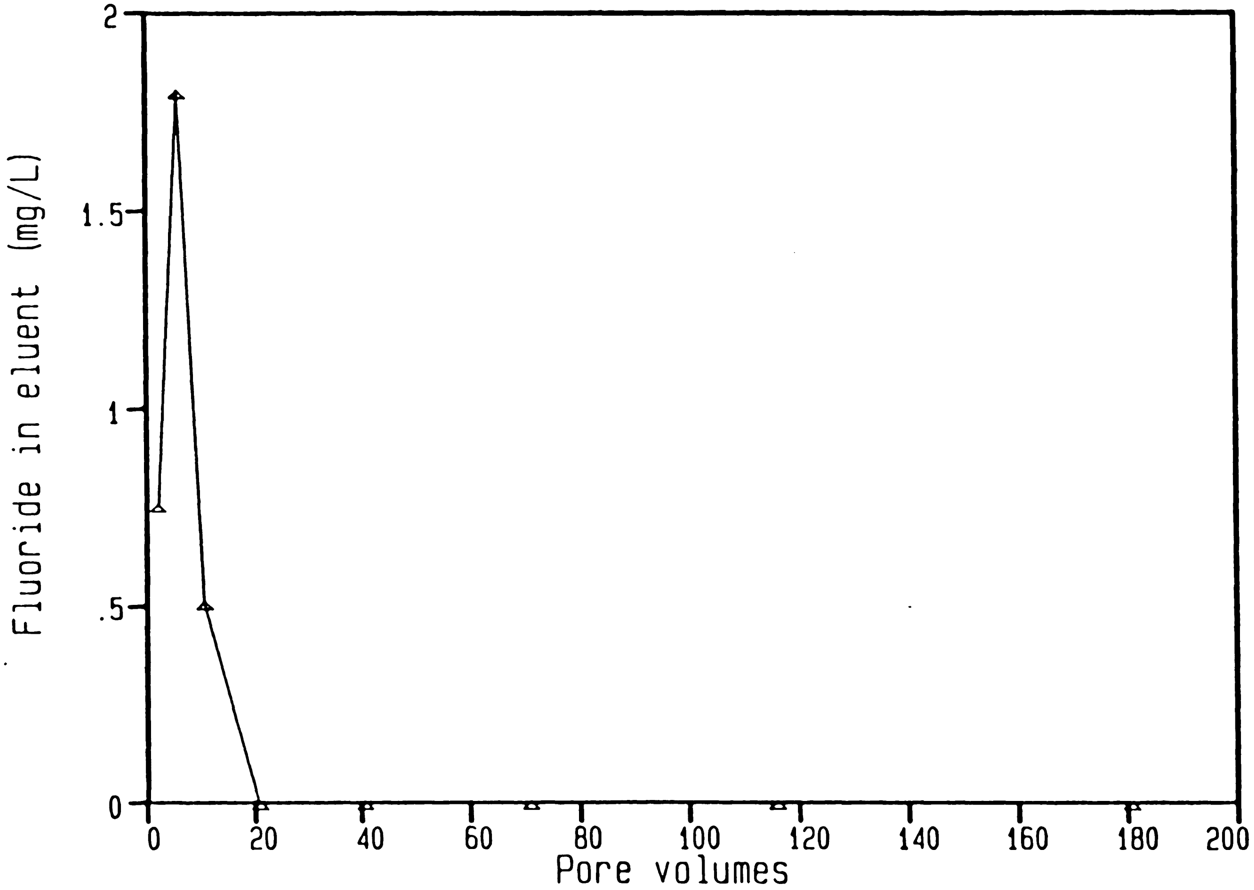

Figure 45. Variation in concentration of F in soil eluent

Table 17. Properties of soil eluents

Pore volume	pH	Conductivity[1]	Redox pontential[2]	Alkalinity[3]
2.39	7.5	0.250	212.5	98.0
6.21	7.6	0.150	194.2	98.0
10.99	7.4	0.117	200.8	58.8
16.25	7.3	0.084	218.1	58.8
21.02	7.3	0.072	220.3	58.8
30.10	7.3	0.063	219.0	58.8
40.61	7.1	0.049	224.6	29.4
50.65	7.1	0.052	227.5	29.4
71.19	7.0	0.038	217.0	29.4
91.26	6.8	0.038	227.1	39.2
116.10	6.9	0.043	219.9	29.4
141.42	6.9	0.040	230.6	29.4
180.84	6.9	0.038	227.9	29.4

Feed solution: distilled, deionized water.

[1] mmho/cm.

[2] mV.

[3] mg/L as $CaCO_3$.

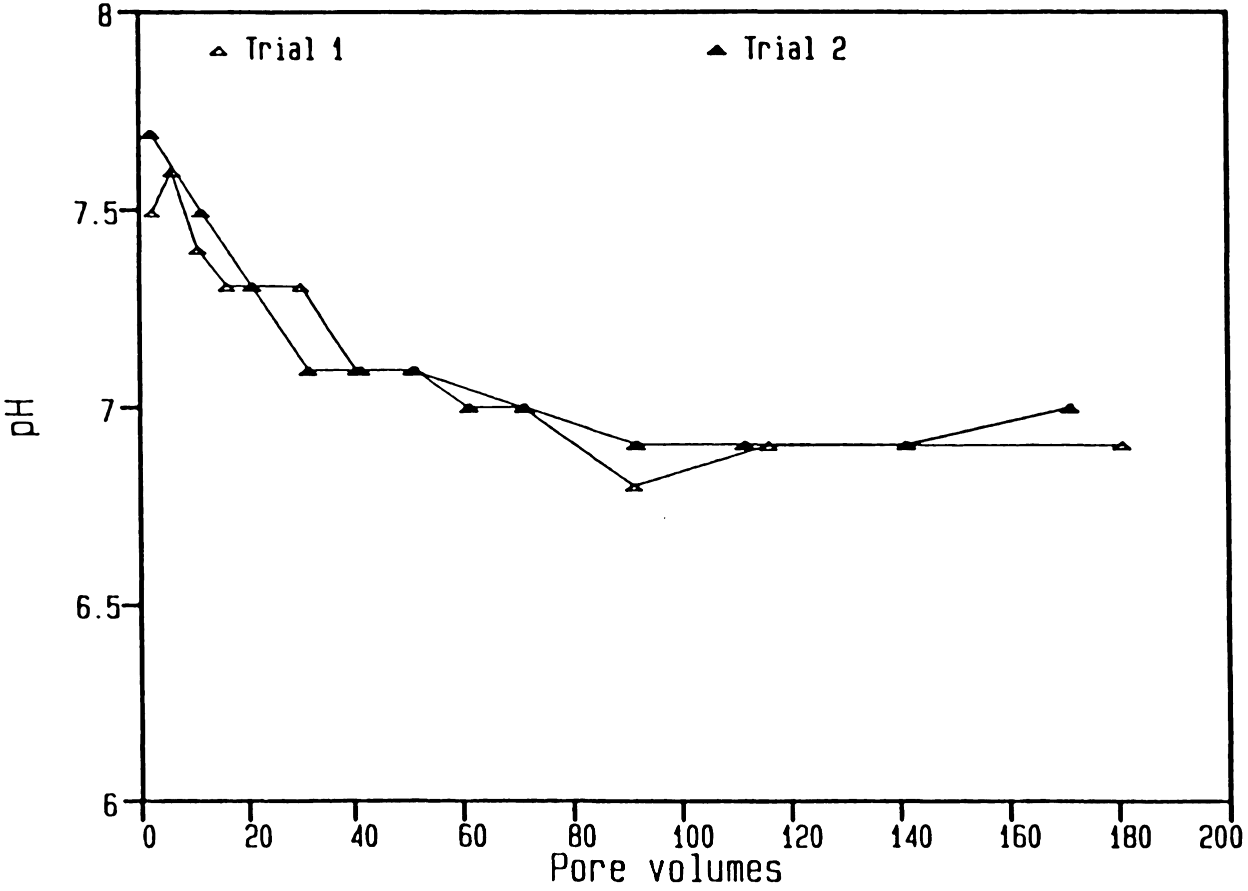

Figure 46. Variation of pH in soil eluent

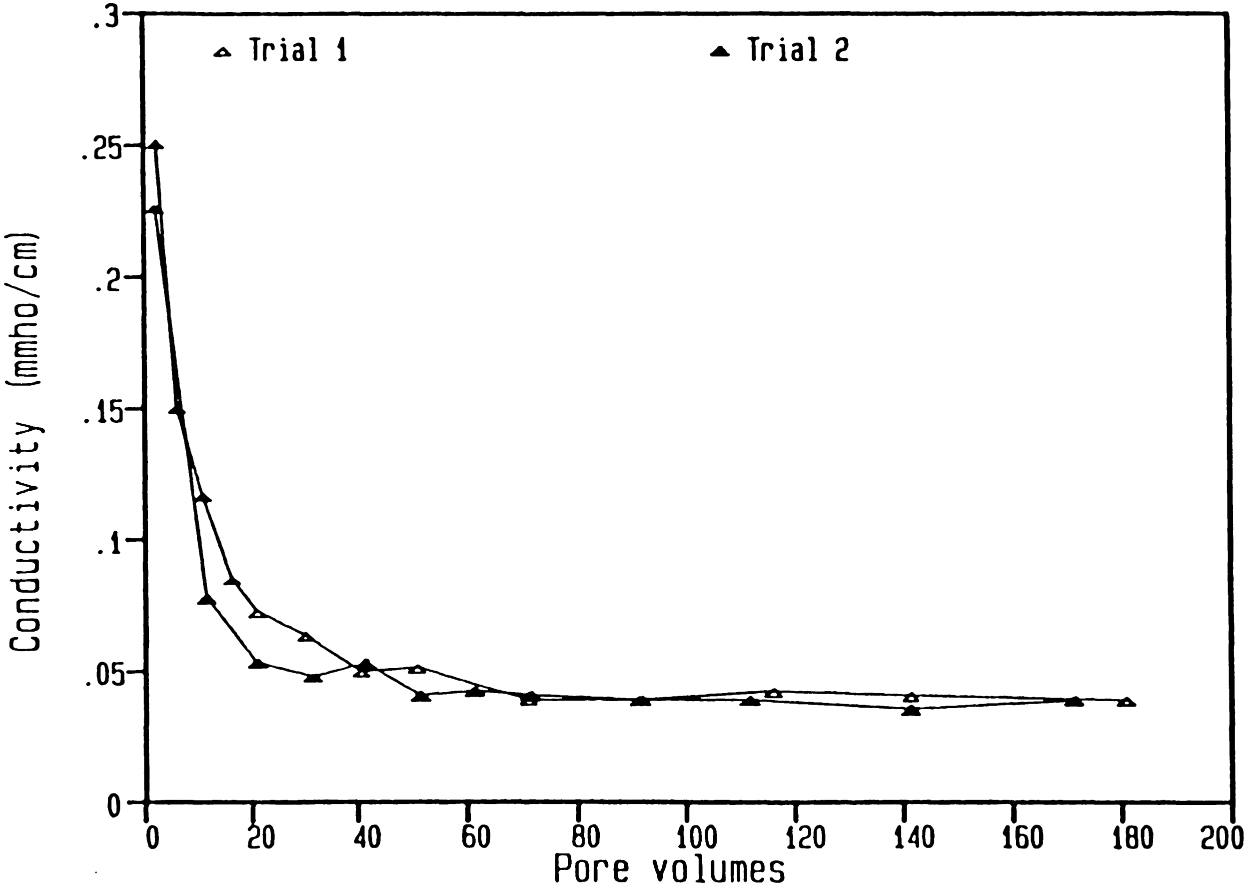

Figure 47. Variation of conductivity in soil eluent

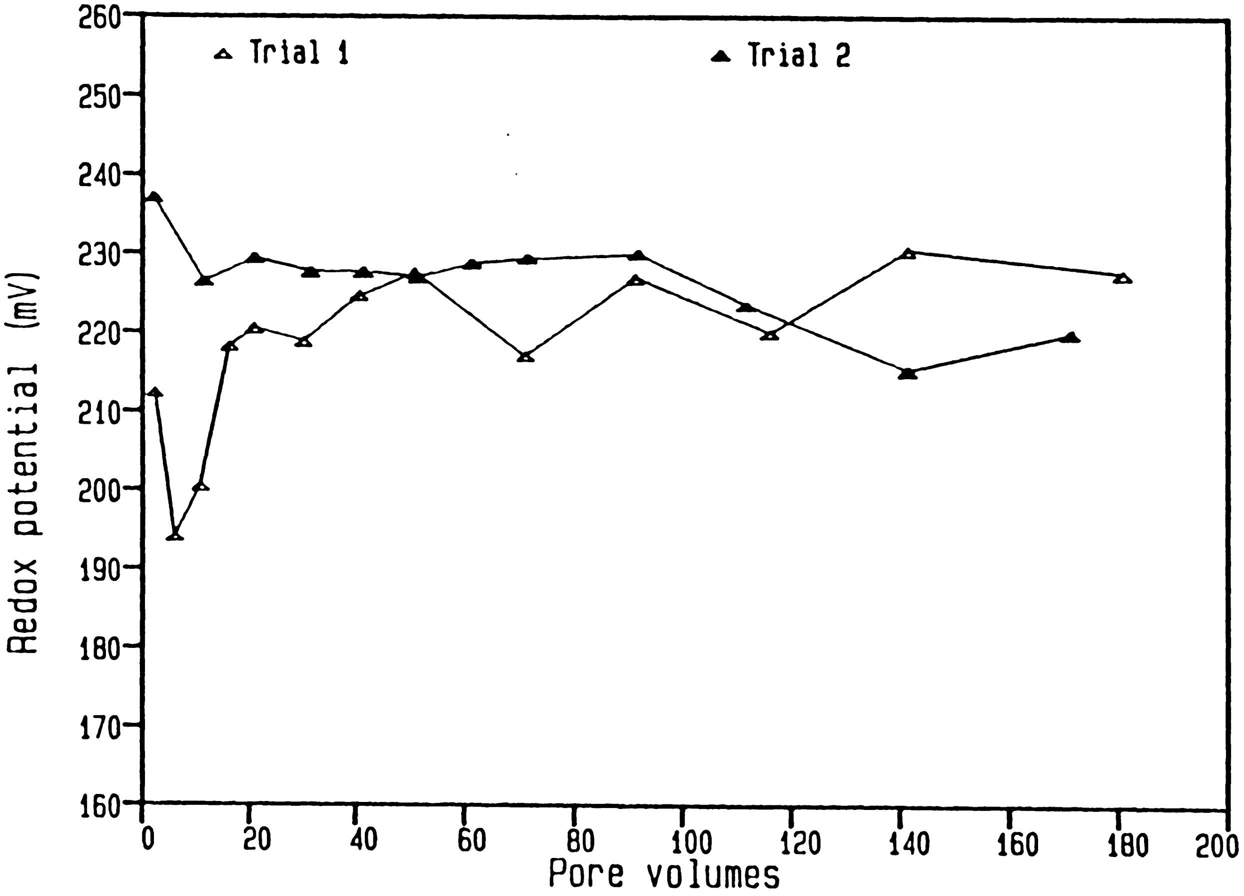

Figure 48. Variation of redox potential in soil eluent

Figure 49 shows that the soil had some affinity for arsenic when a solution containing four cations was pumped through the columns. The arsenic was almost entirely adsorbed within the first 10 pore volumes, followed by a sharp increase in arsenic concentrations of the effluent in the next 10-20 pore volumes to a peak concentration of 9 mg/L (90% of the feeding concentration). Then, the arsenic was sorbed in a gradual manner through the rest of the trial. The concentration of As in the column effluent was in the range of 6.4-7.2 mg/L.

Sorption of As in the case where the feed solution contained a mixture of eight ions was quite different from that described above. This is illustrated in Figure 50. The arsenic was totally adsorbed in the first 15 pore volumes and followed by a sharp increase in the concentration of As in the effluent. However, the peak concentrations in three column trials never exceeded 4 mg/L, less than half of that observed with feed solutions containing only four cations. Only 0.5-0.8 mg/L of As were left in the effluent after 70 to 120 pore volumes. Increase of arsenic concentration in the effluent was observed in two of the three columns after 180 pore volumes.

Figure 51 indicates that considerable quantities of calcium were flushed out of the soil in the first 10 pore volumes. The variance in the data points of three triplicate columns makes it difficult to estimate the average concentrations of calcium in the effluent. Nevertheless, after the point of peak concentration (418-484 mg/L), the concentration of calcium decreased through the experimental period and further decreases in the concentration of calcium was predictable. In the case of feed solutions containing eight ions, the initial flush of calcium again occurred. However, as seen in Figure 52, after the calcium concentration decreased to a level of 380-390 mg/L at approximately 40 pore volumes, a concentration plateau was observed. Further decreases in calcium concentration occurred after 180 pore volumes.

The sorption curves of cadmium by the soil are given in Figures 53 and 54. These figures indicate that the sorption of cadmium was not influenced by the presence of NH_4, SO_4, and F in the feed. In both systems, breakthrough occurred at 30-40 pore volumes and the point of exhaustion was at 50-60 pore volumes.

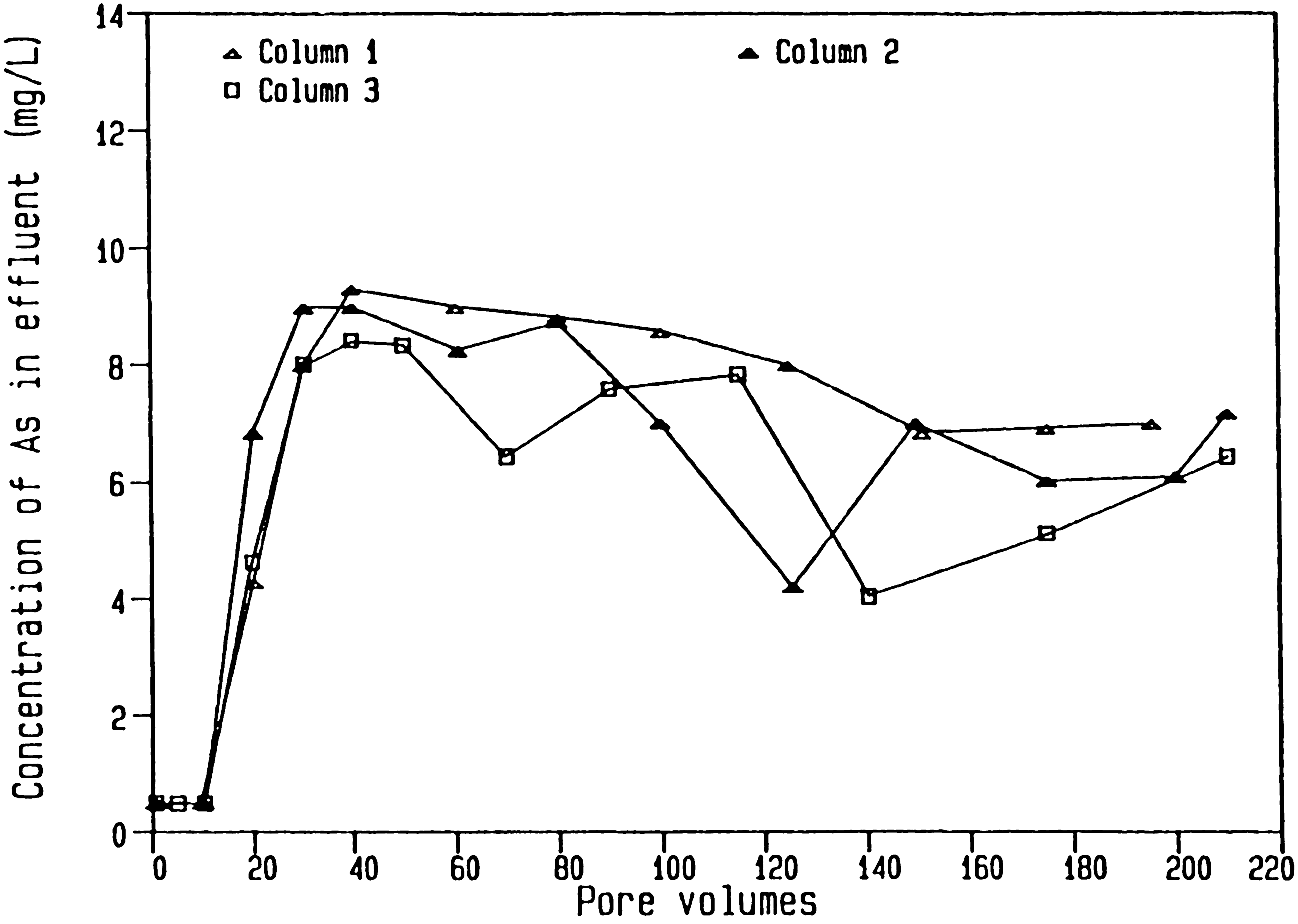

Figure 49. Sorption of arsenic in solutions containing four cations: (C_0 = 10 mg/L)

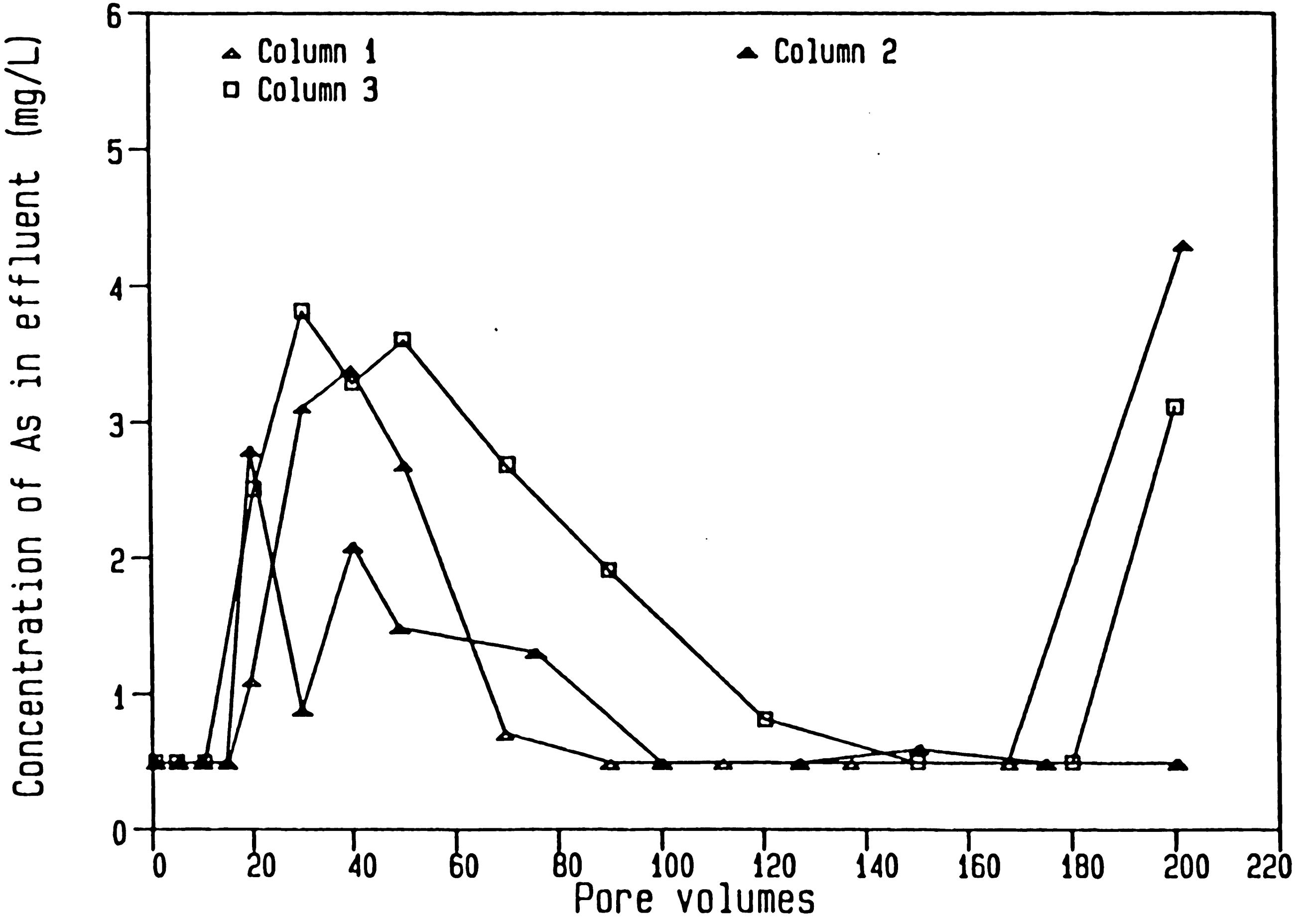

Figure 50. Sorption of arsenic in solutions containing eight ions: (10 mg/L)

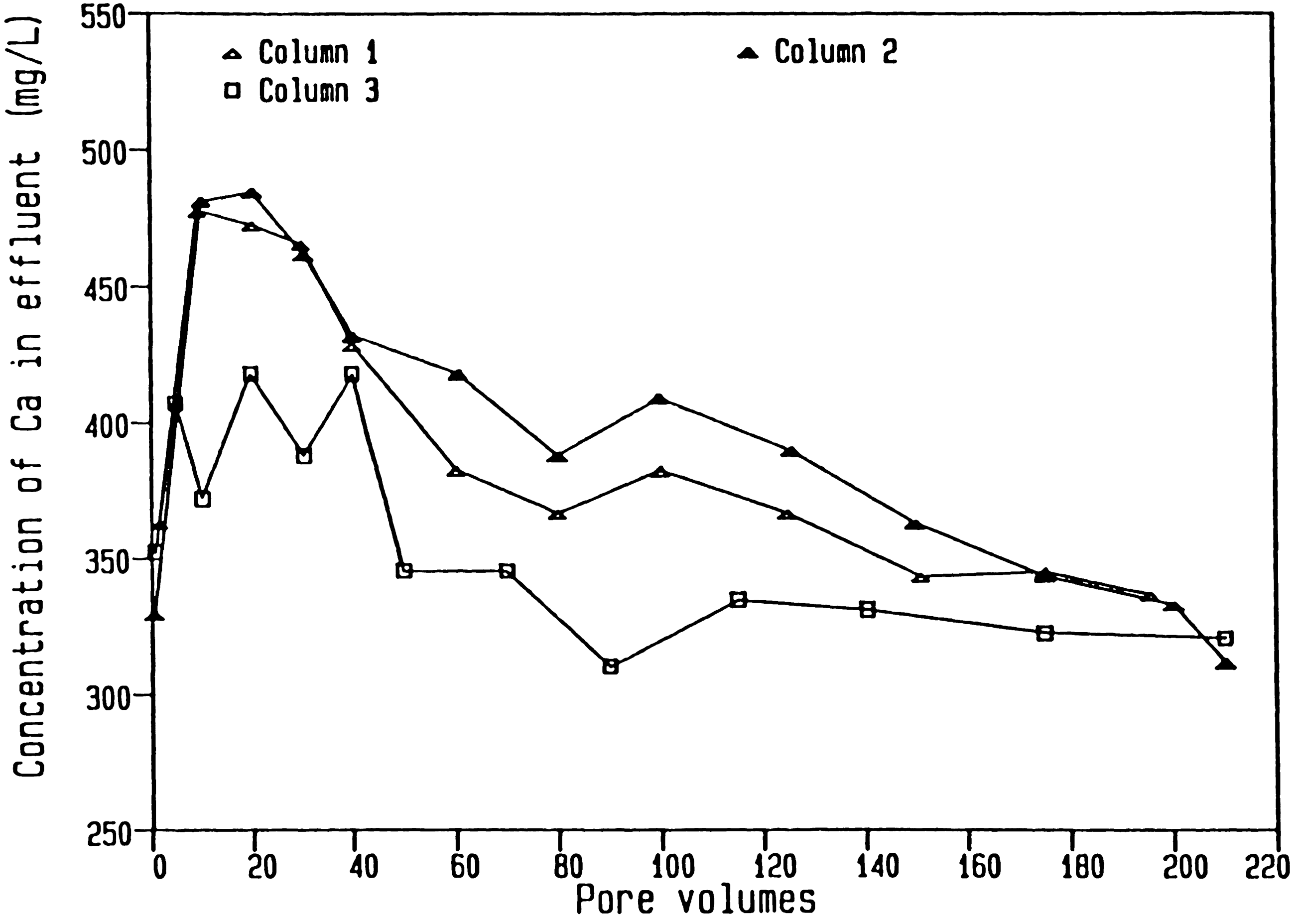

Figure 51. Sorption of calcium in solutions containing four cations: (C_0= 10 mg/L)

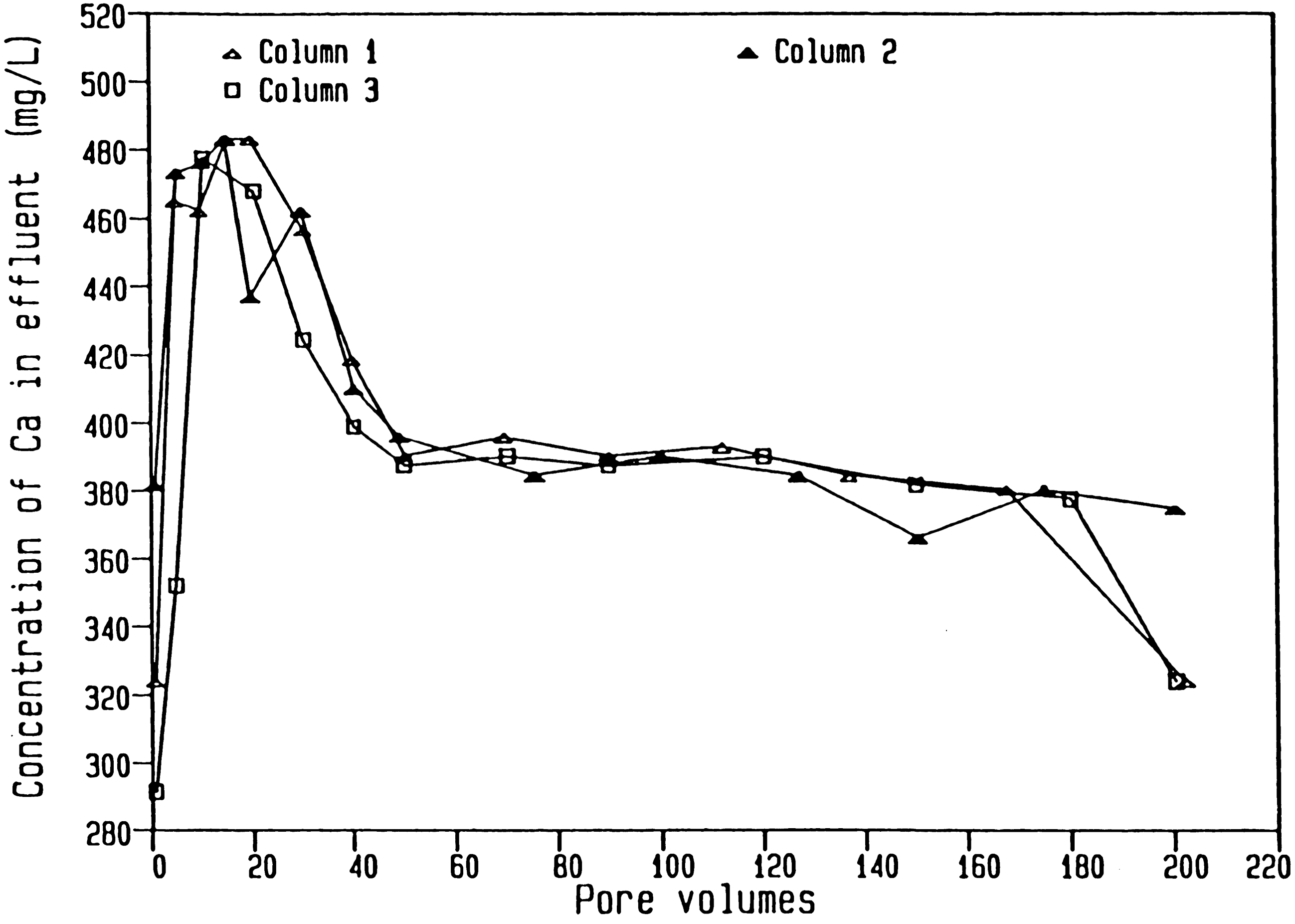

Figure 52. Sorption of calcium in solutions containing eight ions: (C_0= 10 mg/L)

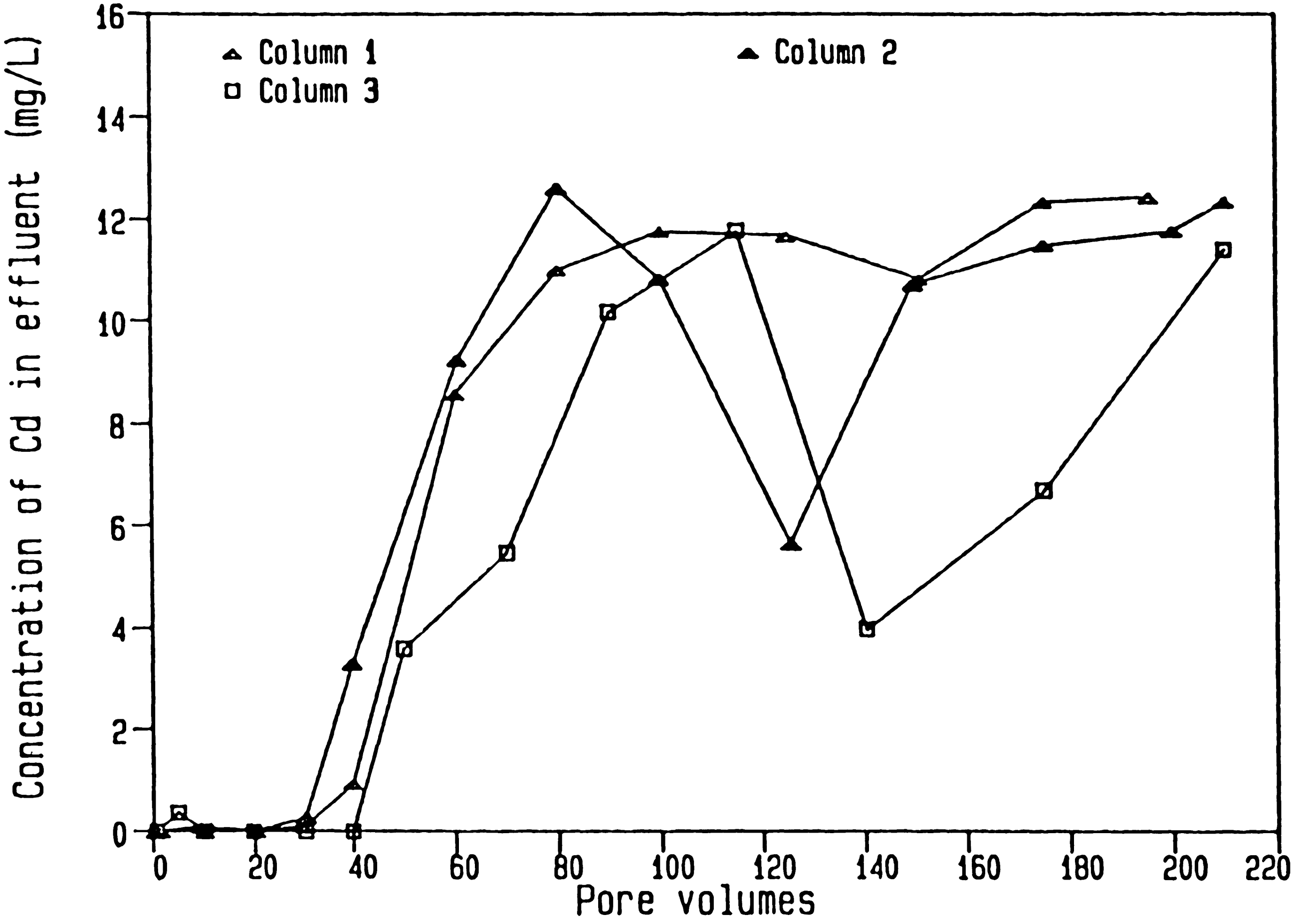

Figure 53. Sorption of cadmium in solution containing four cations: (C_0= 10 mg/L)

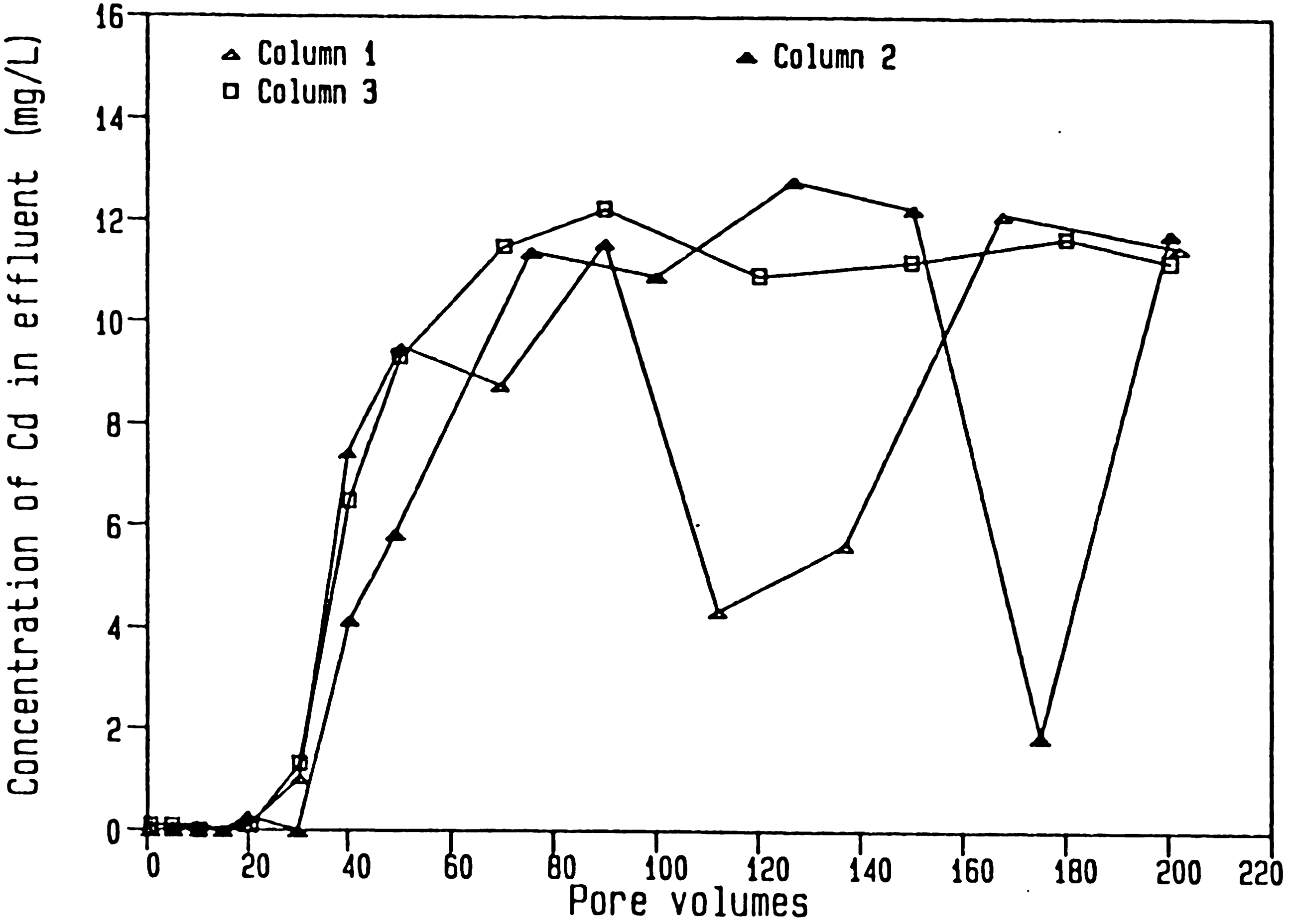

Figure 54. Sorption of cadmium in solution containing eight ions: (C_0 = 10 mg/L)

The data presented in Figures 55 and 56 indicate that a great deal of potassium was released from soil (up to 120 mg/L) initially. The amount of potassium dramatically decreased to approximate 11 mg/L within 20 pore volumes. The addition of NH_4, SO_4, and F in the feed solution did not show any influence on the concentration of potassium in the column effluent.

The soil showed some affinity for the ammonium ions. Sorption capacity of soil for ammonium was not exhausted over the course of the experiment (Figures 57 and 58). When the feed solution only contained NH_4, F, and SO_4, breakthrough occurred at 10 pore volumes. Ammonium levels in the effluent remained in the range between 7.0-8.0 mg/L to the end of the experiment. In the case where cations were, in addition to NH_4, SO_4, and F, added to the feed solution (Figure 58), it is evident that less ammonium ions were sorbed by the soil. The effluent concentration of ammonium was initially at 1.6-2.3 mg/L and then sharply increased to 8.2-9.4 mg/L. Ammonia levels at the end of the experiment were in the range of 8.5-9.2 mg/L.

The fluoride reached breakthrough within one pore volume when the feed solution was composed of NH_4, SO_4, and F (Figure 59). The capacity was exhausted within five pore volumes. The addition of cations in the feed solution, as shown in Figure 60, somewhat delayed the breakthrough of fluoride. Point of exhaustion was reached at 30-40 pore volumes.

Sorption of sulfate is illustrated in Figures 61-62. In the case where the feed solution contained only NH_4, SO_4, and F (Figure 61), the sorption capacity of the soil was exhausted in 25-30 pore volumes. However, when cations were added to the feed, a great deal of sulfate was released from the soil, but the levels of sulfate in effluents rapidly decreased to 10-11 mg/L within five pore volumes (Figure 62).

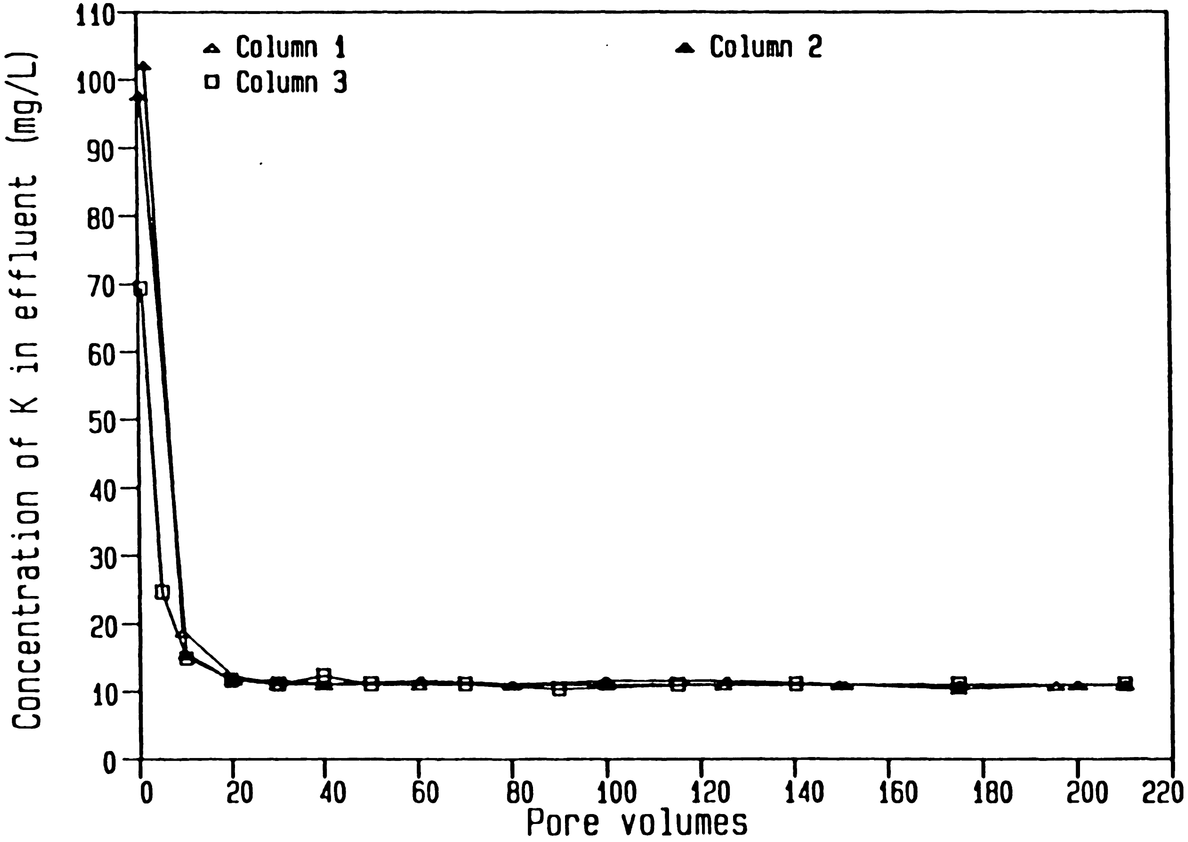

Figure 55. Sorption of potassium in solution containing four cations: (C_0= 10 mg/L)

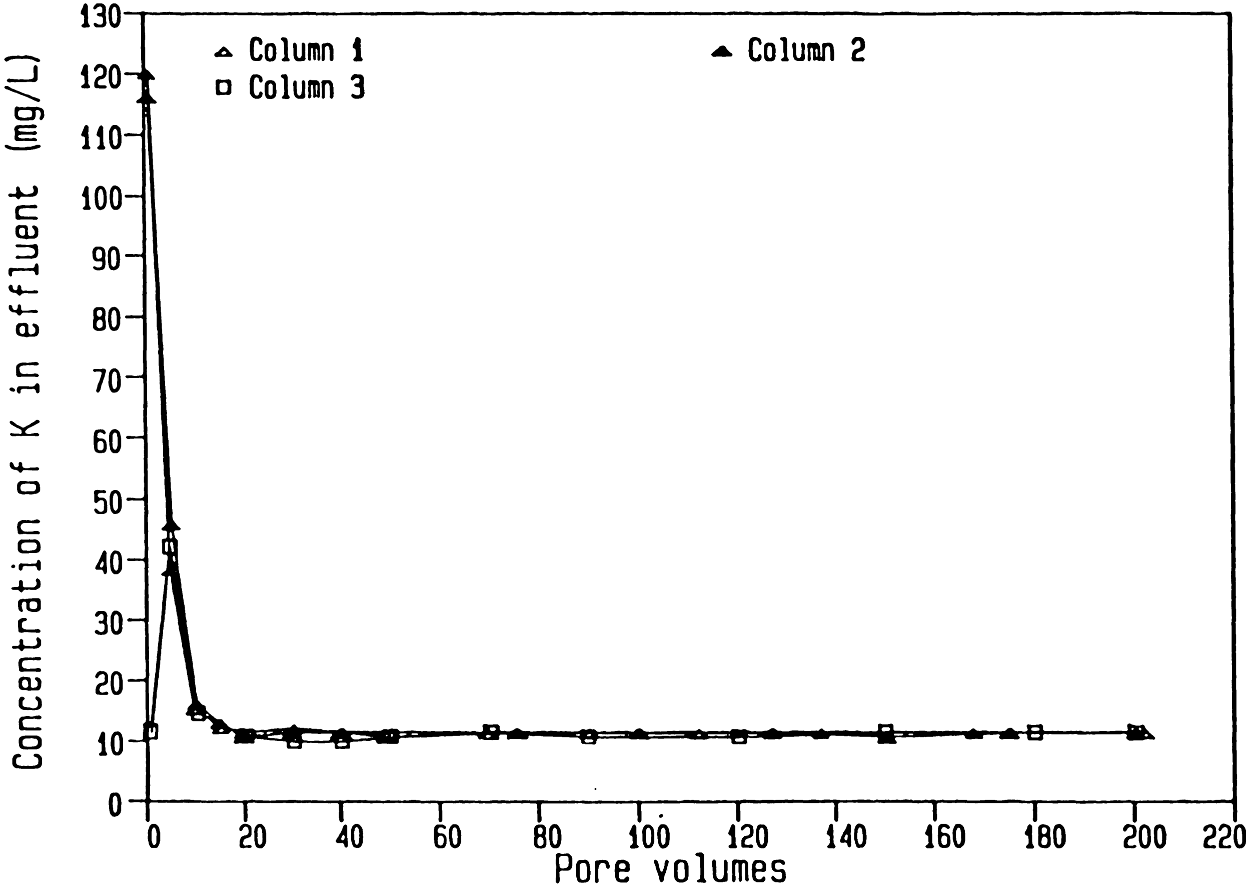

Figure 56. Sorption of potassium in solution containing eight ions: (C_0 = 10 mg/L)

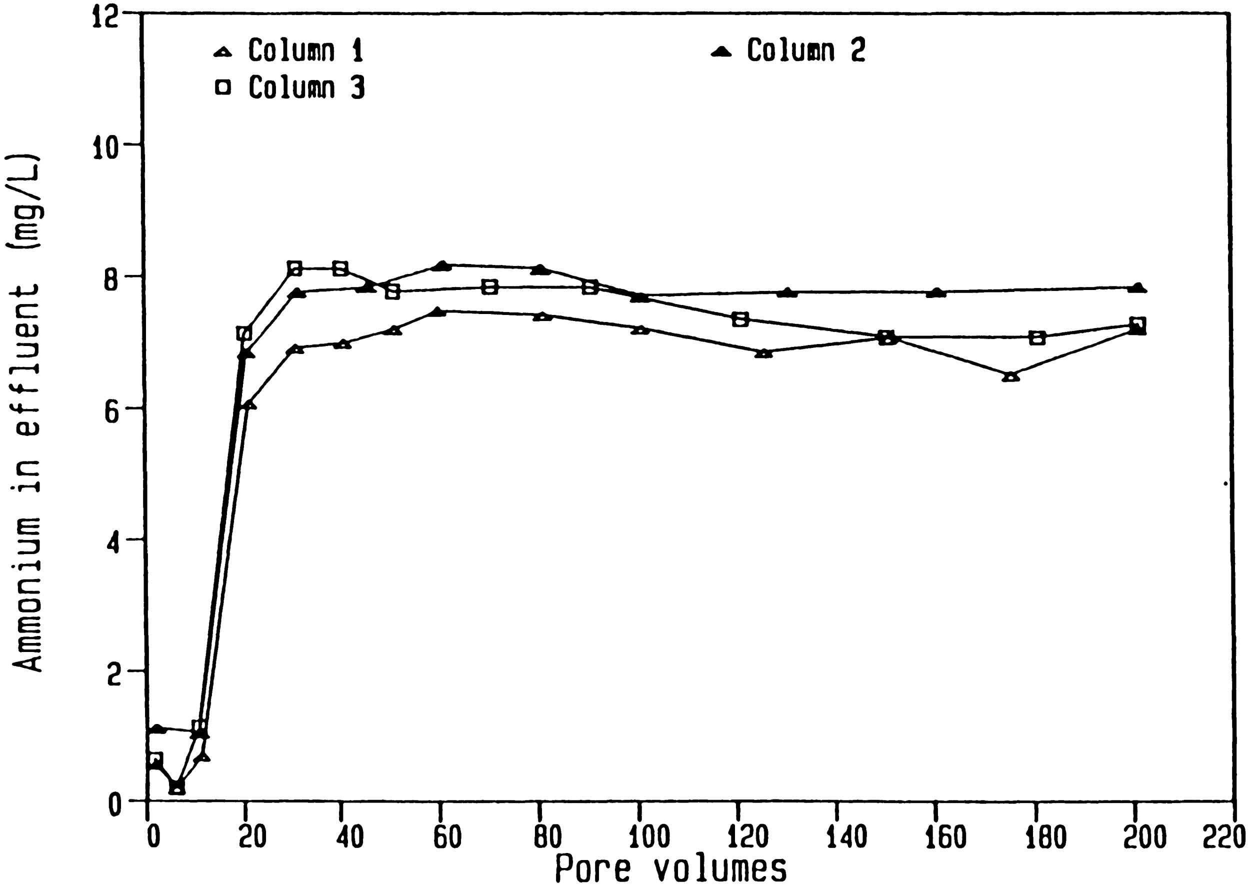

Figure 57. Sorption of ammonium in solution containing NH_4, SO_4, and F: ($C_0 = 10$ mg/L)

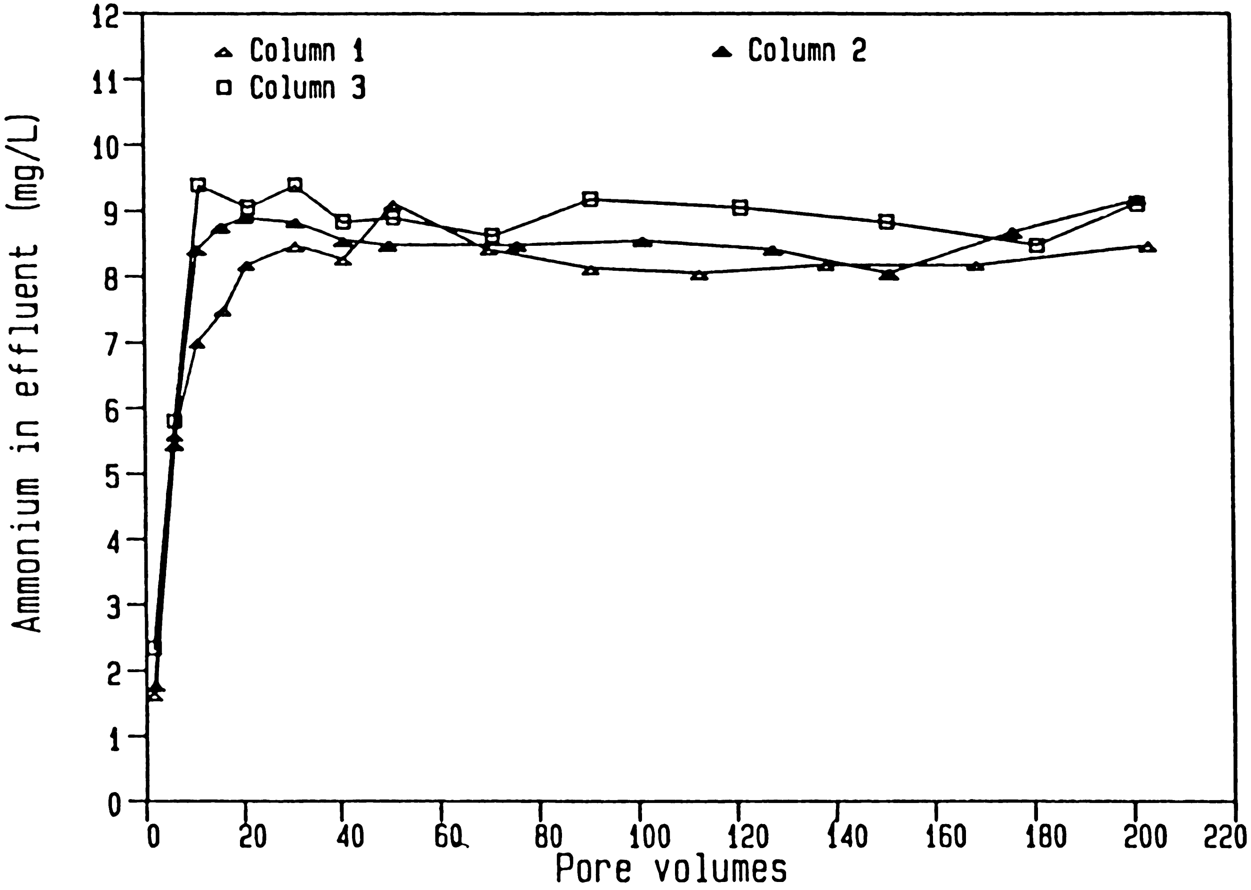

Figure 58. Sorption of ammonium in solution containing eight ions: (C_0 = 10 mg/L)

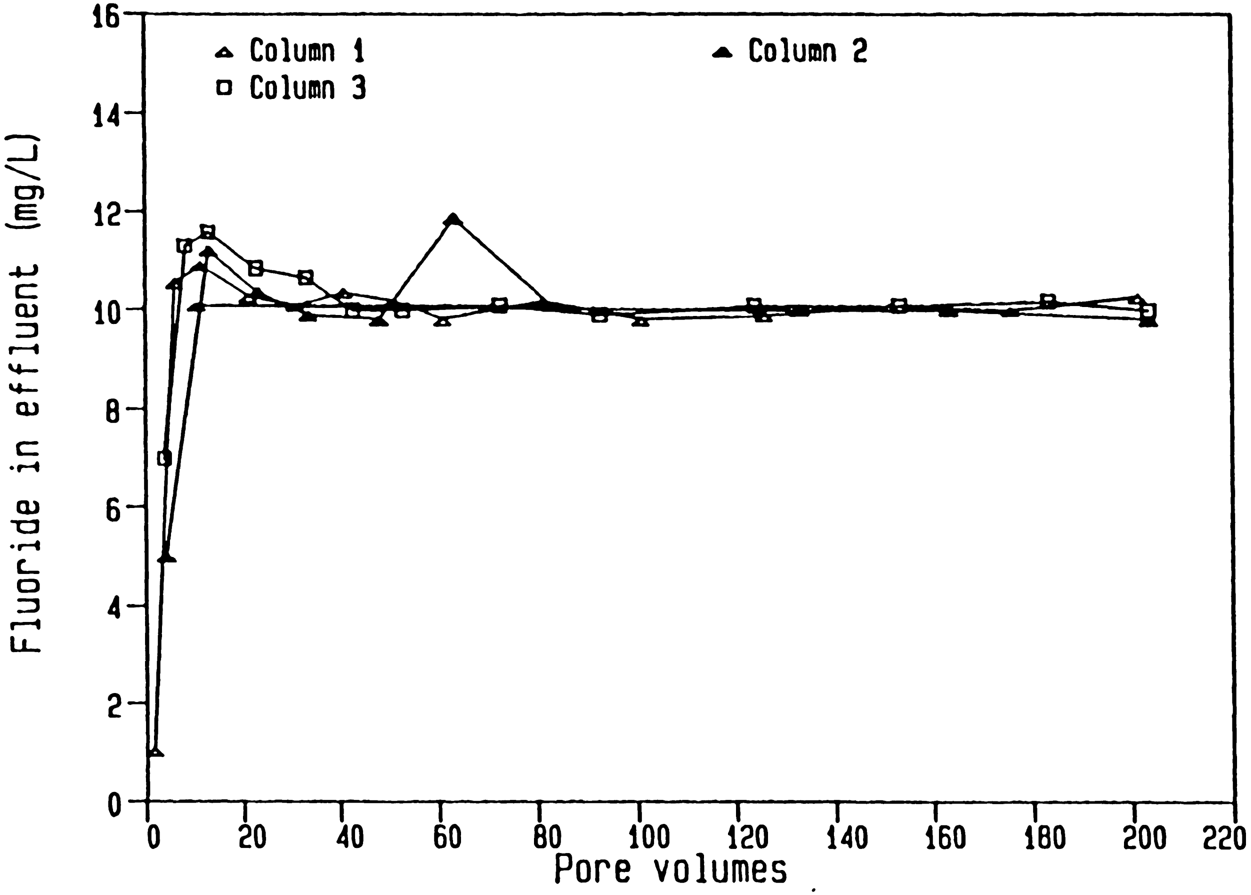

Figure 59. Sorption of fluoride in solution containing NH_4, SO_4, and F: (C_0 = 10 mg/L)

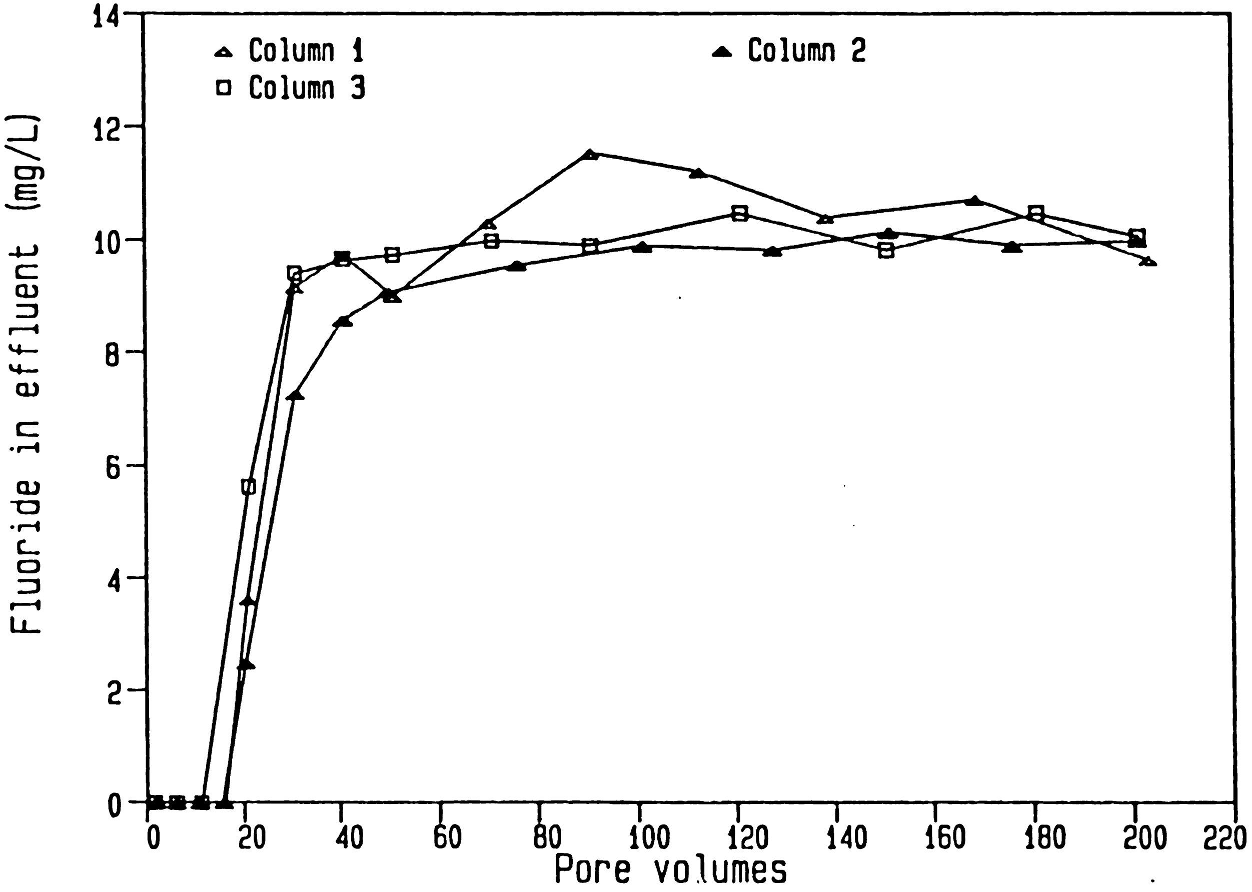

Figure 60. Sorption of fluoride in solution containing eight ions: (C_0 = 10 mg/L)

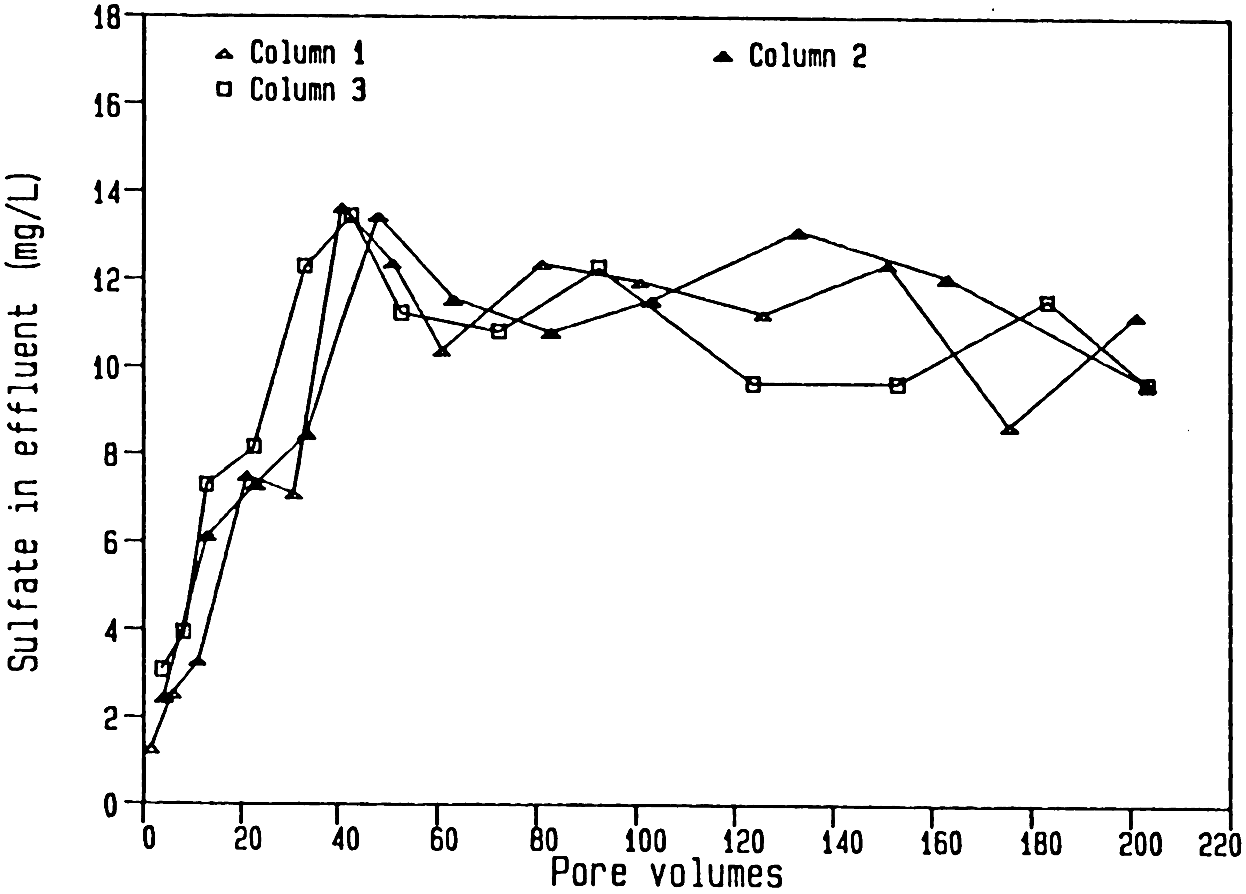

Figure 61. Sorption of sulfate in solution containing NH_4, SO_4, and F: (C_0= 10 mg/L)

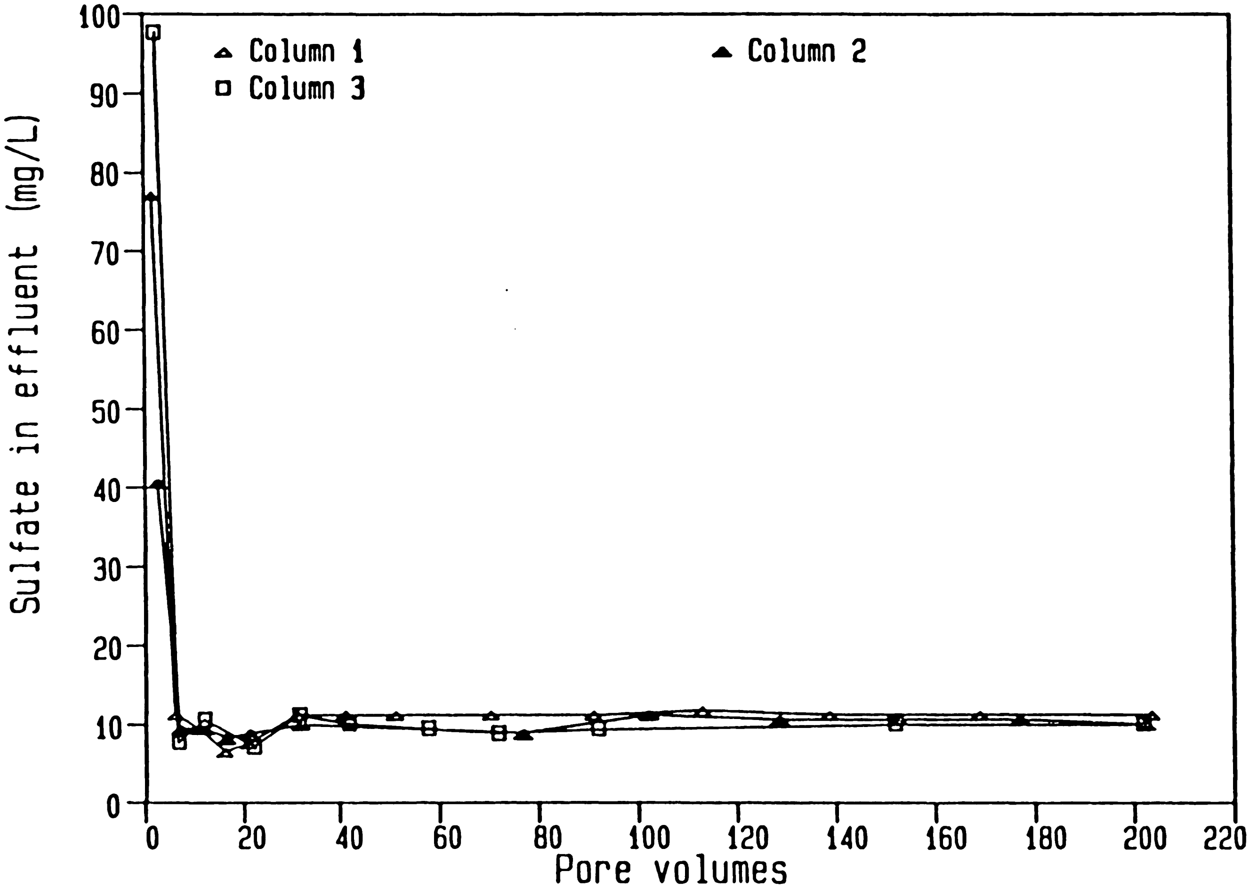

Figure 62. Sorption of sulfate in solution containing eight ions: (C_0 = 10 mg/L)

Chapter V

DISCUSSION

5.1 *Sorption of Organic Compounds by the Shales and the Western Soil*

Sorption of organic compounds in batch experiments was investigated with three types of solutions: single-sorbate solutions (containing each organic compound alone), three-component solutions (containing HN, THQ and TMP), and four-component solutions (containing HN, THQ, TMP and DMP). Two types of feed solutions were used in column experiment: (1) a mixture of HN, DMP, THQ, and TMP; and (2) a mixture of HN, THQ, and TMP. Although DMP in the solutions could not be determined quantitatively, the influence of DMP on the sorptive behavior of other organic compounds may be considered.

5.1.1 Analysis of Batch Experimental Results

The batch sorptive behavior of HN, THQ, and TMP in the presence of Antrim, Anvil Points, Oxy 6, and Run 16 shales and the western soil are analyzed in this section.

Antrim shale sorbed nearly all of the three organic compounds in the single-sorbate trials. In multi-sorbate systems, HN was sorbed best followed by THQ and then TMP. Competition effects largely depressed the sorption of THQ and TMP, especially for TMP. The influence of DMP on the other three compounds was noticeable.

In single sorbate trials, the preference of sorption of organic compounds by Anvil shale followed the order of: HN > TMP > THQ. Desorption occurred after maximum adsorption which was probably due to the effect of solvent competition for the sorption sites. In multi-sorbate trials, TMP was sorbed better than THQ initially. However, TMP exhibited greater desorption rates which caused more THQ to be retained on Anvil raw shale at the end of experiments. Competition for sorption sites apparently had a negative effect on both adsorption and the desorption of THQ and TMP on Anvil raw shale.

HN was sorbed better by Oxy 6 shale than THQ and TMP in both single- and multi-sorbate solutions. THQ and TMP were sorbed to approximate the same extent in single-sorbate trials. However, sorption of TMP was greatly depressed by the competition of other agents in multicomponent solutions. This mutual inhibition effect was even more significant in four-component solutions than in three-component solutions.

Relative sorptive quantities of organic compounds by Run 16 shale can be ranked as HN > THQ > TMP. Actually, Run 16 appeared to be a poor sorbent for TMP in batch trials. Effect of competition caused more TMP to desorb from the shale. Influence of DMP on the system was little.

Each organic compounds was sorbed well by the soil in single-sorbate trial. In multi-sorbate systems, competition effects had a greater influence on the sorption of TMP and THQ than on HN. THQ and TMP were sorbed to a similar extent from the three component solutions. The presence of DMP in the four-component system depressed the uptake of THQ.

Based on the data developed in batch experiments, sorption of the three organic compounds on the five sorbents can be ranked in the following order:

Antrim	HN > THQ > > TMP
Anvil	HN > THQ > TMP
Oxy 6	HN > THQ ≅ TMP
Run 16	HN > THQ > > TMP
Soil	HN > THQ > > TMP

5.1.2 Analysis of Column Experimental Results

Throughout the column experiments with organic compounds, the oil shales and the western soil showed that sorption capacity for the three organic compounds decreased in the following order:

HN > THQ > TMP.

The presence of DMP generally increased sorption of HN and decreased sorption of THQ which tended to enlarge the relative sorption capacity differences between the two compounds. Both batch and column data showed that HN was sorbed best of the organic compounds. This stronger sorption tendency is probably related to the ability of HN to form hydrogen bonds with the sorbent. Another factor which may have enhanced the sorption of HN is its greater molecular weight. Generally the sorption capacity may be increased with molecular weight increases.

Although TMP also has the capability to form hydrogen bonding, bond strength appears to be weakened due to the three methyl groups attached on the aromatic ring. The effect of steric hindrance caused by the three methyl substitutes may be the primary reason for the less effective adsorption of TMP. THQ is a Lewis base, i.e. an electron doner, which can form a coordination bond between the nitrogen on the aromatic ring and the metals on the surface of the shales and the soil. This might explain why THQ was sorbed better than TMP, yet poorer than HN. In addition, DMP is also a Lewis base containing a free electron pair which can be shared with metals on the soil surfaces. Therefore, it might be expected that DMP would exert a greater negative effect on sorption of THQ.

5.1.3 Competitive Effect on Sorption Capacity of the Oil Shales and the Soil

The results for sorption of organic compounds in single- and multi-sorbate trials indicated that the effect of competition varied with the characteristics of sorbates as well as sorbents. Table 18 summarized the adsorbed amount of three organic compounds on the oil shales and the soil at the end of each type of experiment. Mutual inhibition of adsorption capacity for each organic compound in the presence of other solutes was evident. The depression of sorption capacity was more pronounced for less effectively sorbed compounds, such as TMP. Because of the competition of HN and THQ, the decrease in the number of available sorption sites for TMP made it even more difficult to effectively approach the sorbent surfaces because of steric hindrance.

Although the sorptive capacity for each organic compound was decreased in multisorbate systems, the accumulative sorption capacity of the oil shales and the soil for the three organic compounds was higher than the individual adsorption capacities for HN, THQ, and TMP. The enhancement in solid-phase loading was more pronounced for Antrim shale and the soil, yet less effective for the poorer sorbents, such as Run 16.

Table 18. **Amount of organic agents retained on the sorbent surfaces**

Type of Sorbent	Type of Trial	Final Sorbed Quantity[1], mg/L			
		HN	THQ	TMP	Total
Antrim	A[3]	25.0	24.2	25.0	—
	B[3]	23.6	22.8	13.9	60.3
	C[3]	23.0	17.3	8.5	48.8[2]
Anvil	A[3]	21.6	13.9	17.6	—
	B[3]	20.1	10.4	8.7	39.2
	C[3]	20.3	14.5	9.1	43.9[2]
Run 16	A[3]	19.5	14.4	2.3	—
	B[3]	11.9	6.7	5.0	23.6
	C[3]	13.1	8.2	6.3	27.6[2]
Oxy 16	A[3]	23.8	17.3	16.6	—
	B[3]	21.5	13.6	7.8	42.9
	C[3]	21.7	14.8	7.8	44.3[2]
Soil	A[3]	25.0	23.6	—	—
	B[3]	23.3	11.6	10	44.9
	C[3]	23.7	11.4	4.3	39.4[2]

[1] The amount of organic compounds sorbed after 96 hrs.

[2] The quantity of DMP sorbed on the oil shales or the soil was not included.

[3] Type A: Single sorbate system. Type B: Three-component system (HN, THQ, and TMP). Type C: Four-component system (HN, DMP, THQ, and TMP).

When the overall sorption capacities of the five sorbents in the single- and multi-component trials were evaluated, the efficiency of the oil shales and the soil for sorption of organic compounds can be ranked as:

Antrim shale > Western soil > Oxy 6 shale > Anvil raw shale > Run 16 shale

5.2 Sorption of Inorganic Ions by the Western Soil

Before analyzing the experimental data, it is important to note that some of the reagents used to prepare stock solutions were in the their cloro-salt forms, e.g., NH_4Cl and $CaCl_2$. In addition, HNO_3 is generally added to the AA standard solutions of the caions (As, Cd, Fe, and K) to keep the solutions at low pHs. Therefore, significant quantities of nitrate (NO_3^-) and chloride (Cl^-) were actually involved in the sorption/desorption processes. The presence of Cl^- and NO_3^- in the effluent were identified by ion chromatography.

5.2.1 Analysis of Batch Experimental Results

The elution study provided background information about the ions that may be leached from soil. Both batch and column experiments showed that large quantities of calcium and potassium were leached from the soil. However, the column eluent concentrations of Ca and K decreased sharply, relative to the initial concentrations, whereas the batch eluent concentrations of Ca and K reached their equilibrium concentrations gradually. In addition, sulfate concentration was high in the batch eluent, yet insignificant in the column eluent. This might have been due to high sulfate concentrations in the distilled water used in the batch trials. The distilled water boiler is sometimes washed with sulfuric acid. Sulfur-free distilled water was used as leachent in the column elution trials.

In single-sorbate trials, iron was the only specie that was totally removed from the solution, i.e., approximately 66.7 mg/L of iron was attenuated by the soil. The concentration of iron was probably reduced by precipitation of amorphous iron hydroxide ($Fe[OH]_3$) since the solution pHs (7.2-7.5) favored the predominance of ferric iron over ferrous iron in the solution. Because iron removal is most likely controlled by precipitation and the pHs in multi-sorbate trials were between 6.5-7.1, it is not surprising that the addition of cations did not affect the iron concentration significantly. The initial gradual decrease of iron level in multi-sorbate solution indicated the conversion of Fe(II) to Fe(III) while $Fe(OH)_3$ was forming as pH values shifted from 6.5 to 7.1.

The amount of As sorbed by the soil in single-sorbate trials was relatively small, relative to the sorption quantities of other cations. However, a dramatic increase in the attenuation of As was evident in multi-sorbate trials. Precipitation with Ca^{2+} forming $Ca_3(AsO_4)_2$ was not likely to be the reason for As removal because this requires that the pH of solutions remain above 12. By comparing the multi-sorbate sorption curves of As and Fe in Figures 22 and 25, it appears that both species shared almost the same sorption trend. This indicates some proportionality existed between the reduction of solution As and the reduction of solution Fe (or the formation of $Fe[OH]_3$). Therefore,the reduction of As in the multi-sorbate trial was probably contributed to by the coprecipitation of As with ferric hydroxide, i.e., the arsenic was sorbed on the bulk-precipitated $Fe(OH)_3$. This also explains why no appreciable amount of As was sorbed in the single sorbate system when iron was absent.

Substantial amounts of Cd were adsorbed in single-sorbate trials. Evidence from control tests showed that the cadmium concentration remained relatively constant in the absence of soil, indicating that the removal of Cd was due to adsorption by soil colloids, hydrous oxides and organic matter, rather than by precipitation. The uptake of Cd was significantly reduced in the multi-sorbate trial. Benjamin and Leckle [8] noted Cl^- and SO_4^{2-} were capable of forming complexes with Cd in multi-sorbate system. Due to the high concentration of chloride and sulfate in the system, reduction of Cd adsorption was probably due to formation of chloro and sulfato complexes of cadmium in addition to competition for adsorption sites with other compounds in the mixture.

In single-sorbate sorption, Ca^{2+}, K^+, and NH_4^+ were sorbed to a notable extent. One would expect that these ions, without interference of other competing species, would be bound by the clay minerals, e.g., hydrated aluminum and iron silicates. However, the attractive forces between these ions and the soil apparently were relatively weak. When other compounds were added to the solution, all of the three cations eluted from the soil. Ions with higher charge are expected to replace monovalent K^+ and NH_4^+. Dissolution of CO_3^{2-} and competition by other divalent cations, such as Cd^{2+}, for sorption sites may be responsible for the desorption of Ca^{2+} from the soil. Other compounds in the mixture such as Fe and/or As may also contribute to the inhibition Ca sorption.

The soil showed a noticeable adsorption capacity for fluoride. The mechanism for the removal of fluoride from solution was probably due to anion exchange, since precipitation of CaF_2 was not likely to occur under weakly alkaline condition. The results showed that significant quantities of sulfate eluted from soil; however, solution sulfate decreased through the course of experiments, probably by complexation and precipitation.

5.2.2 Analysis of Column Experimental Results

Sorption of As from cation mixtures which contained As, Ca, Cd, and K followed a typical breakthrough curve up to a peak point. Then, probably because As associated with other compounds in the mixture, more adsorption of As occurred which is generally referred to as an "undershoot". When the feed solution contained all of the eight ions, i.e. As, Ca, Cd, Fe, K, F^-, NH_4^+, and SO_4^{2-}, the sorption pattern of As changed dramatically. The peak concentration of As in effluents after breakthrough was much less than that found in the cationic multi-sorbate trials. More sorption of As, probably due to coprecipitation with $Fe(OH)_3$, after the peak point caused nearly total removal of As in the effluent. It is noted that some of the arsenic precipitate tended to redissolve in the solution which increased the arsenic level in the effluent.

High quantities of Ca in the soil eluent was probably due to dissolution of CO_3^{2-}. Dramatic increases of calcium in the effluent of both types of multi-sorbate trials indicated that large quantities of exchangeable Ca in soil were replaced by other ions in the feed mixtures. The reduction of effluent Ca was due to the exhaustion of total exchangeable Ca on the soil surface.

The sorption of Cd in both types of multi-sorbate trials were relatively comparable, indicating that the addition of Fe, F, NH_4, and SO_4 only had a minor influence on Cd sorption, e.g., slightly faster breakthrough. Batch data from multi-sorbate trials showed that the soil only sorbed small amounts of Cd in solutions when high concentrations ($\cong$ 66.7 mg/L) of Cd were present, whereas in column trials the Cd in the feed solution ($\cong$ 10 mg/L) was significantly sorbed by the soil. Apparently, the continually renewing soil-solution interface provided more available sorption sites for cadmium.

The results of eluting K from soil columns were consistent with the batch results. Since K, Ca, and Mg are generally predominant in alkaline soil, exchangeable K may be rapidly replaced by cations with a higher charge. However, the concentration of K in the effluent decreased rapidly with percolating flow, since less and less exchangeable K was available.

Sorption of NH_4 was characterized by its rapid breakthrough and sharp increase of ammonium concentration in the effluent. Nevertheless, the concentration of ammonium in the effluent never exceeded the feed concentration ($\cong$ 10 mg/L). In multi-sorbate trials where feed solutions contained F, NH_4, and SO_4, the plateau concentration was approximately 8 mg/L, whereas with the addition of cations in the feed, a higher plateau concentration of approximately 9 mg/L was reached due to the competition of other cations. Note that some NH_4^+ in the form of ammonia (NH_3) might have escaped from the effluent during operation and sample collection which would lead to an overestimate of the sorption capacity for ammonium.

The results of sulfate sorption from mixtures of NH_4, SO_4, and F indicated that sulfate was sorbed within the first 30 pore volumes of feed solution and then desorbed from the soil.

In the presence of the other cations, sulfate was initially released from soil which implied that some salt associated with sulfate might be replaced by cations in the percolating flow.

Chapter VI

CONCLUSIONS

The sorptive behavior of 2-Hydroxynaphthalene, 1,2,3,4-Tetrahydroquinoline, and 2,3,5-Trimethylphenol in the presence of Antrim, Anvil Points, Oxy 6, and Run 16 shales and the western soil was studied through batch and continuous flow column experiments. The sorption study was also conducted to evaluate the sorption capacity of the western soil for inorganic ions including arsenic, cadmium, calcium, iron, potassium, ammonium, fluoride, and sulfate.

Based on the experimental data, the following conclusions were developed:

1. All of the five sorbents studied demonstrated a substantial sorption capability for 2-Hydroxynaphthalene and 1,2,3,4-Tetrahydroquinoline, yet poor sorption capacity for 2,3,5-Trimethylphenol.

2. Considering the overall sorption capacity, Antrim shale was a better sorbent for the organic compounds than the other three shales. Sorption capacity of the Run 16 shale appeared to be relatively poor.

3. The sorptive behavior of each organic compound was adversely affected by the presence of the other organics. Competition effects among the organic compounds increased with increases in the number of solutes. The less effectively adsorbed the compound was the more adversely it was affected by competition.

4. The overall sorptive capacities of the oil shales and the soil increased with the number of organic compounds in the solution. The increase in adsorption capacity of the oil shales with increases in number of solutes in solution emphasized the importance of this factor on the performance of spent shales in the co-disposal option where spent shales are used for the removal of complex mixtures of organic constituents in retort waters.

5. The western soil appeared to be a good sorbent for arsenic, cadmium, and iron, and possessed some affinity for fluoride. Potassium, calcium, ammonium, and sulfate were sorbed poorly and eluted well from soil.

6. Sorption of inorganic agents in multicomponent solutions by the soil was influenced not only by competition for sorption sites by solutes, but also by intramolecular interactions between the solutes. The inorganic solute interaction can be very significant in effecting multisorbate sorption of cations by the soil.

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Appendix A. Summary of Data Derived from Batch and Column Experiments

Table A1. Variation of pH in batch sorption of organic compounds

		Type of Trial						
Type of Sorbent	Time, hr	Elution[1]	Single Sorbate				Multi-component	
			HN	DMP	THQ	TMP	HN, THQ & TMP	HN, DMP THQ & TMP
Antrim	4	8.5	9.0	9.1	8.9	7.6	8.4	9.2
	12	9.5	9.3	9.4	9.1	9.2	9.0	9.3
	24	9.8	9.9	9.7	9.5	9.9	9.3	9.5
	48	10.0	9.8	9.9	9.5	4.1	9.8	9.6
	96	9.7	9.6	8.5	8.9	9.3	9.1	8.6
Anvil	4	9.1	9.2	9.1	9.1	9.1	8.9	8.7
	12	8.1	4.3	6.5	6.4	6.1	8.2	8.3
	24	6.9	7.8	7.7	7.9	8.3	7.3	7.4
	48	7.9	6.7	5.1	6.9	3.4	7.7	6.1
	96	7.4	6.3	7.5	7.3	7.0	6.3	6.5
Oxy 6	4	8.0	7.9	7.7	7.7	7.7	7.9	7.8
	12	7.9	7.8	7.7	7.8	7.8	7.6	7.7
	24	7.6	7.3	7.1	7.5	7.3	6.8	7.0
	48	7.4	8.2	8.1	6.7	7.0	7.6	7.6
	96	8.2	7.4	8.3	8.4	8.4	8.4	8.2
Run 16	4	10.6	10.5	10.5	10.7	10.1	10.2	9.9
	12	10.7	10.8	10.8	10.8	9.9	10.7	10.7
	24	11.0	11.0	11.1	11.1	11.1	10.9	10.9
	48	11.1	10.9	11.2	11.0	11.0	11.0	11.0
	96	11.3	11.3	11.3	11.2	11.2	11.3	11.3
Soil	4	7.5	8.1	8.3	8.4	8.3	8.3	8.1
	12	7.1	5.5	4.0	6.5	4.1	7.3	7.3
	24	6.6	7.3	7.4	7.6	7.4	7.2	7.1
	48	7.2	7.3	7.3	7.2	7.2	7.1	7.4
	96	6.5	6.7	7.1	6.7	6.9	6.7	7.0

[1] Containing soil-water suspension with no chemical added.

Table A2. Sorption of HN, THQ, TMP in the batch experiments

Type of Trial	Time, hr	Concentration in Solution, mg/L														
		Antrim			Anvil Points			Run 16			Oxy 6			Soil		
		HN	THQ	TMP	HN	THQ	TMP	HN	THQ	TMP	HN	THQ	TMP	HN	THQ	TMP
Four-component[1,2]	4	11.8	16.3	17.4	8.8	12.3	11.7	8.7	8.0	40.4	8.6	13.8	17.6	8.9	16.1	17.0
	12	7.7	8.1	11.5	4.6	11.6	8.2	0.0	20.9	21.4	4.3	13.1	20.7	3.7	13.7	11.5
	24	5.5	11.5	13.4	4.0	7.8	7.6	19.3	12.4	29.8	2.6	12.2	14.0	1.0	6.3	7.8
	48	2.6	6.9	11.4	2.8	10.4	8.5	20.0	22.1	34.1	1.6	7.2	1.2	1.2	10.9	6.2
	96	2.0	7.7	16.5	4.7	10.5	15.9	11.9	16.8	18.7	3.3	10.2	17.2	1.3	13.6	10.7
Three-component[1,3]	4	10.9	14.8	14.0	8.3	11.9	11.3	8.9	8.1	15.1	3.5	7.9	9.3	8.2	16.3	16.8
	12	0.0	9.6	13.3	5.6	11.7	8.6	4.4	10.9	13.3	6.9	16.9	13.5	3.2	13.8	11.5
	24	2.5	8.4	8.2	3.9	8.2	6.5	19.0	16.3	30.0	20.4	20.0	30.3	2.0	8.3	8.1
	48	1.1	6.4	10.5	1.4	8.3	7.0	21.8	20.8	30.0	3.0	7.6	19.3	1.8	10.9	8.2
	96	1.4	3.2	11.1	4.9	14.6	16.3	13.1	18.3	20.0	3.5	11.4	17.2	1.7	13.4	15.0
Single sorbate[3]	4	4.2	8.3	4.3	---	9.7	---	14.2	8.8	25.7	5.3	12.7	10.8	2.7	12.7	14.2
	12	0.0	1.9	7.4	6.9	11.3	9.0	0.0	15.2	18.1	5.9	9.7	7.8	2.3	8.8	5.3
	24	0.0	0.3	0.0	1.7	6.1	5.4	17.1	10.9	18.7	0.2	9.0	6.3	0.3	4.6	7.9
	48	0.0	0.7	0.0	2.2	8.2	4.4	18.0	12.0	17.1	2.7	6.7	5.9	0.4	5.3	6.3
	96	0.0	0.8	0.0	3.4	11.1	7.4	5.5	10.6	22.7	1.2	7.7	8.4	0.0	1.4	31.8

[1] Intial concentration of indivial compound: 25 mg/L

[2] Containing HN, DMP, THQ, and TMP.

[3] Containing HN, THQ, TMP.

Table A3. Conductivity and pH associated with the soil batch trials

	Time (hr)	As[1]	Ca[1]	Cd[1]	Fe[1]	K[1]	NH$_4$[1]	F[1]	SO$_4$[1]	Multi-sorbate[1,2]	Soil-water suspension[3]
pH	4	7.9	6.6	6.4	7.4	6.2	8.1	8.2	7.3	6.7	6.5
	8	7.6	6.9	6.4	7.4	6.4	8.0	6.5	7.2	6.6	6.7
	12	7.8	6.7	6.3	7.3	6.5	8.0	6.5	7.2	6.5	6.8
	24	7.6	6.8	6.4	7.2	6.7	7.8	7.2	7.2	7.0	6.8
	48	7.6	6.9	6.3	7.5	7.3	8.0	7.3	7.1	6.7	6.8
	72	7.9	7.5	6.4	7.4	7.3	7.6	6.4	7.2	7.1	6.8
	96	7.9	6.4	6.3	7.5	7.4	7.3	7.5	7.3	7.1	7.1
Conductivity (mmho/cm)	4	11.10	0.41	6.60	5.50	5.30	0.72	0.38	0.28	12.40	0.19
	8	10.90	1.13	7.90	4.40	6.50	0.63	0.34	0.30	11.60	0.19
	12	10.20	0.39	8.00	7.60	6.40	0.69	0.42	0.31	11.90	0.19
	24	10.48	0.41	7.70	7.20	6.60	0.67	0.37	0.32	12.61	0.20
	48	9.76	0.45	6.90	11.30	6.30	0.68	0.36	---	12.71	0.22
	72	10.78	0.62	7.80	11.00	5.30	0.69	0.38	0.34	12.90	0.21
	96	11.39	0.45	6.30	17.30	11.90	0.72	0.38	0.34	12.91	0.22

[1] Initial concentration of individual ion in solution: 67.7 mg/L.

[2] Solution contained As, Ca, Cd, Fe, and K.

[3] Containing 7.5g soil in 150 mL distilled water, but no chemicals added.

Table A4. Variation of pH in batch control tests

Time, hr	As[1]	Ca[1]	Cd[1]	Fe[1]	K[1]	NH_4[1]	F[1]	SO_4[1]	Multi-sorbate[1,2]	Blank[3]
0	7.0	7.3	6.8	6.7	6.4	7.3	7.0	7.2	6.7	6.7
4	6.6	6.9	6.2	5.7	6.7	7.2	6.9	7.1	6.9	6.6
8	6.2	7.0	6.2	5.5	6.4	7.1	6.9	7.0	6.5	6.7
12	6.5	6.9	6.3	5.5	6.9	7.5	6.8	7.1	6.8	6.7
24	6.7	7.0	6.3	5.6	7.0	6.9	6.5	7.0	6.9	6.8
48	6.8	6.8	6.4	5.3	7.2	7.1	6.8	7.2	6.9	6.9
72	6.6	7.1	6.3	7.1	6.7	7.6	6.7	7.2	6.8	7.0
96	6.8	7.1	6.7	6.7	7.2	7.5	8.0	7.3	6.7	7.3

[1] 67.7 mg/L of each ion were added to eluate prepared by shaking soil-water suspension for 96 hours and then removing the soil.

[2] Solution contained As, Ca, Cd, Fe, and K.

[3] Containing soil-water eluate with no chemicals added.

Table A5. Sorption of inorganic ions in the batch experiments

Trial Type	Time, hr	Concentration in Solution, mg/L As	Ca	Cd	Fe	K	F	NH_4	SO_4
Sorption trials[1]:									
1. Singlesorbate	4	56.00	44.30	45.20	0.05	58.60	65.50	67.00	106.00
	8	60.00	46.80	39.20	0.04	55.70	61.90	63.40	106.00
	12	53.50	46.00	36.60	0.05	54.00	62.20	58.70	99.20
	24	52.50	51.20	30.80	0.06	55.90	60.70	52.10	95.00
	48	52.00	51.70	24.80	0.06	54.10	57.80	60.90	95.00
	72	59.00	53.00	20.00	0.06	53.40	60.30	56.40	87.50
	96	58.50	52.90	18.80	0.07	55.20	57.80	60.70	70.00
2. Multicomponent[2]	4	45.50	79.30	62.10	28.10	85.40			
	8	35.60	77.20	63.30	14.80	85.30			
	12	30.00	76.10	58.00	7.20	76.50			
	24	27.60	83.70	60.10	3.80	73.80			
	48	25.70	87.00	61.10	1.60	73.50			
	72	24.10	92.70	58.50	1.20	71.50			
	96	22.30	93.10	58.10	0.80	70.20			
Control trials[3]:									
3. Singlesorbate[1]	4	62.00	61.40	64.00	76.40	76.80	65.59	67.40	83.98
	8	63.00	58.20	64.40	55.80	62.00	61.81	69.60	83.98
	12	58.00	62.40	68.40	48.70	67.60	56.01	67.62	63.98
	24	55.00	64.90	65.60	37.20	68.00	62.40	70.88	72.48
	48	70.00	66.20	66.80	27.70	66.20	64.48	67.43	78.48
	72	66.00	65.80	66.20	24.50	65.20	67.28	73.25	74.48
	96	61.00	64.30	64.00	11.80	63.40	68.53	67.79	76.48
4. Multicomponent[1]	4	49.00	54.40	54.80	49.30	63.80			
	8	59.00	54.20	61.80	62.00	60.00			
	12	62.00	58.40	65.80	66.30	60.60			
	24	64.00	58.90	67.00	67.80	63.00			
	48	67.00	63.20	65.20	65.40	60.20			
	72	64.00	62.80	64.40	65.20	64.20			
	96	57.00	64.30	63.40	61.60	59.40			

(Continued)

Table A5. Sorption of inorganic ions in the batch experiments (continued)

Trial Type	Time, hr	As	Ca	Cd	Fe	K	F	NH_4	SO_4
		Concentration in Solution, mg/L							
5. Elution trial[4]:	4	<0.500	6.17	<0.005	0.10	9.80	—	0.67	29.50
	8	<0.500	7.44	<0.005	0.42	8.90	0.40	0.69	25.00
	12	<0.500	7.37	<0.005	0.96	9.00	0.42	0.56	29.50
	24	<0.500	9.13	<0.005	0.36	9.30	0.47	0.63	29.50
	48	<0.500	11.10	<0.005	0.14	8.90	0.52	0.69	21.00
	72	<0.500	11.90	<0.005	0.08	10.30	0.49	0.76	12.50
	96	<0.500	12.80	<0.005	0.14	9.40	0.52	0.79	41.50
6. Distilled water:	4	<0.500	0.37	<0.005	0.24	3.32	—	0.42	12.50
	8	<0.500	0.14	<0.005	0.16	3.40	0.35	0.40	21.00
	12	<0.500	0.30	<0.005	0.12	3.40	0.36	0.42	17.00
	24	<0.500	0.29	<0.005	0.16	3.32	0.37	0.37	21.00
	48	<0.500	0.18	<0.005	0.12	3.24	0.38	0.42	21.00
	72	<0.500	0.46	<0.005	0.06	3.00	0.37	0.37	12.50
	96	<0.500	0.15	<0.005	0.08	3.36	0.39	0.45	8.50

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[1] Initial concentration of individual ion in solution : 67.7 mg/L.

[2] Containing 10 mg of each matel ion (As, Ca, Cd, Fe, and K) and 7.5 g soil in 150 mL distilled water.

[3] Containing 8 mg of each ion in 120 mL soil-water eluate (eluate was prepared by shaking the soil-water suspension for 96 hr and removing the soil).

[4] Containing 7.5 g soil in 150 mL water with no chemicals added.

Appendix B. Variatins of pH in Batch Sorption of Organic Compounds

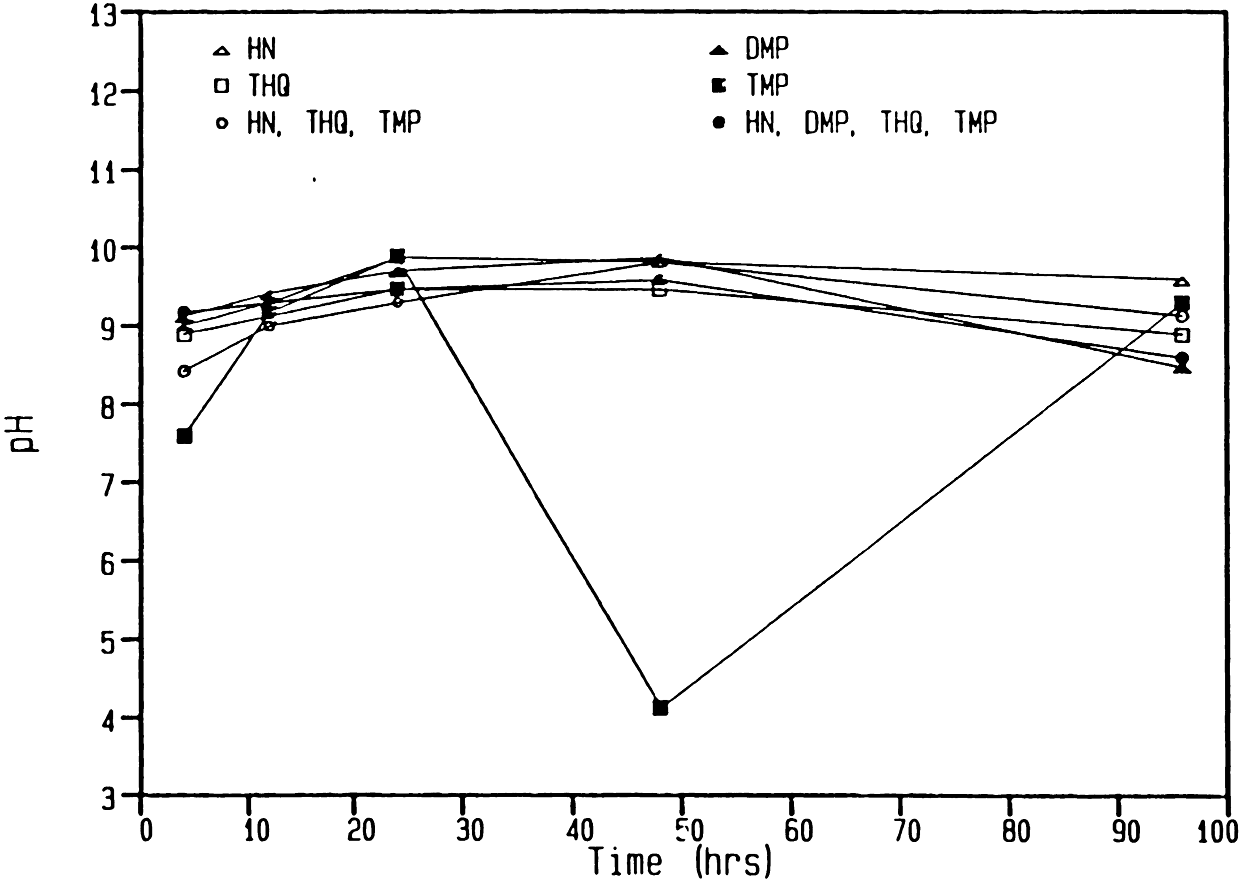

Figure B1. Variation of pH in single-sorbate sorption on Antrim shale

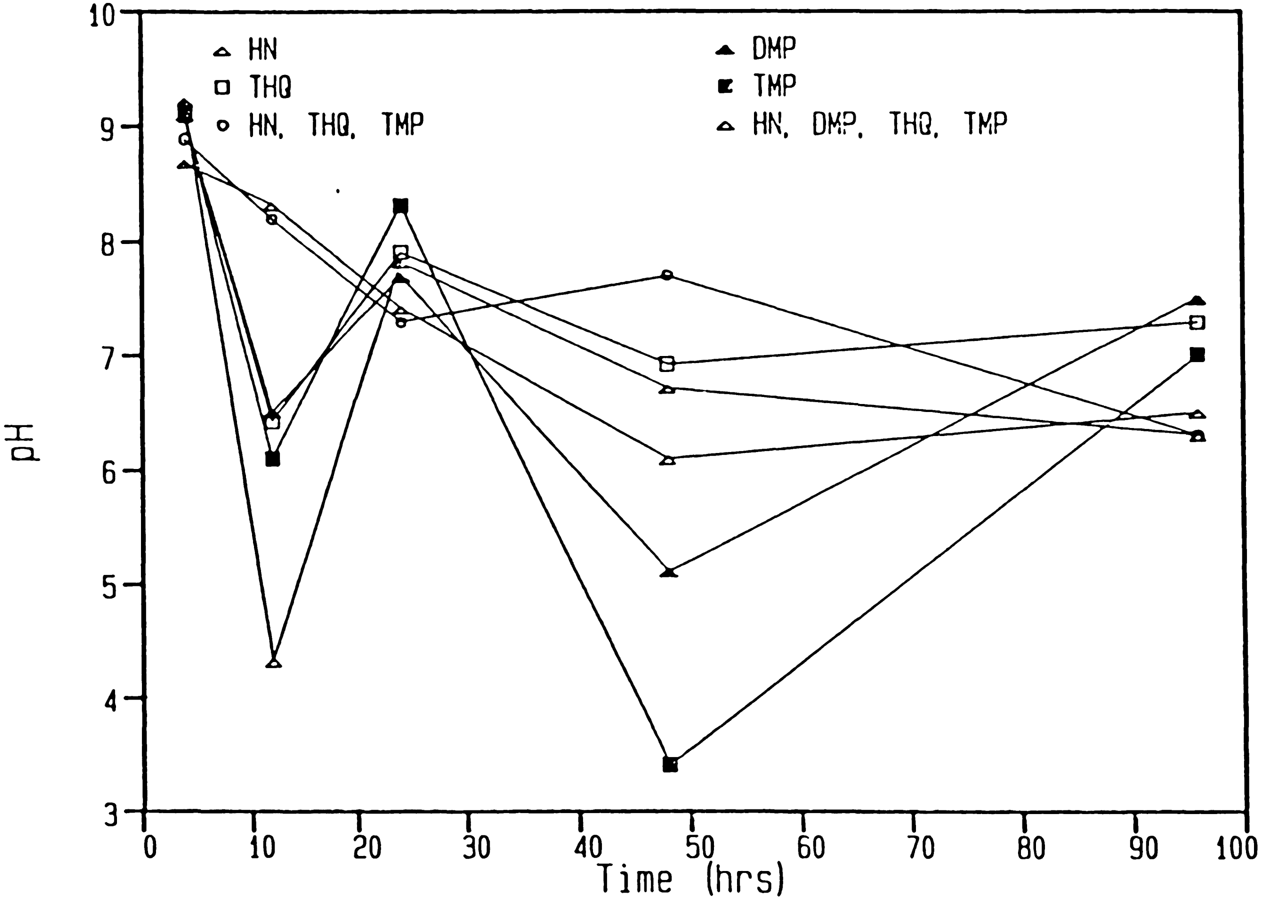

Figure B2. Variation of pH in single-sorbate sorption on Anvil Points shale

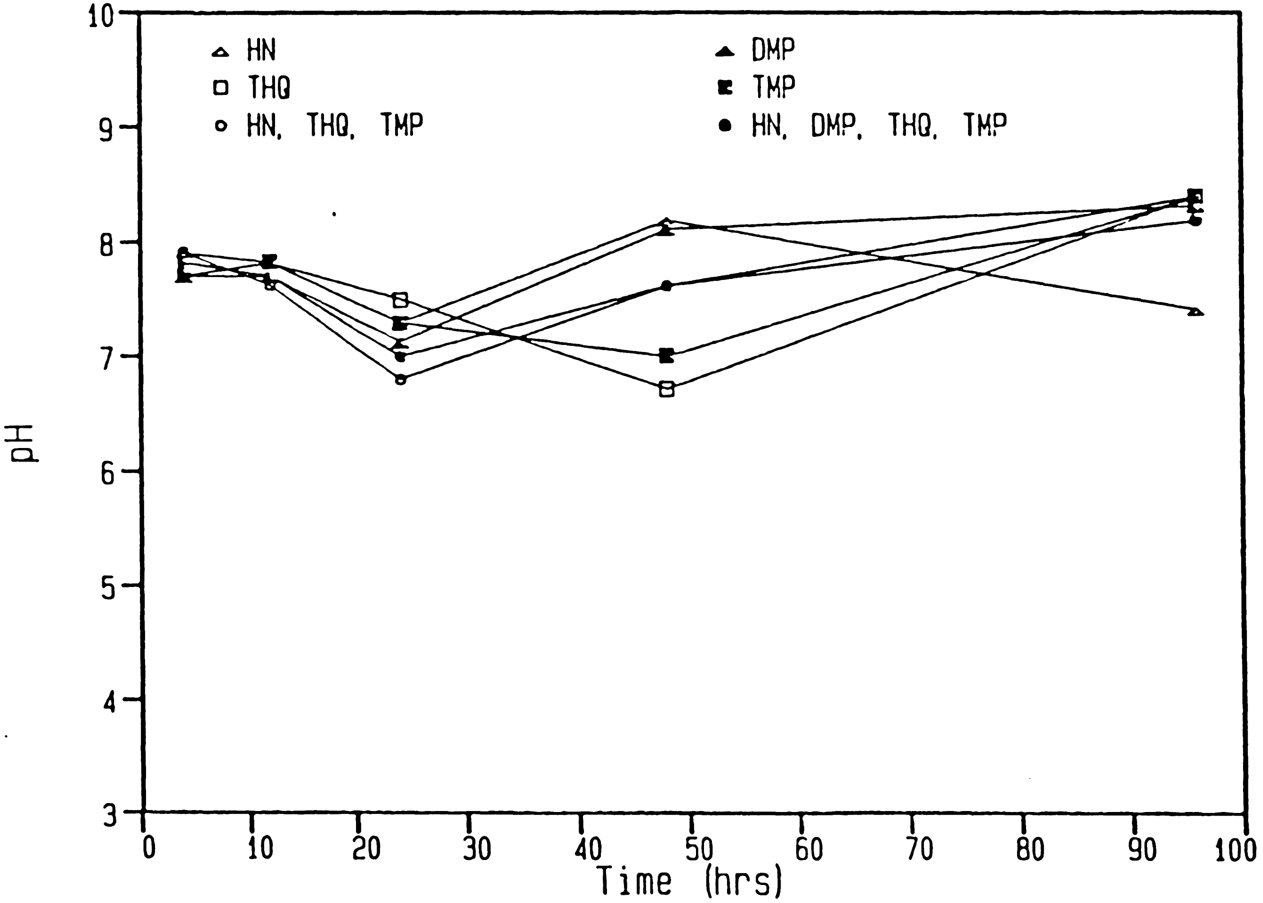

Figure B3. Variation of pH in single-sorbate sorption on Oxy 6 shale

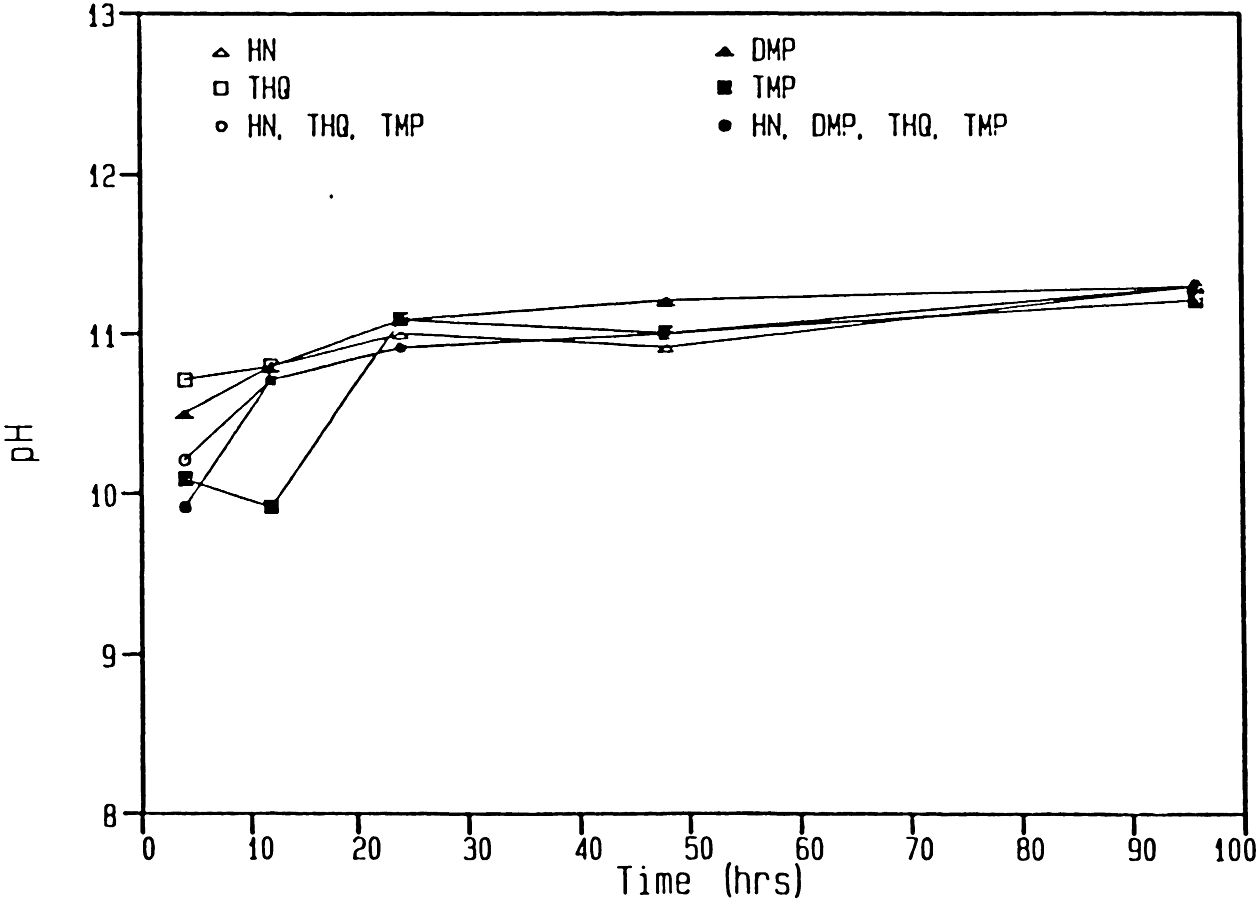

Figure B4. Variation of pH in single-sorbate sorption on Run 16 shale

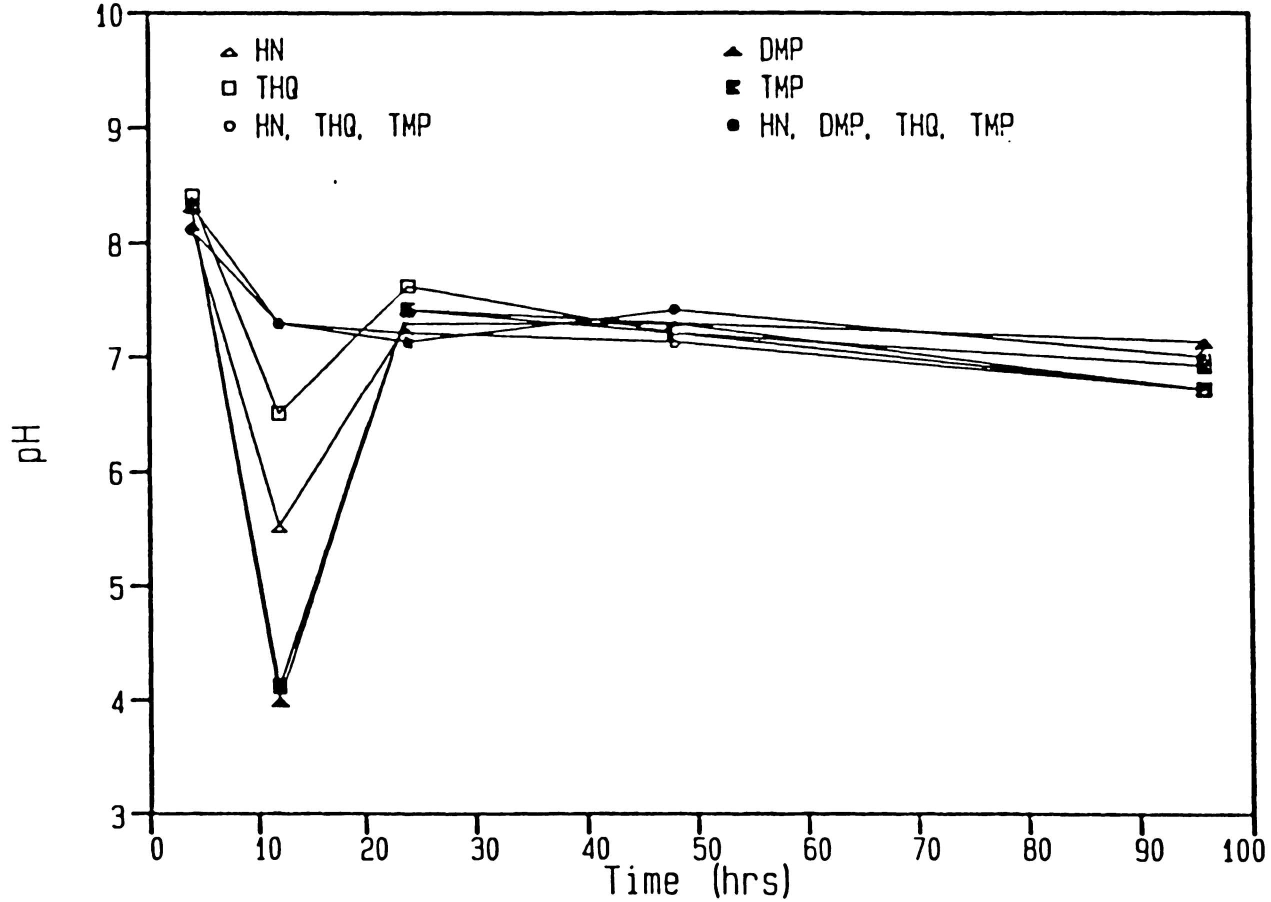

Figure B5. Variation of pH in single-sorbate sorption on the western soil

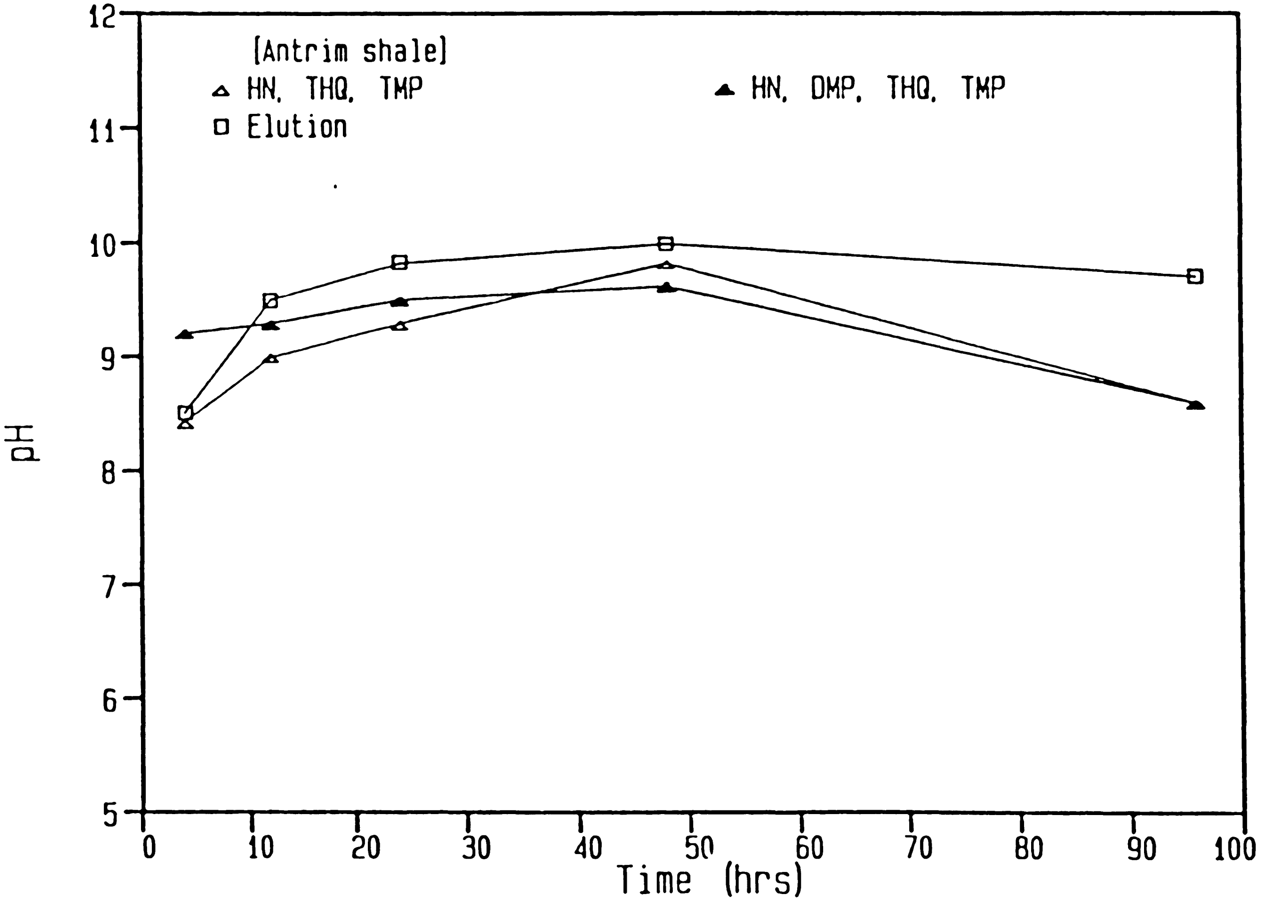

Figure B6. Variation of pH in multicomponent sorption on Antrim shale

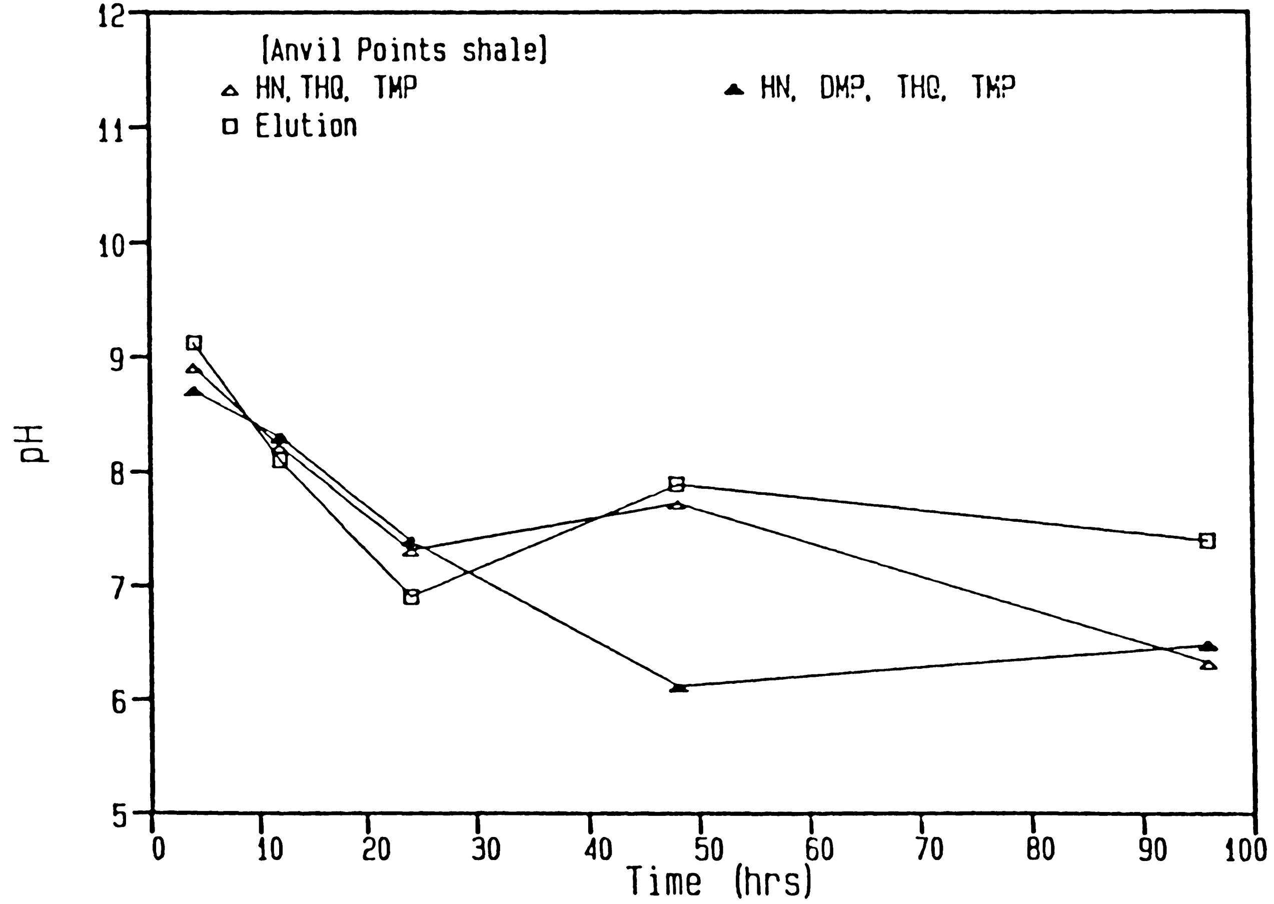

Figure B7. Variation of pH in multicomponent sorption on Anvil Points shale

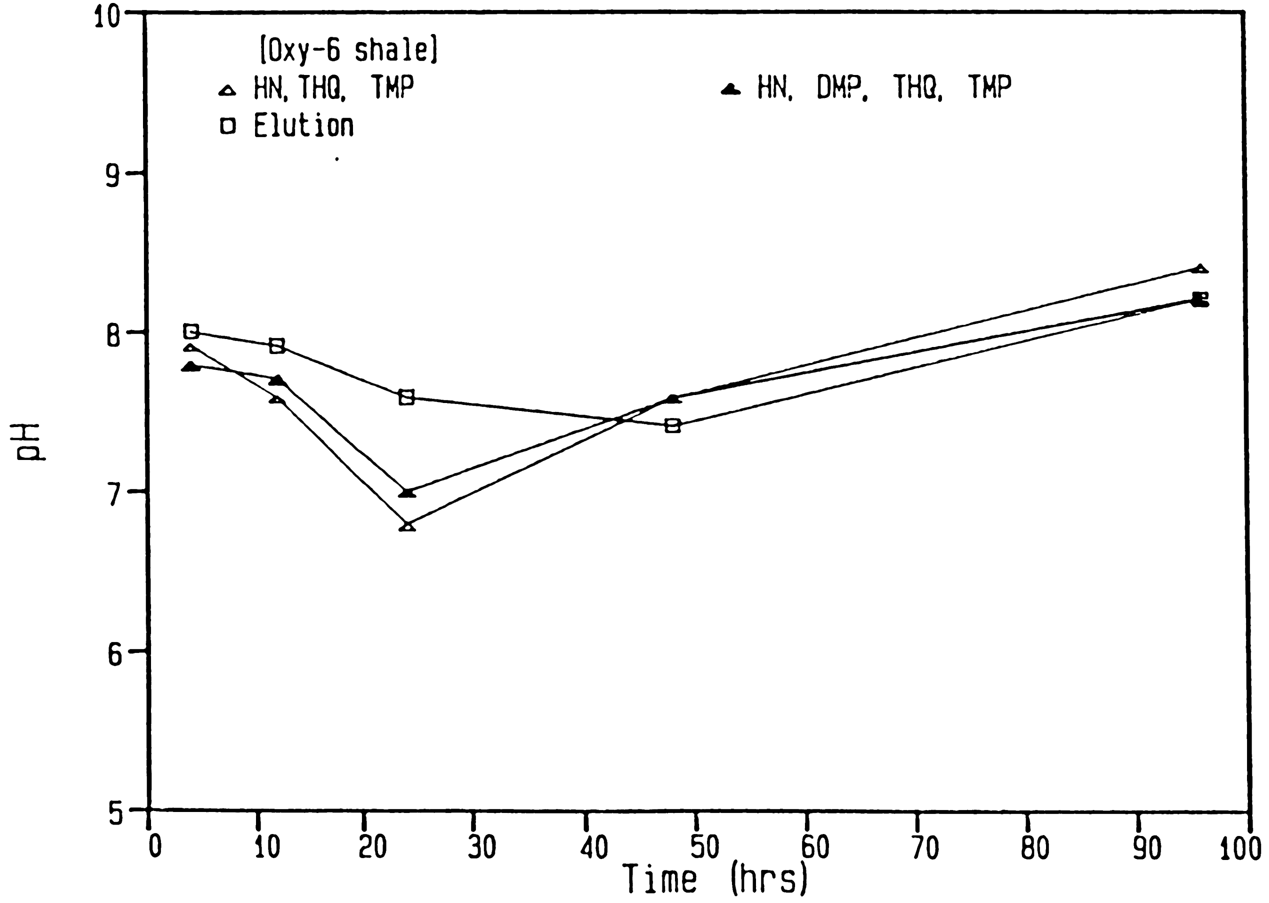

Figure B8. Variation of pH in multicomponent sorption on Oxy 6 shale

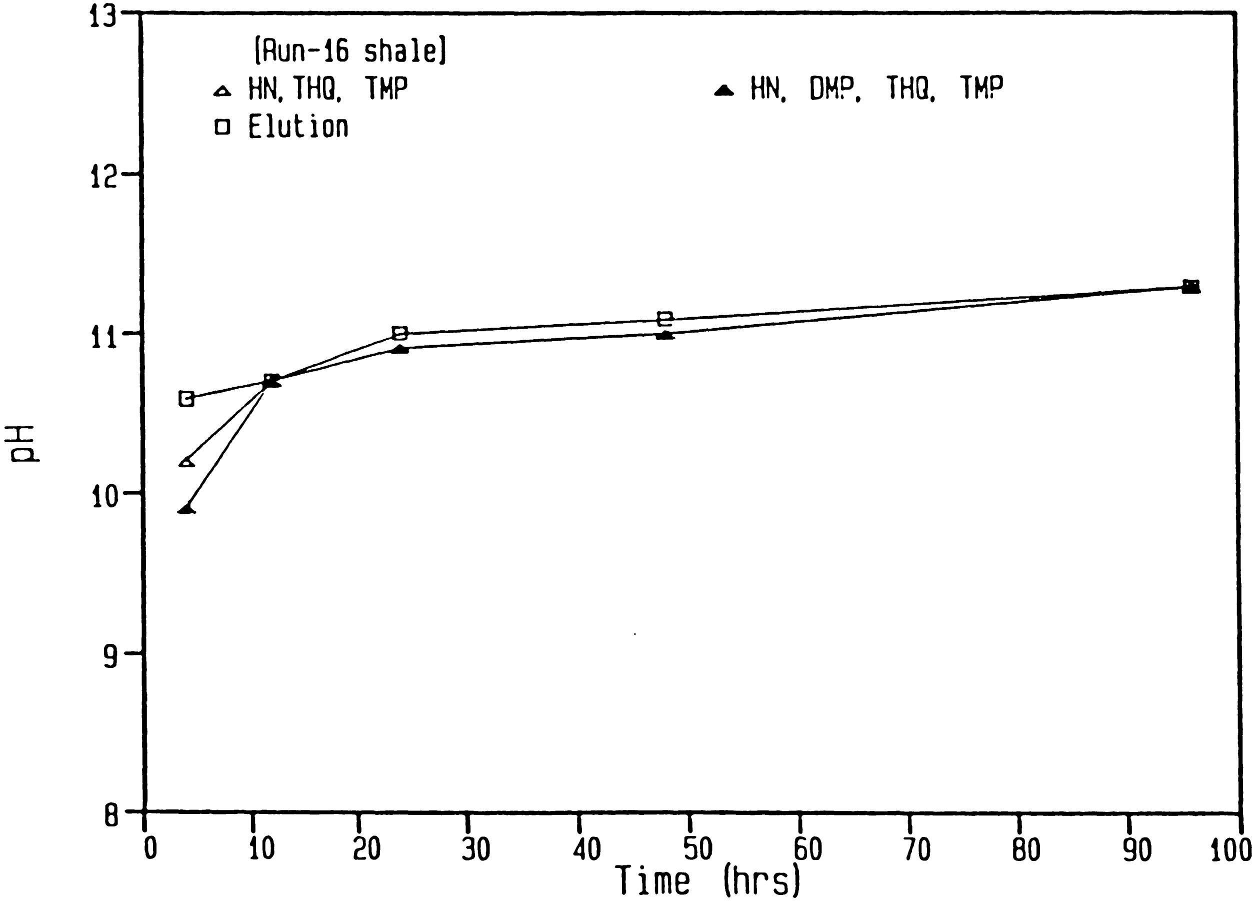

Figure B9. Variation of pH in multicomponent sorption on Run 16 shale

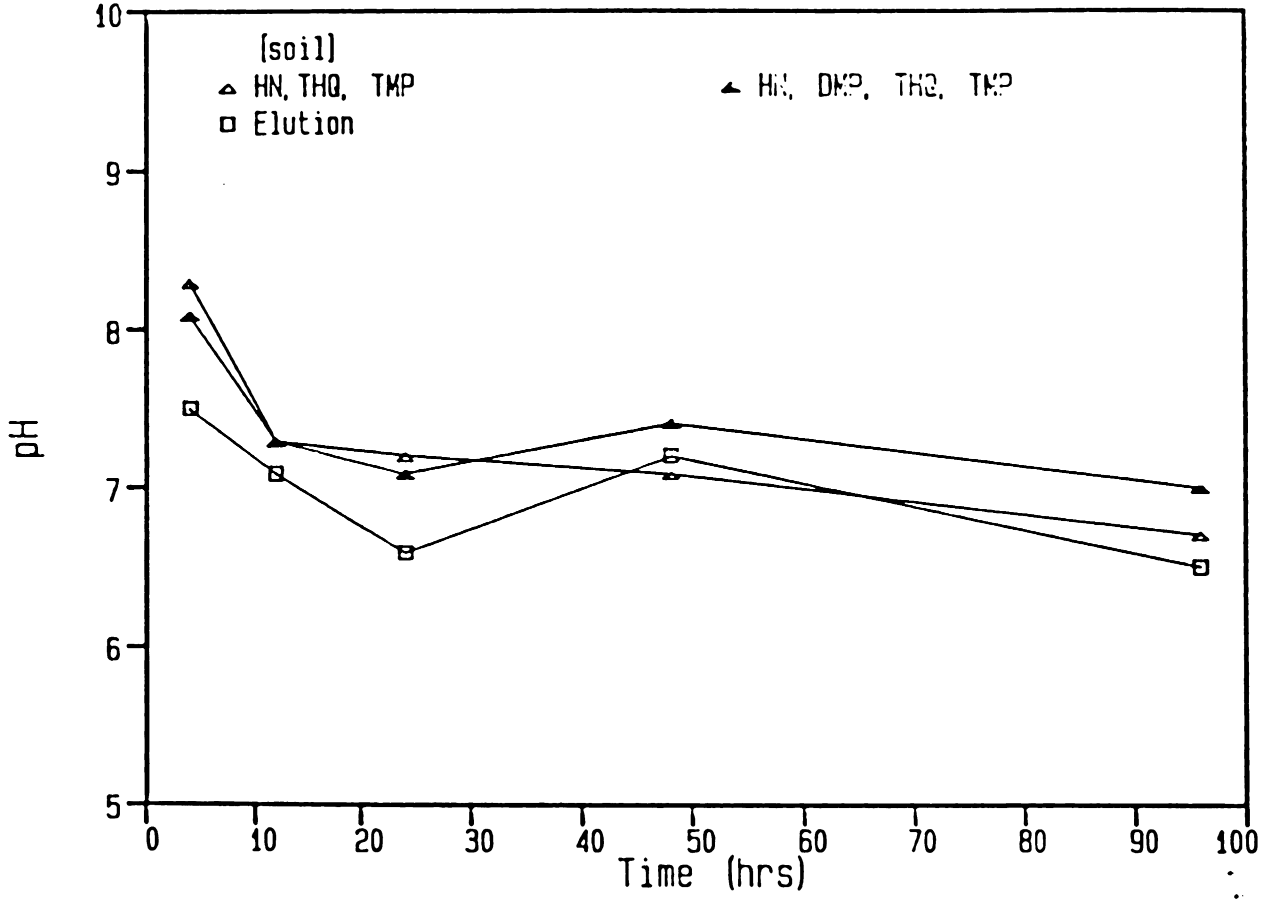

Figure B10. Variation of pH in multicomponent sorption on the western soil

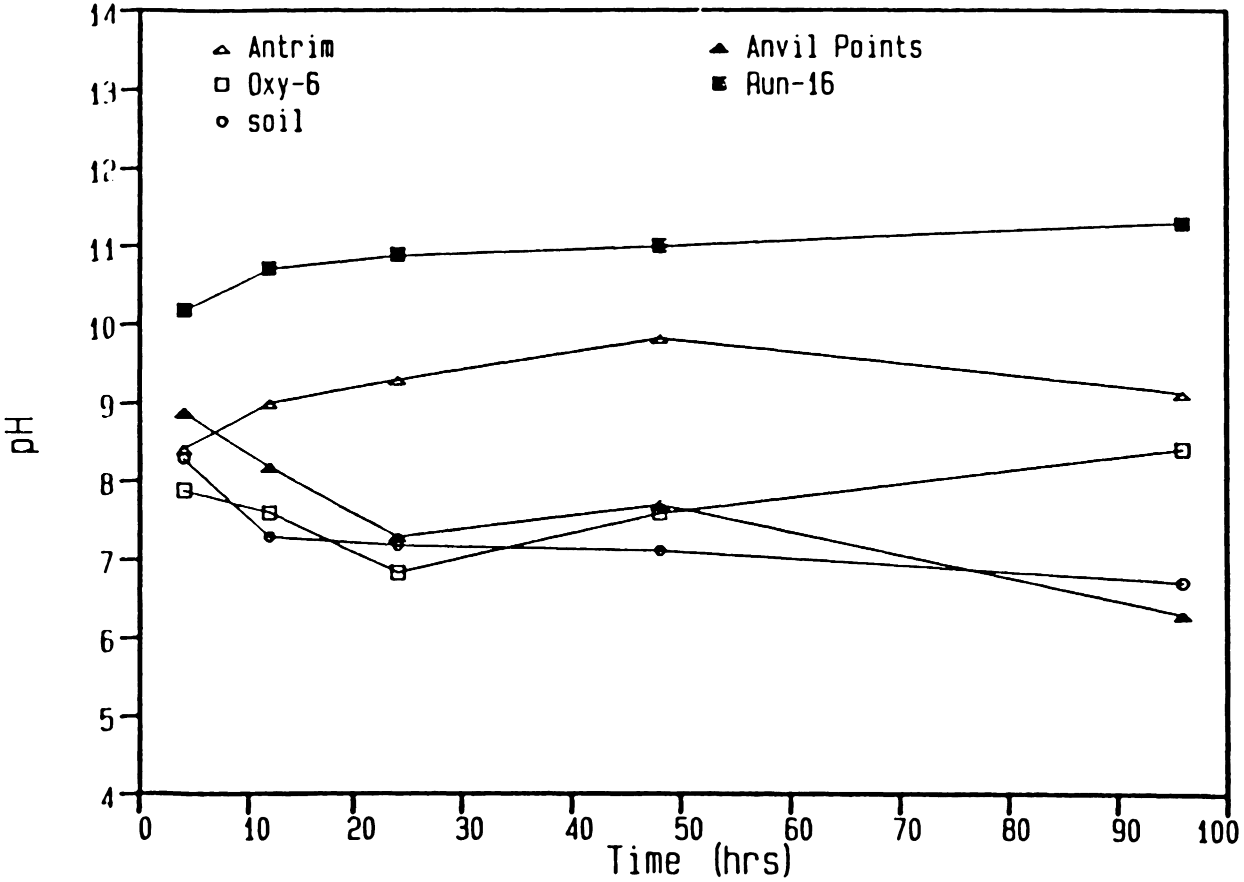

Figure B11. Variation of pH in three component solution

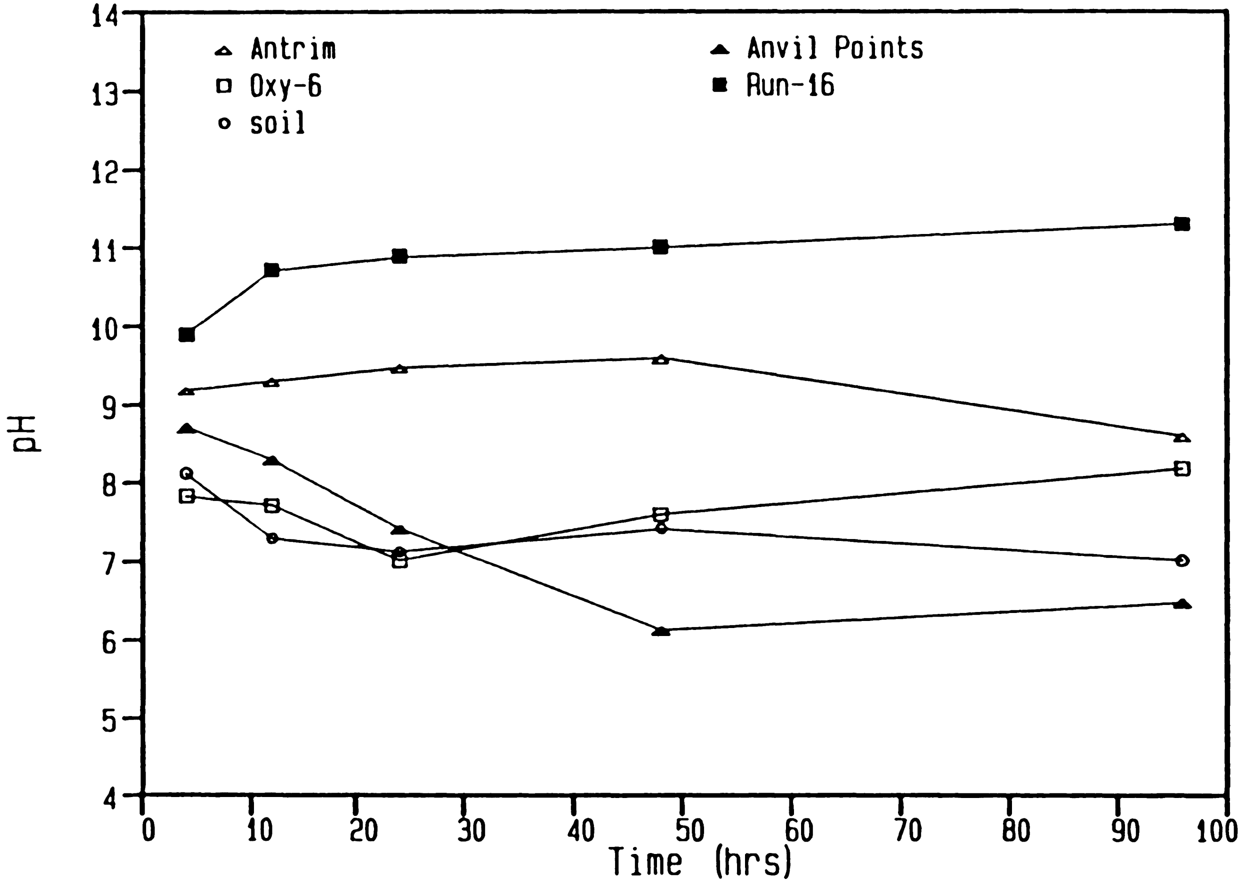

Figure B12. Variation of pH in four component solution

Appendix C. Sorption of HN, THQ, TMP in Single- and Multi-component Solutions

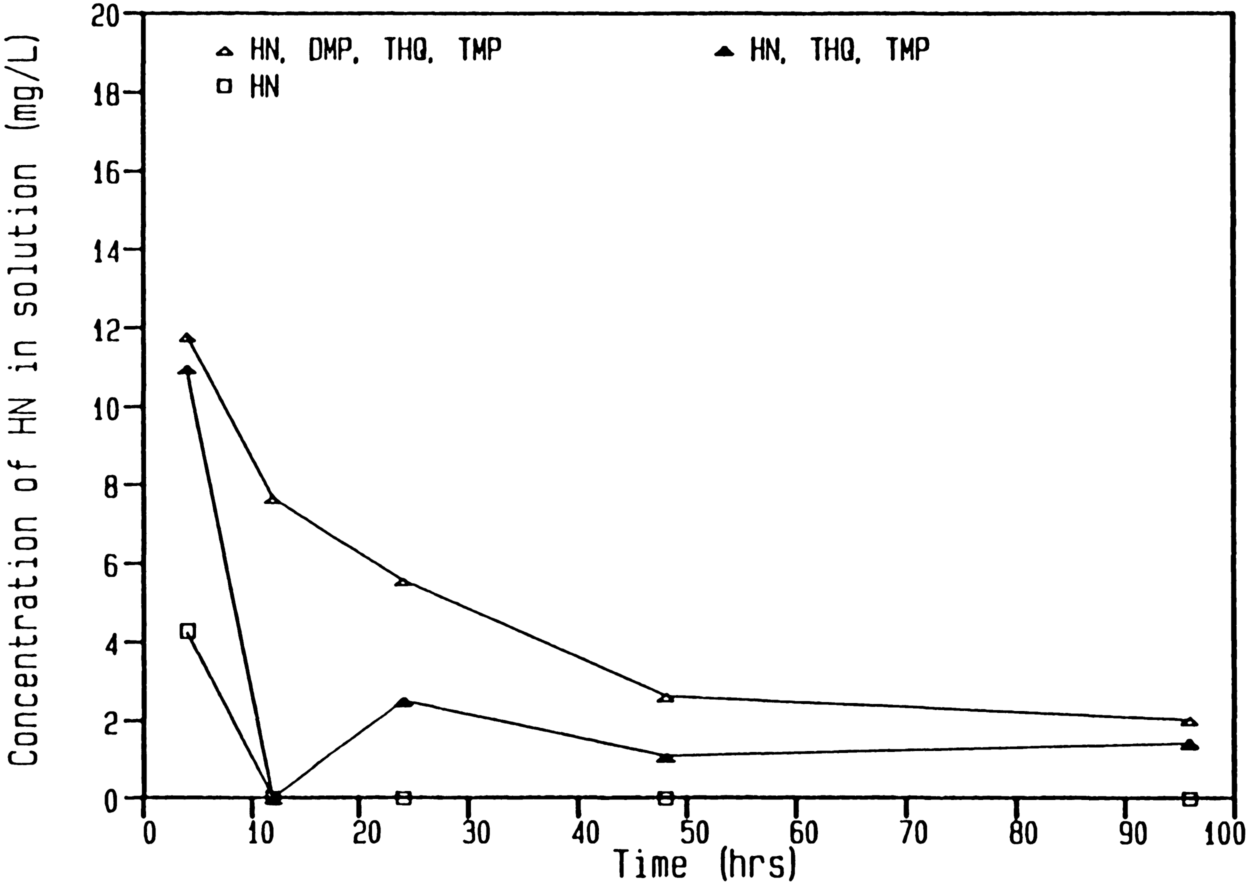

Figure C1. Sorption of HN on Antrim shale: ($C_0 = 25$ mg/L)

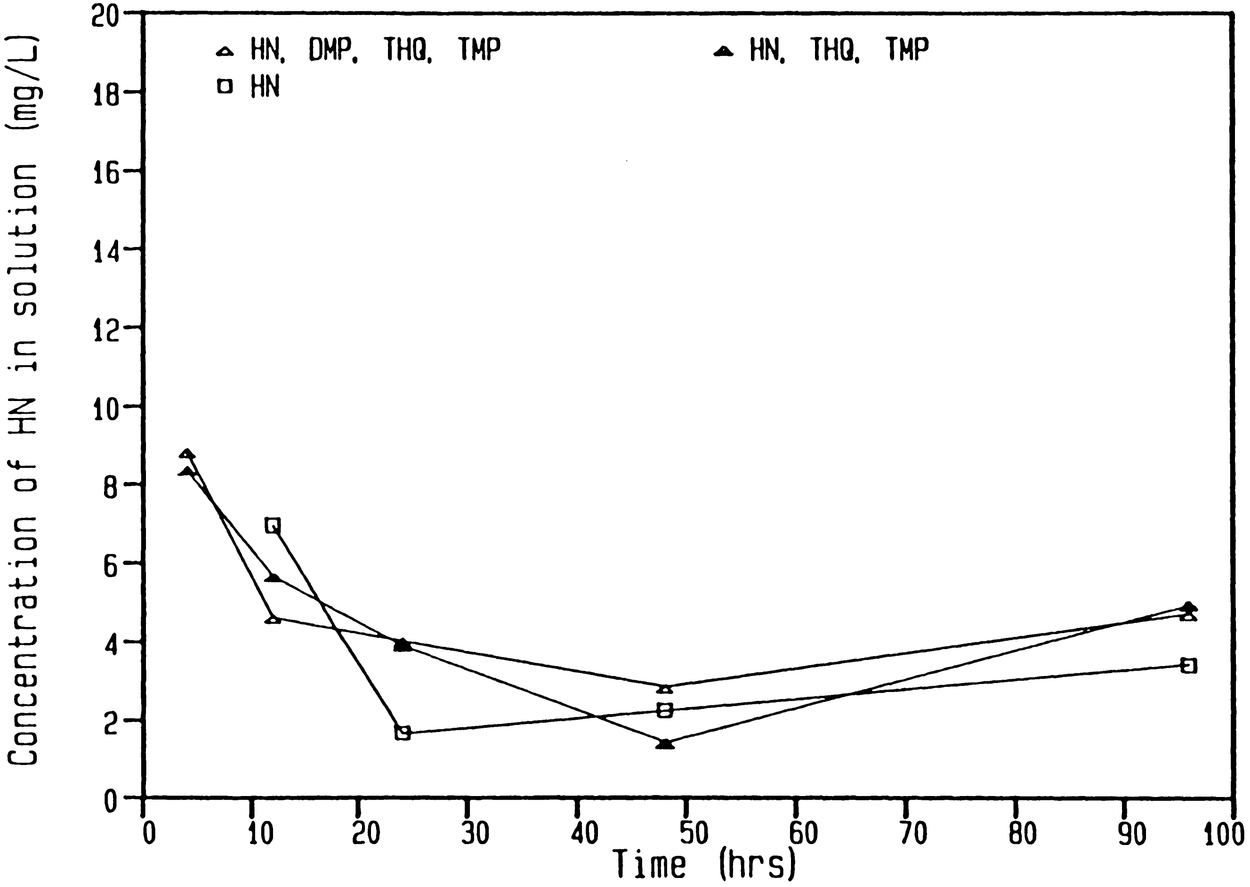

Figure C2. Sorption of HN on Anvil Points shale: (C_0 = 25 mg/L)

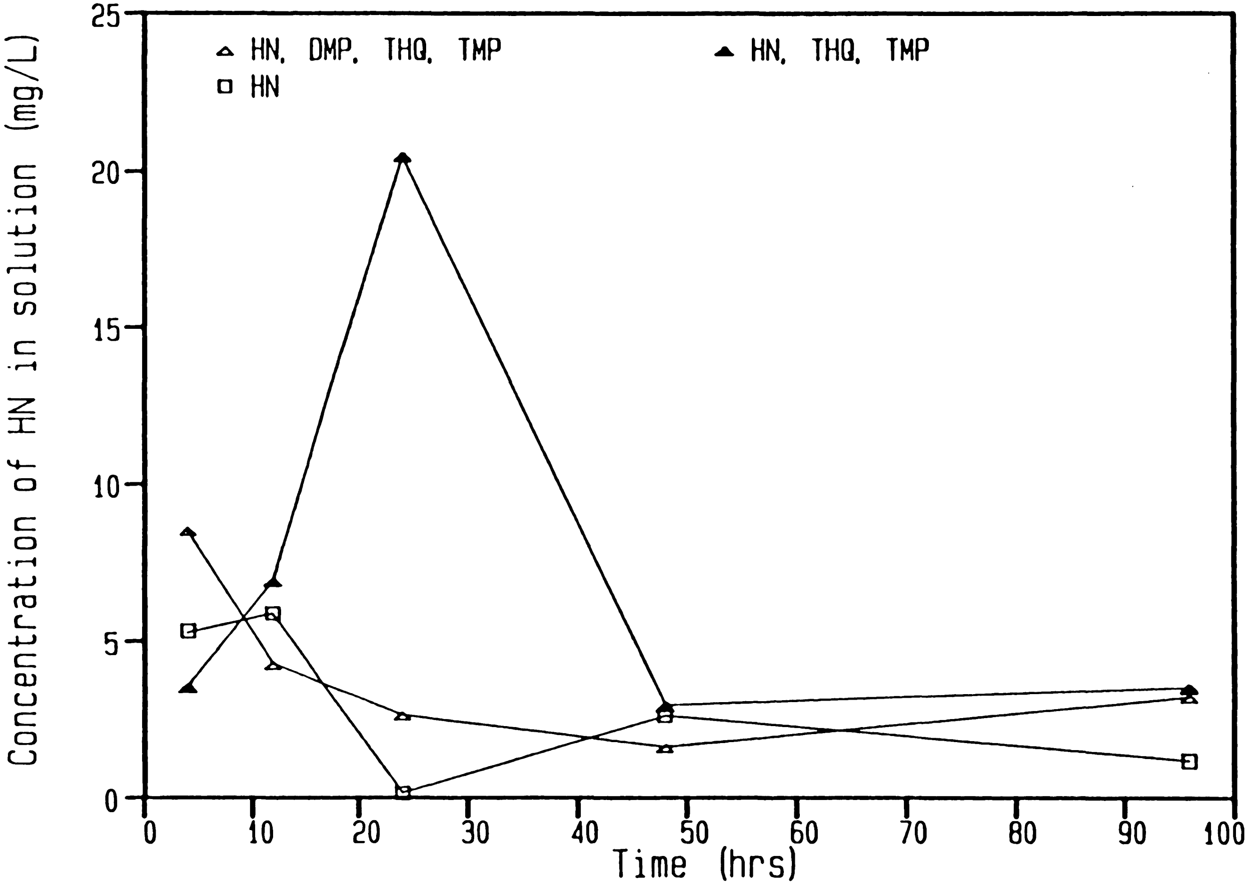

Figure C3. Sorption of HN on Oxy 6 shale: ($C_0 = 25$ mg/L)

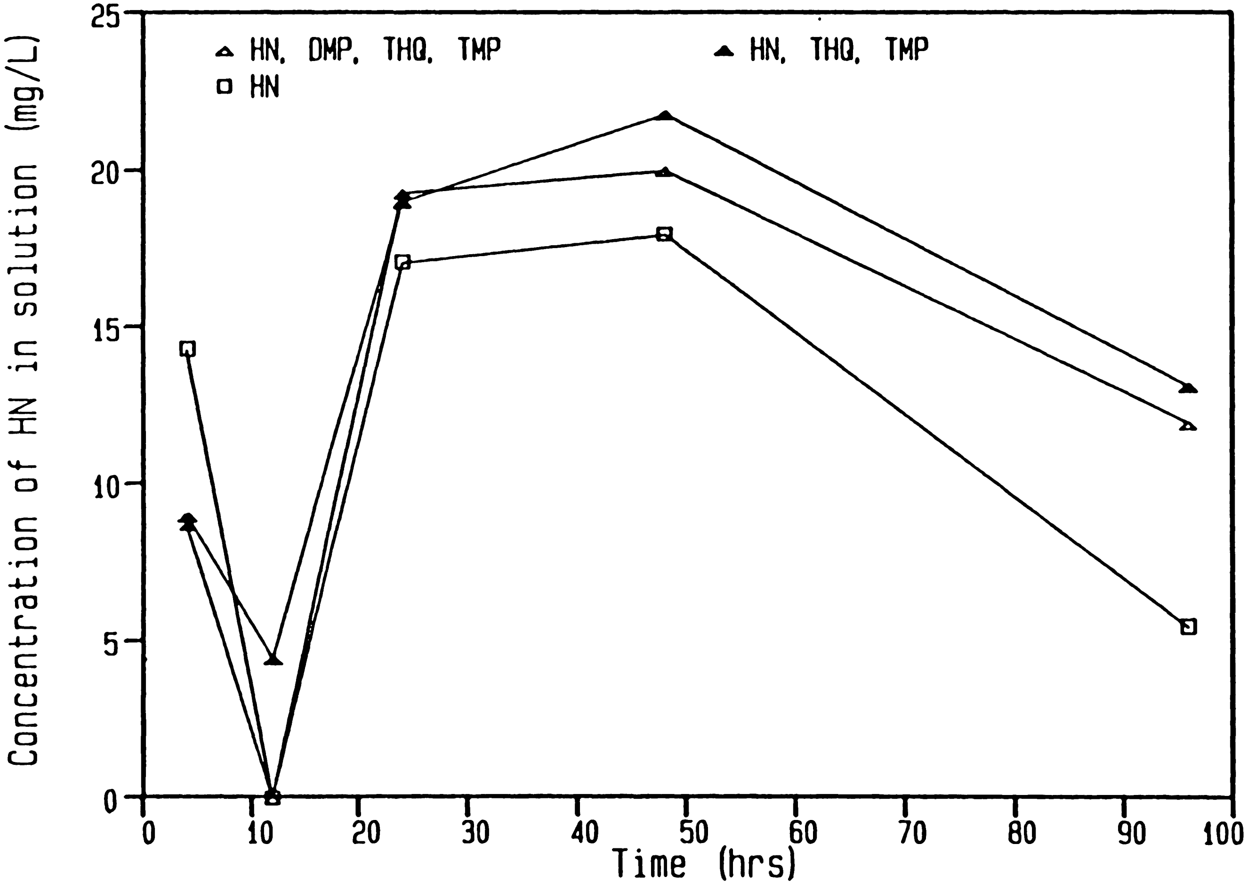

Figure C4. Sorption of HN on Run 16 shale: ($C_0 = 25$ mg/L)

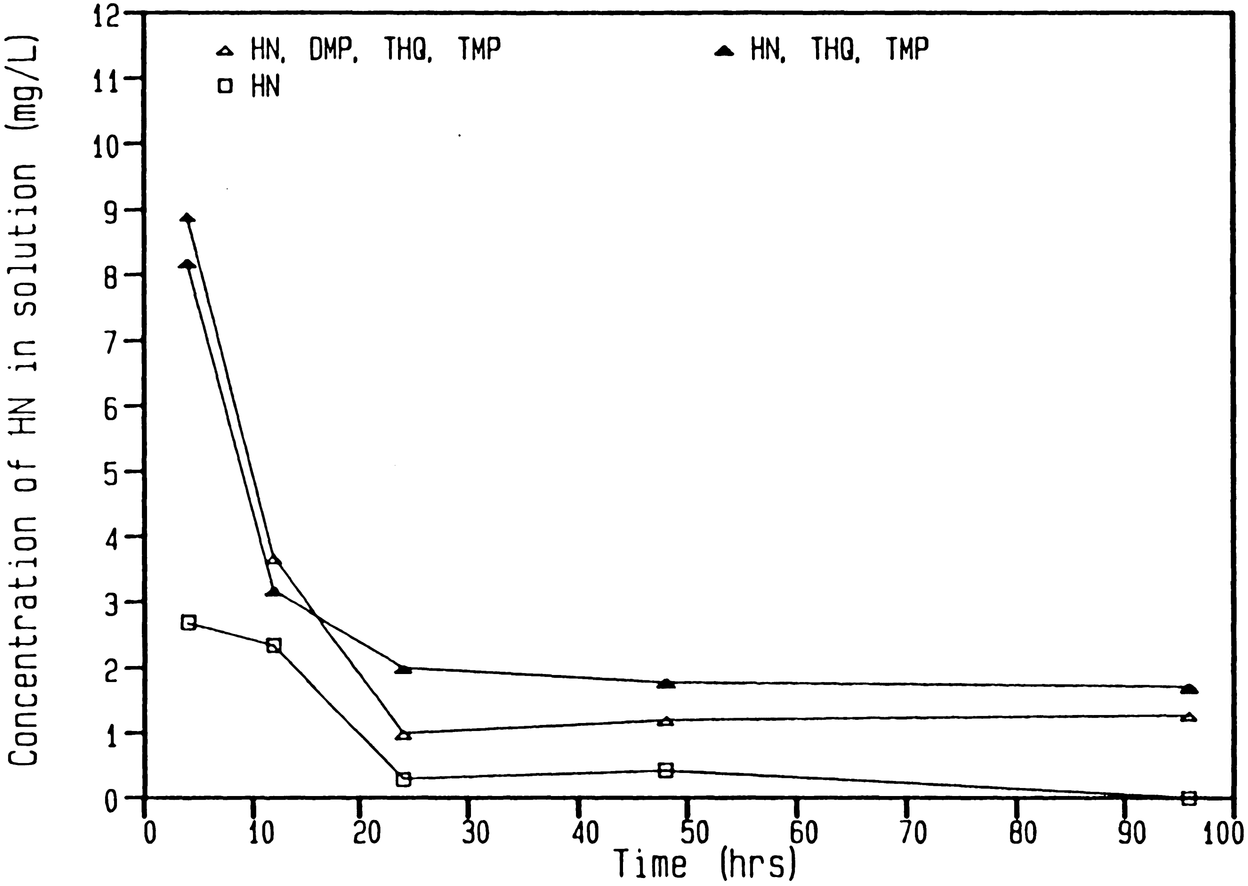

Figure C5. Sorption of HN on the western soil: ($C_0 = 25$ mg/L)

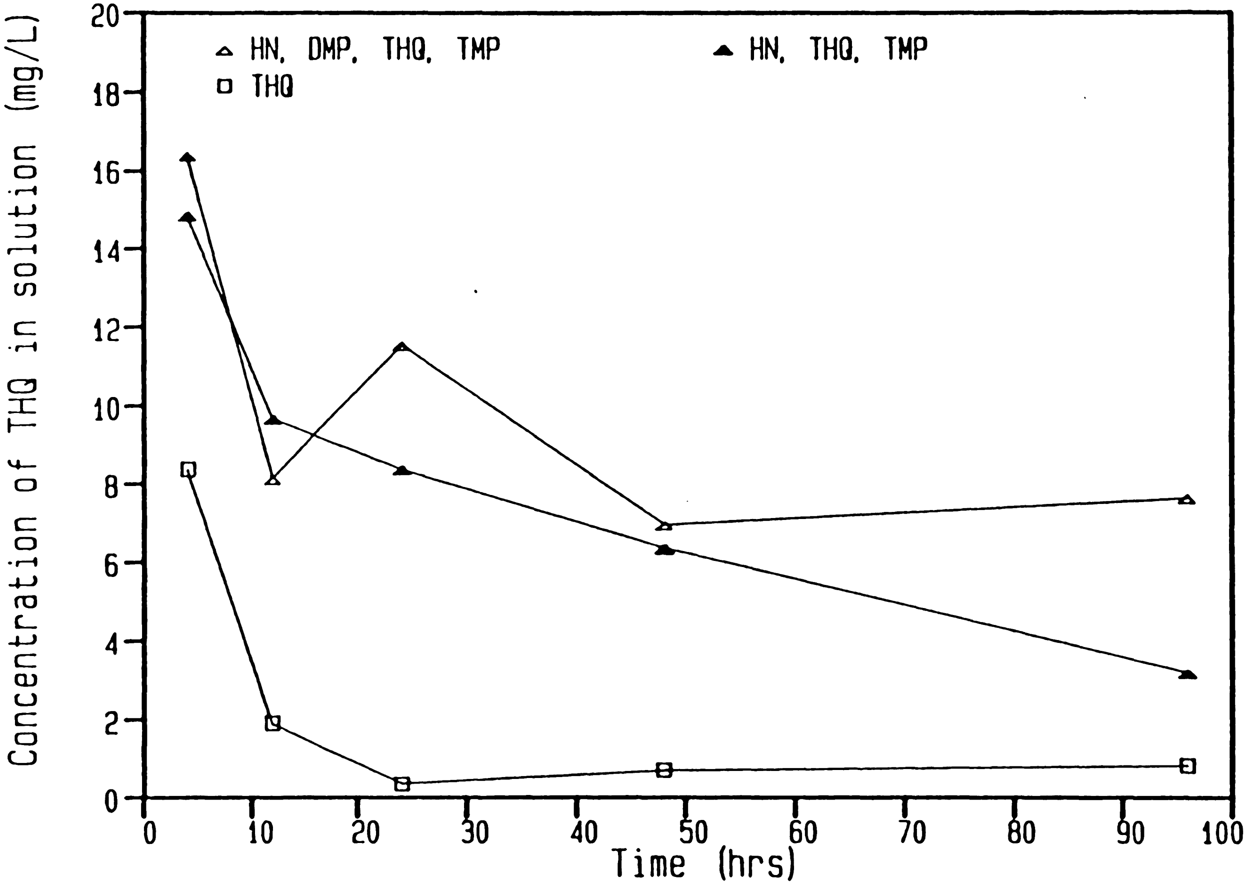

Figure C6. Sorption of THQ on Antrim shale: ($C_0 = 25$ mg/L)

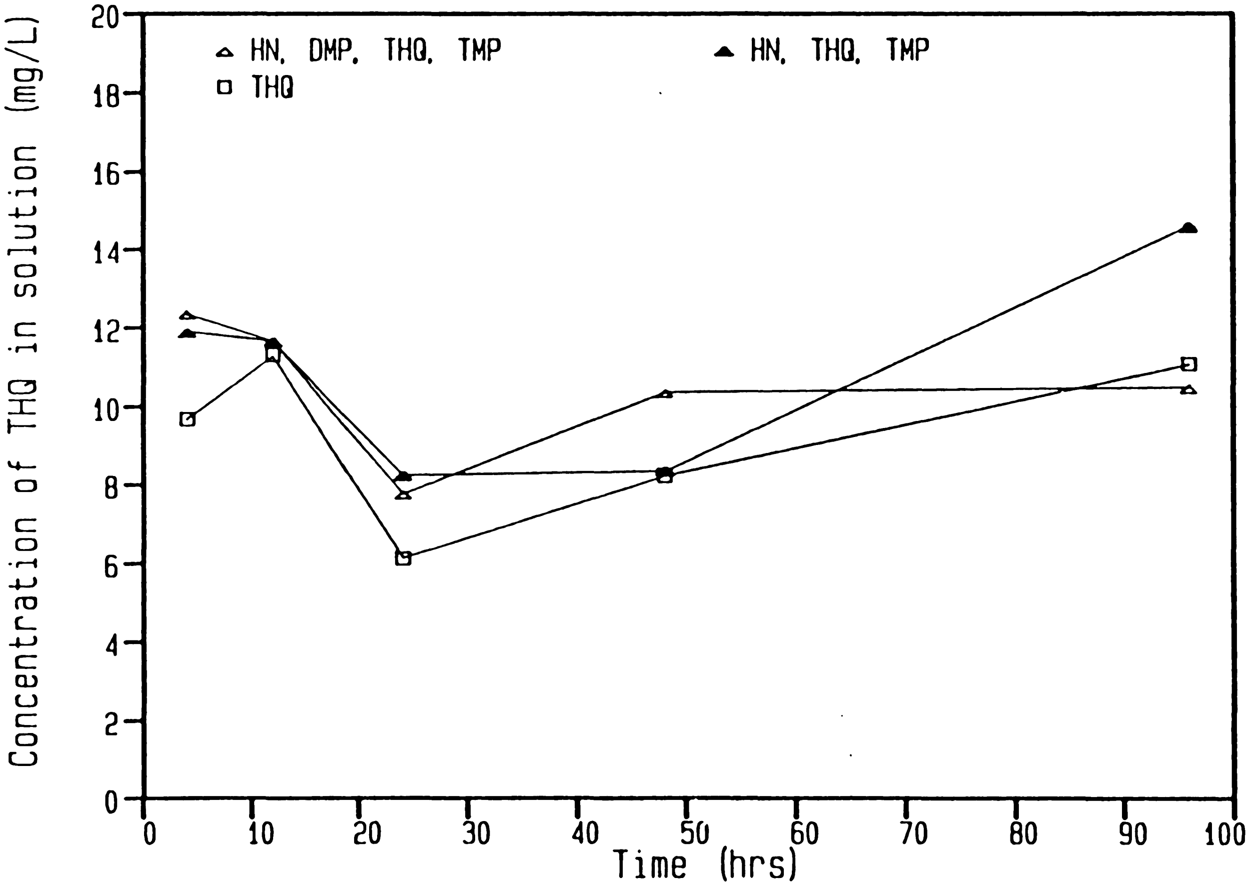

Figure C7. Sorption of THQ on Anvil Points shale: ($C_0 = 25$ mg/L)

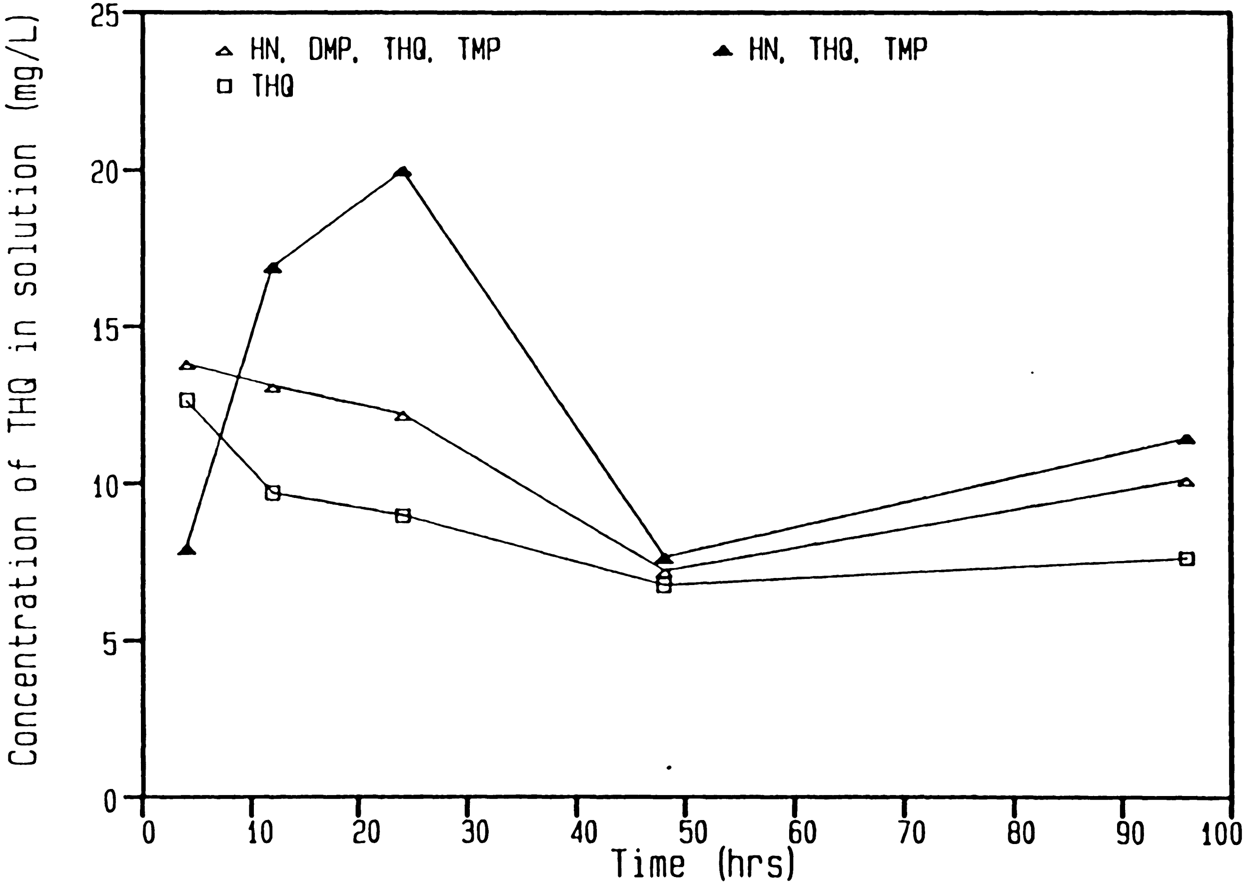

Figure C8. Sorption of THQ on Oxy 6 shale: ($C_0 = 25$ mg/L)

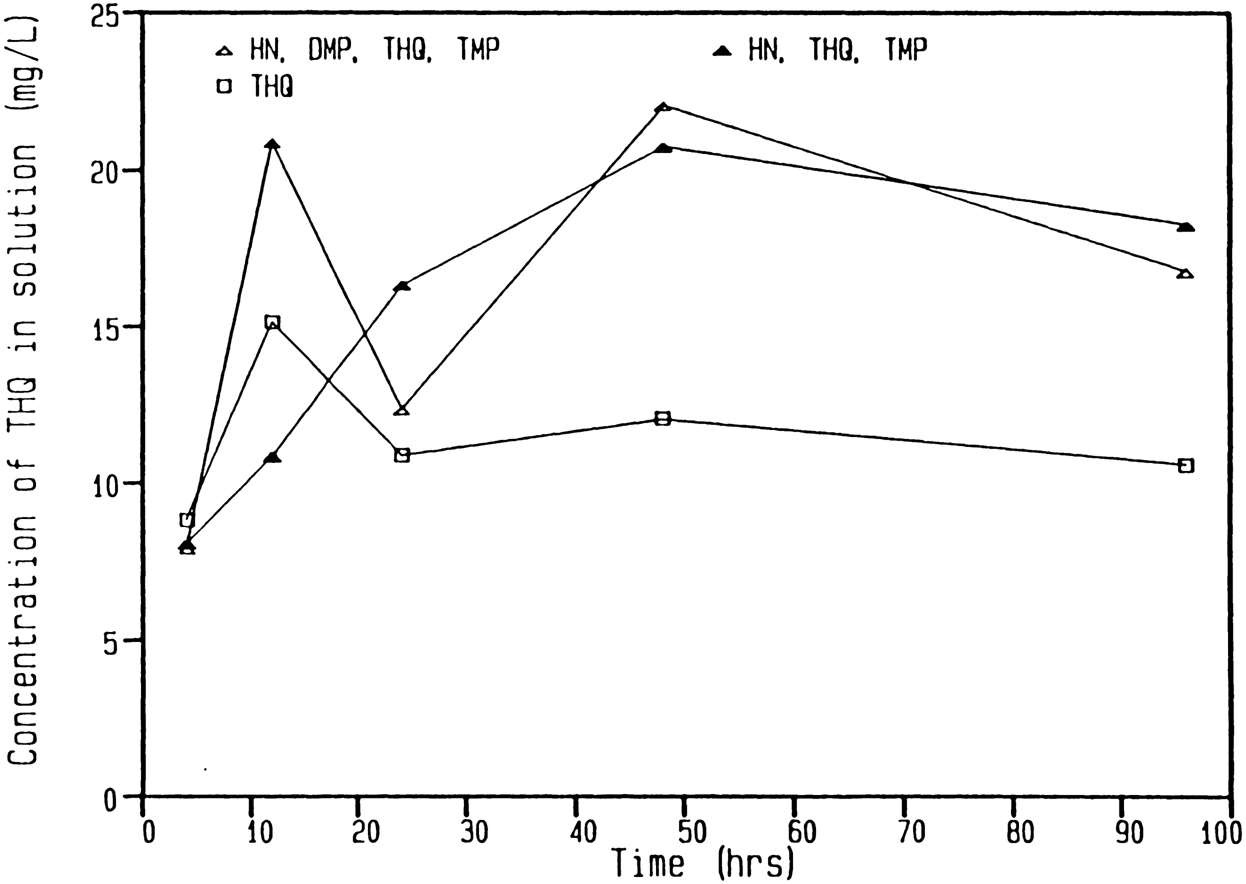

Figure C9. Sorption of THQ on Run 16 shale: ($C_0 = 25$ mg/L)

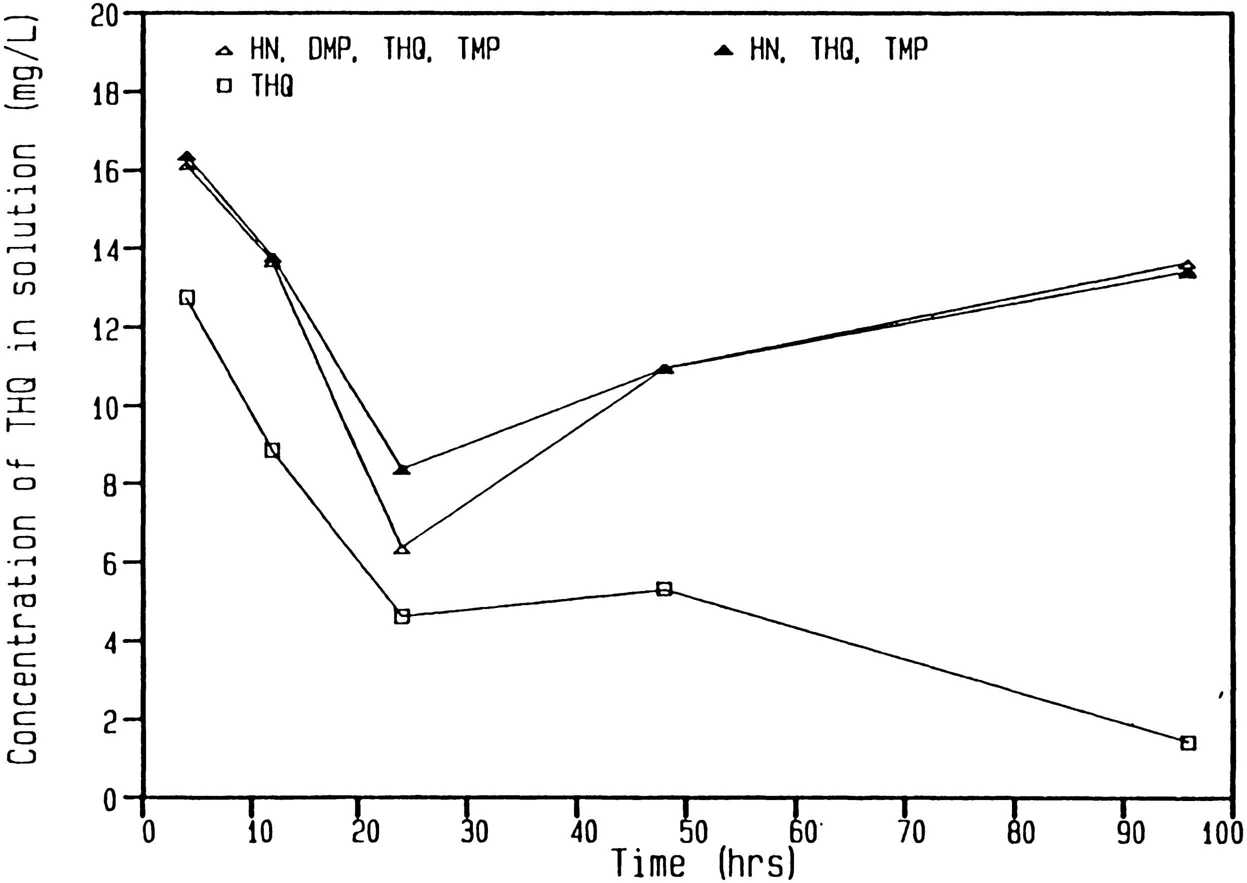

Figure C10. Sorption of THQ on the western soil: ($C_0 = 25$ mg/L)

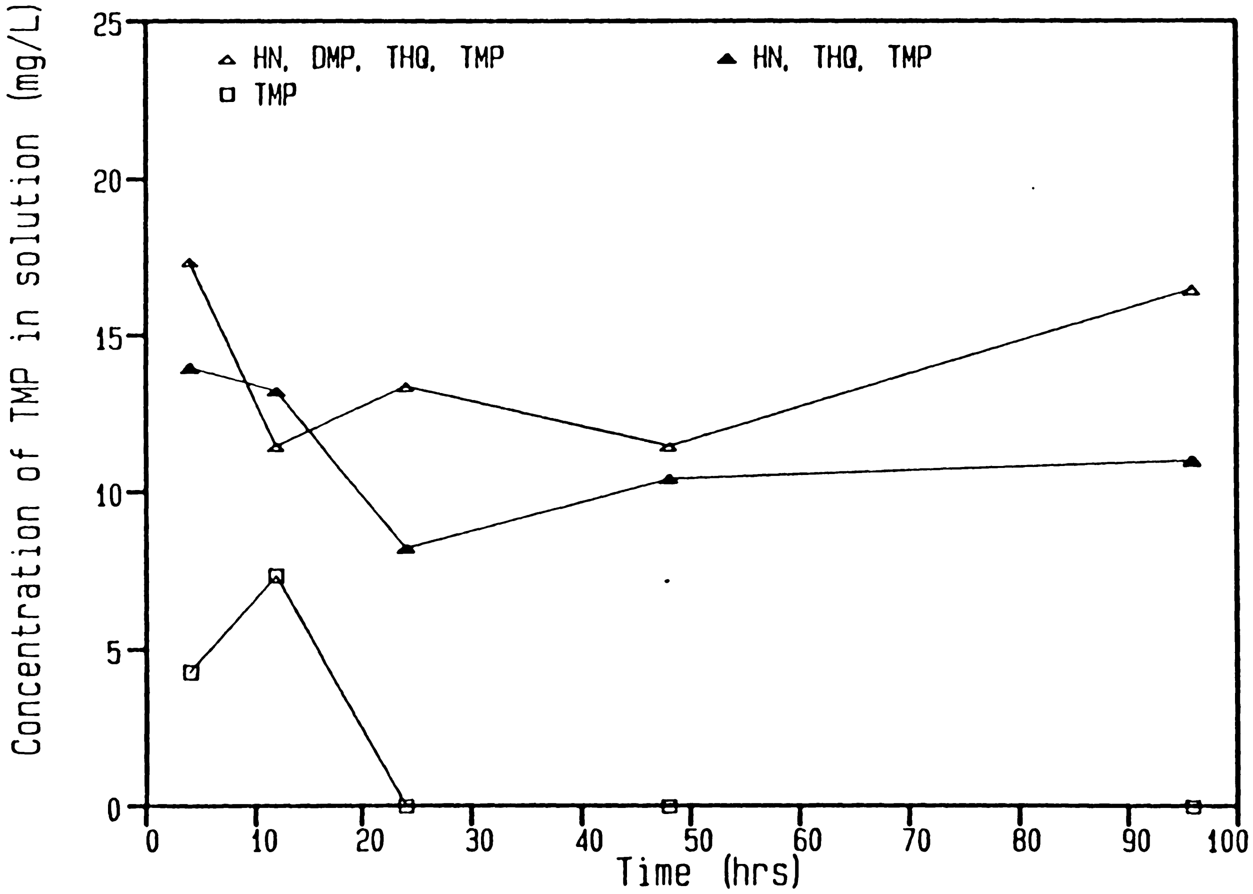

Figure C11. Sorption of TMP on Antrim shale: ($C_0 = 25$ mg/L)

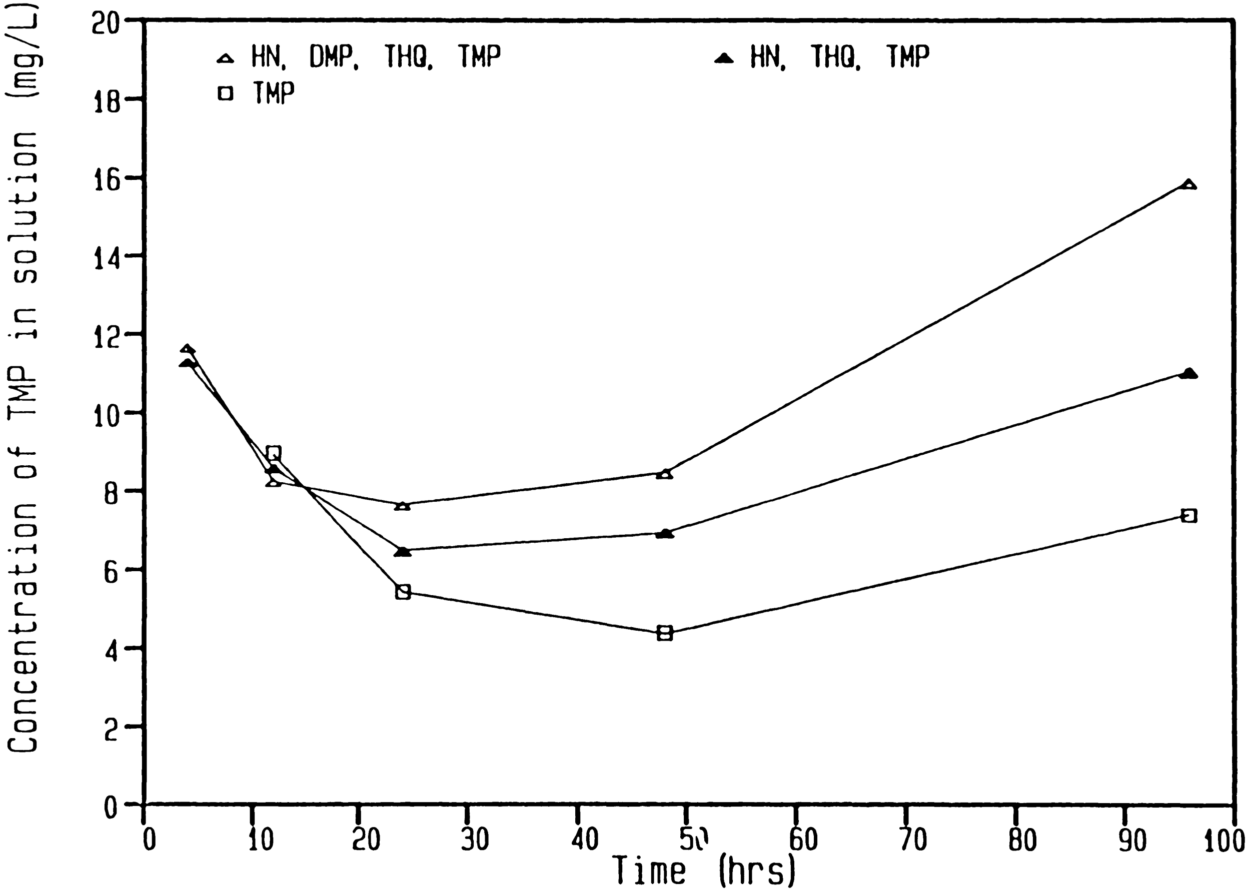

Figure C12. Sorption of TMP on Anvil Points shale: ($C_0 = 25$ mg/L)

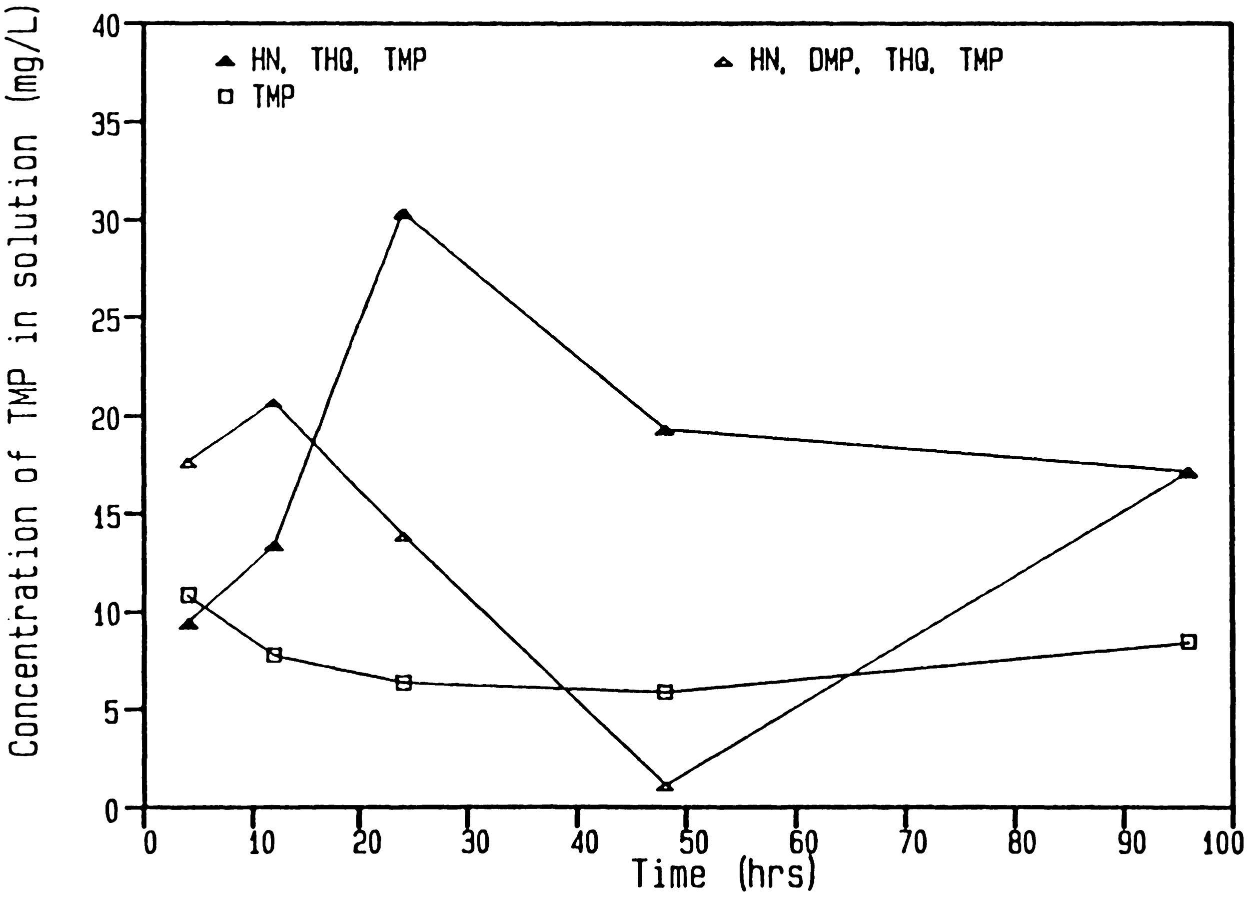

Figure C13. Sorption of TMP on Oxy 6 shale: ($C_0 = 25$ mg/L)

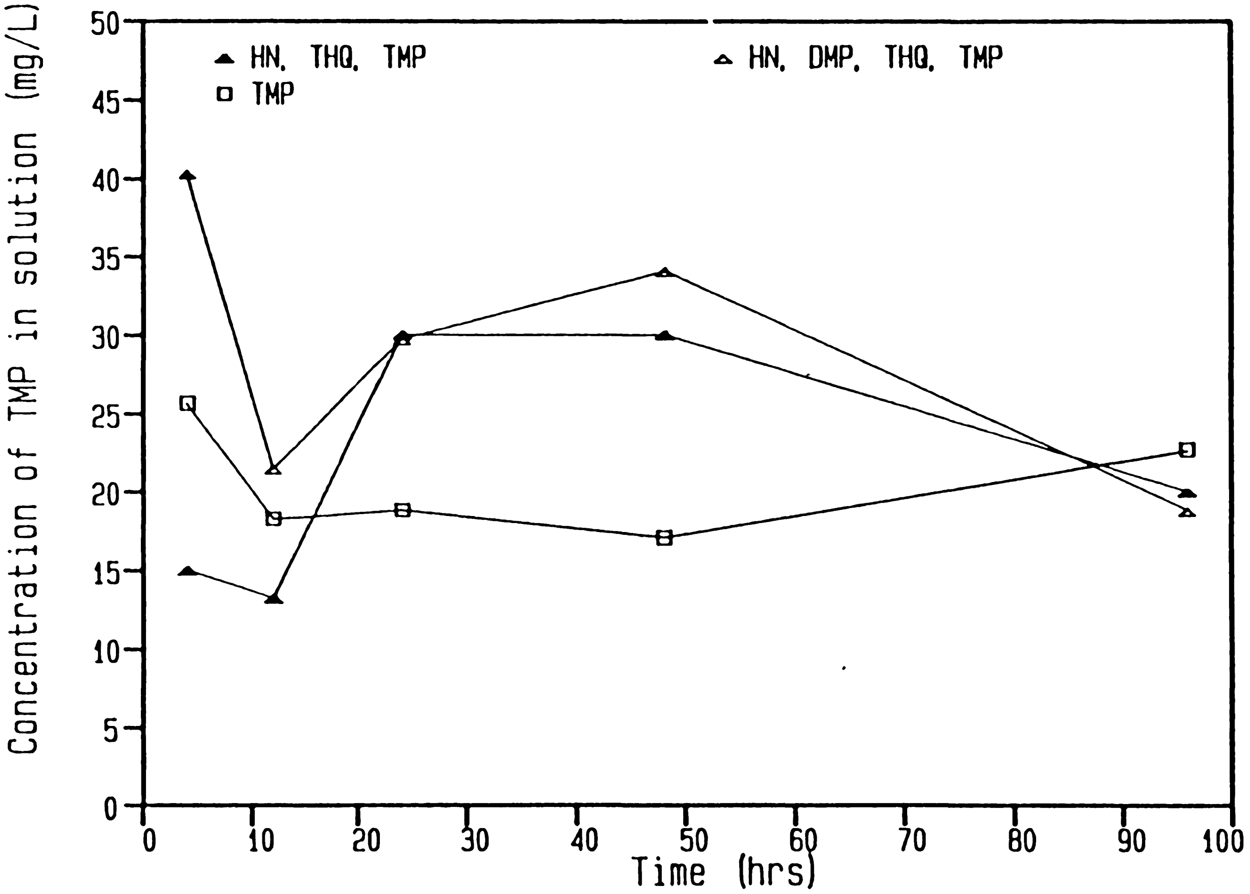

Figure C14. Sorption of TMP on Run 16 shale: ($C_0 = 25$ mg/L)

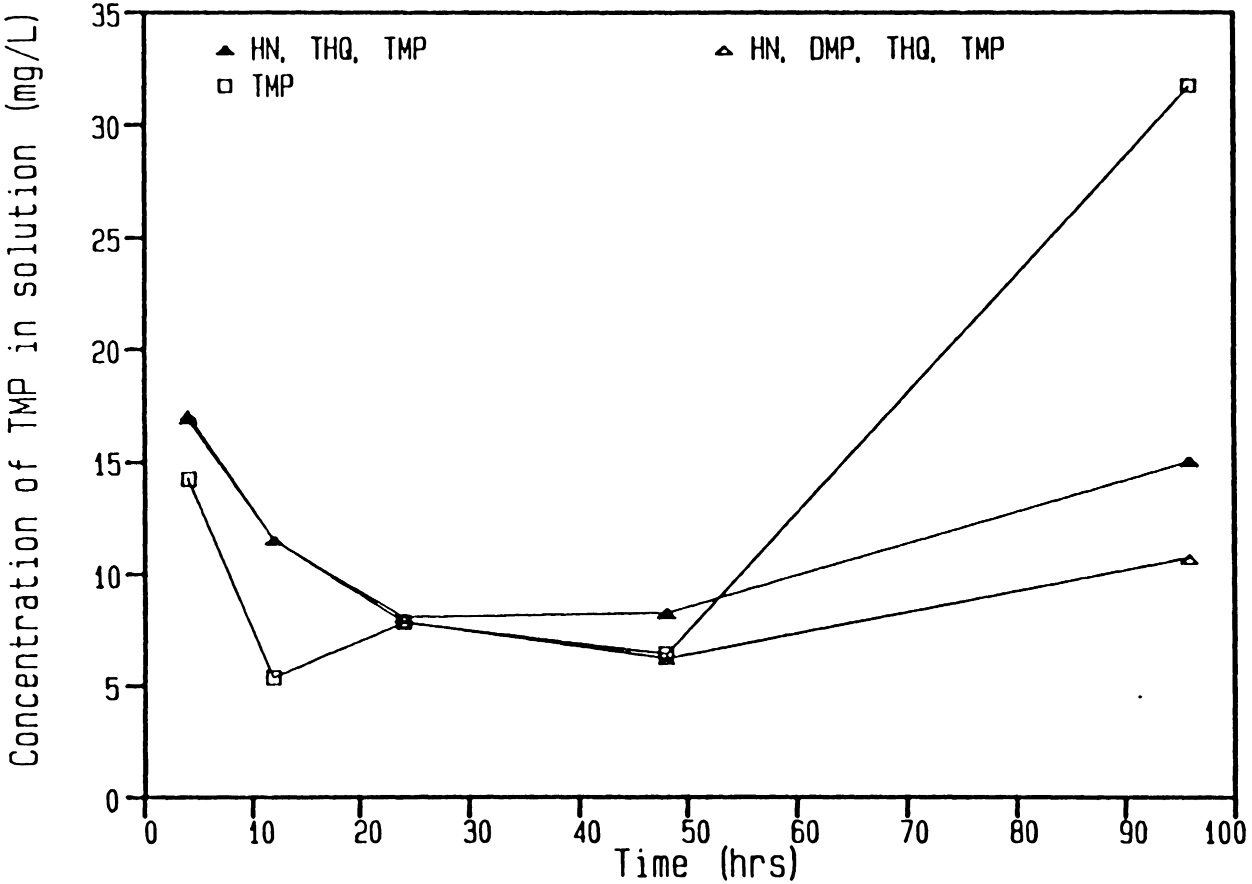

Figure C15. Sorption of TMP on the western soil: (C_0=25 mg/L)

Appendix D. Variation of pH in Batch Sorption of Inorganic Ions

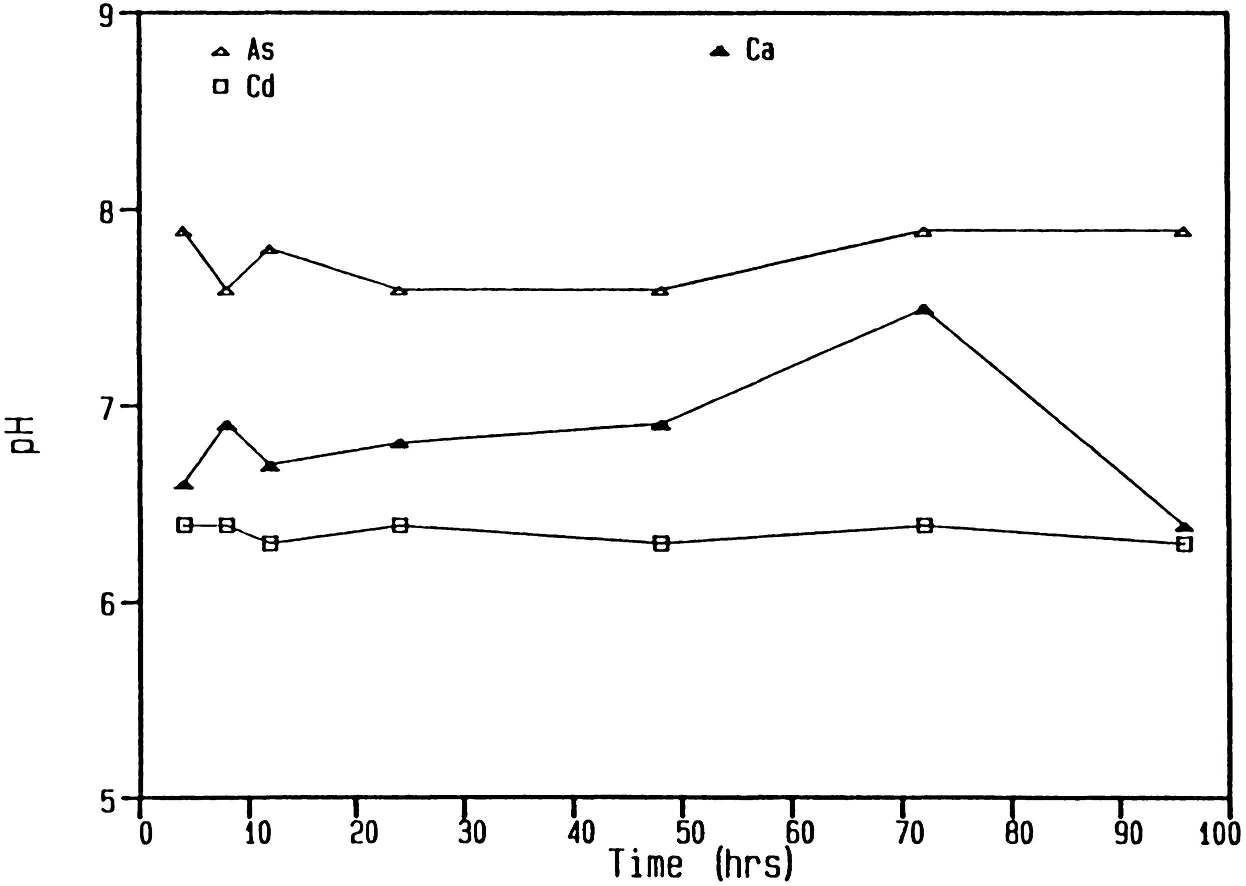

Figure D1. Variation of pH in sorption of cations (I)

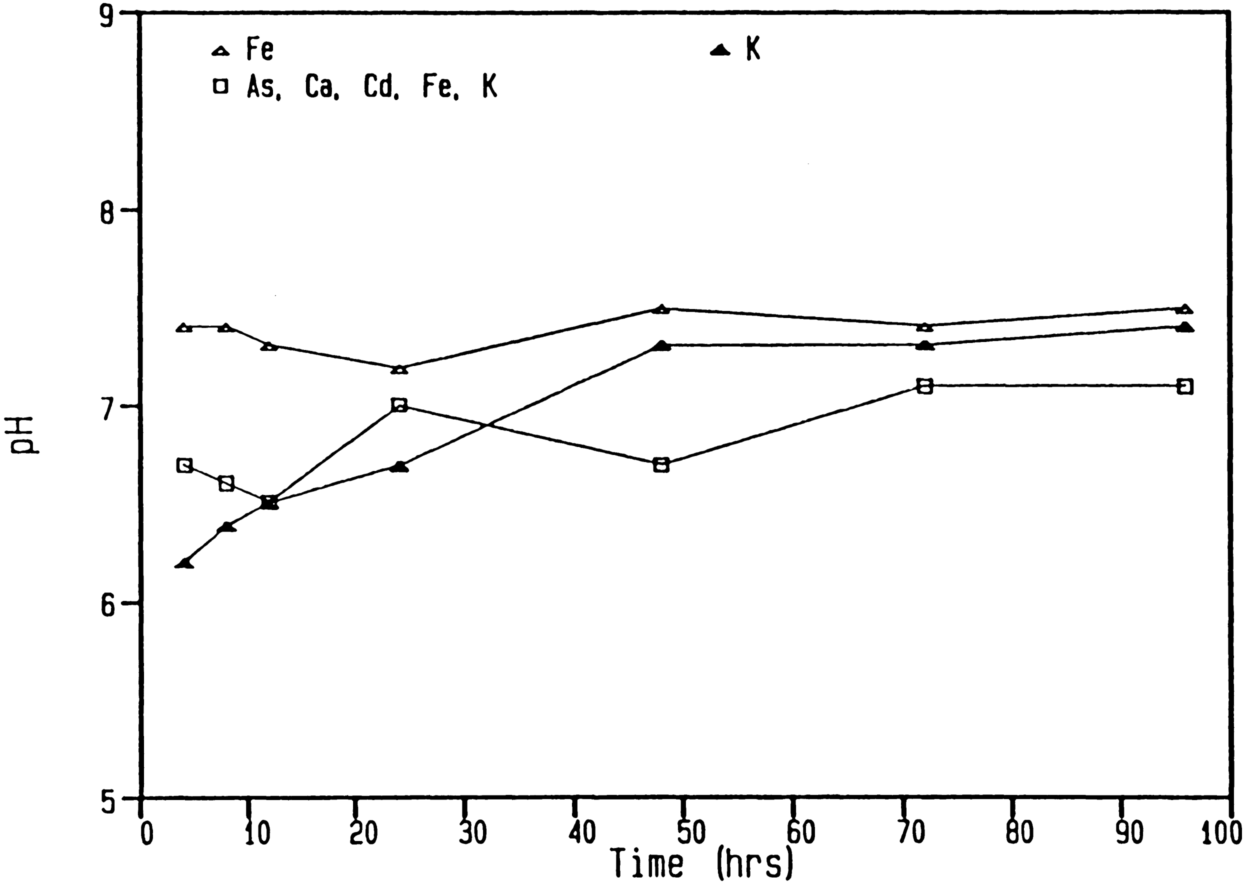

Figure D2. Variation of pH in sorption of cations (II)

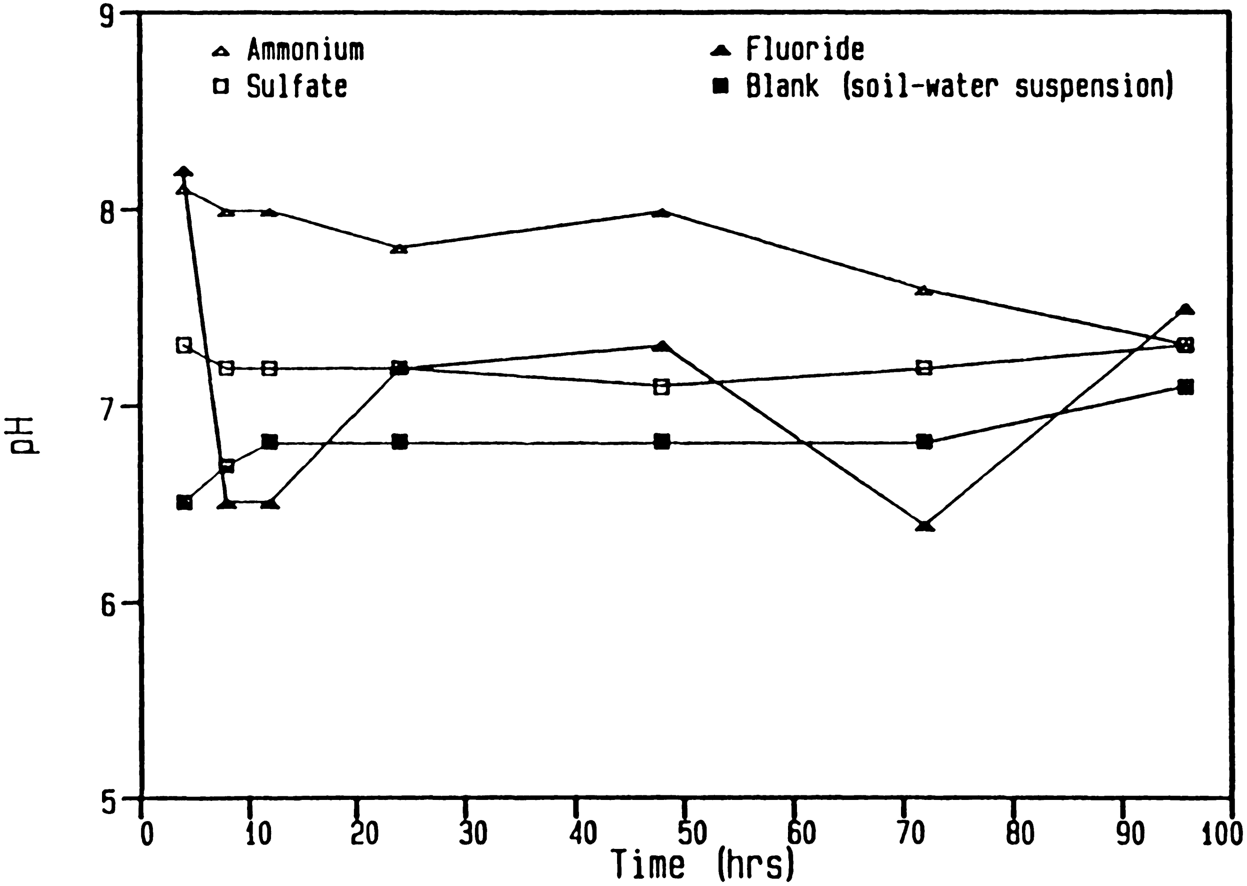

Figure D3. Variation of pH in sorption of NH_4, SO_4, and F

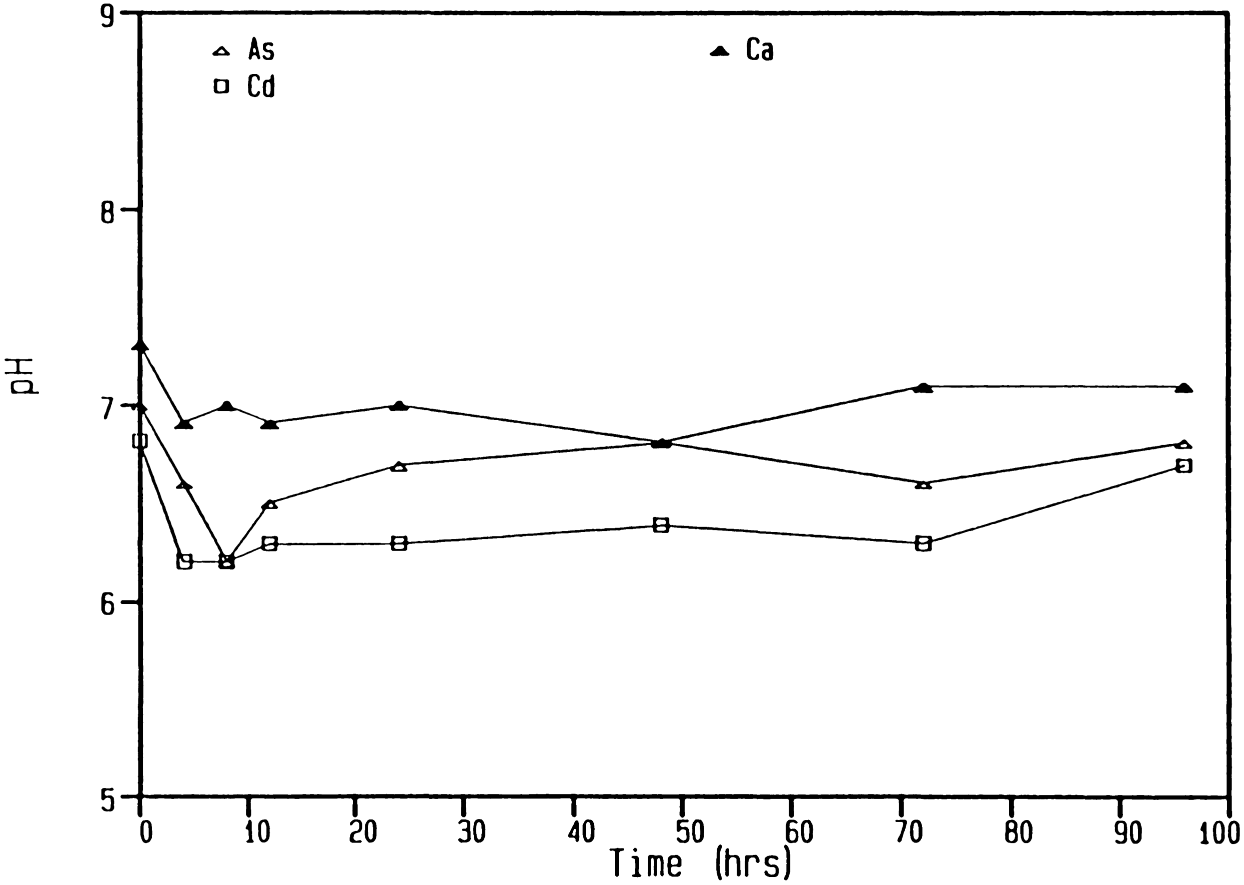

Figure D4. Variation of pH in sorption controls of cations (I)

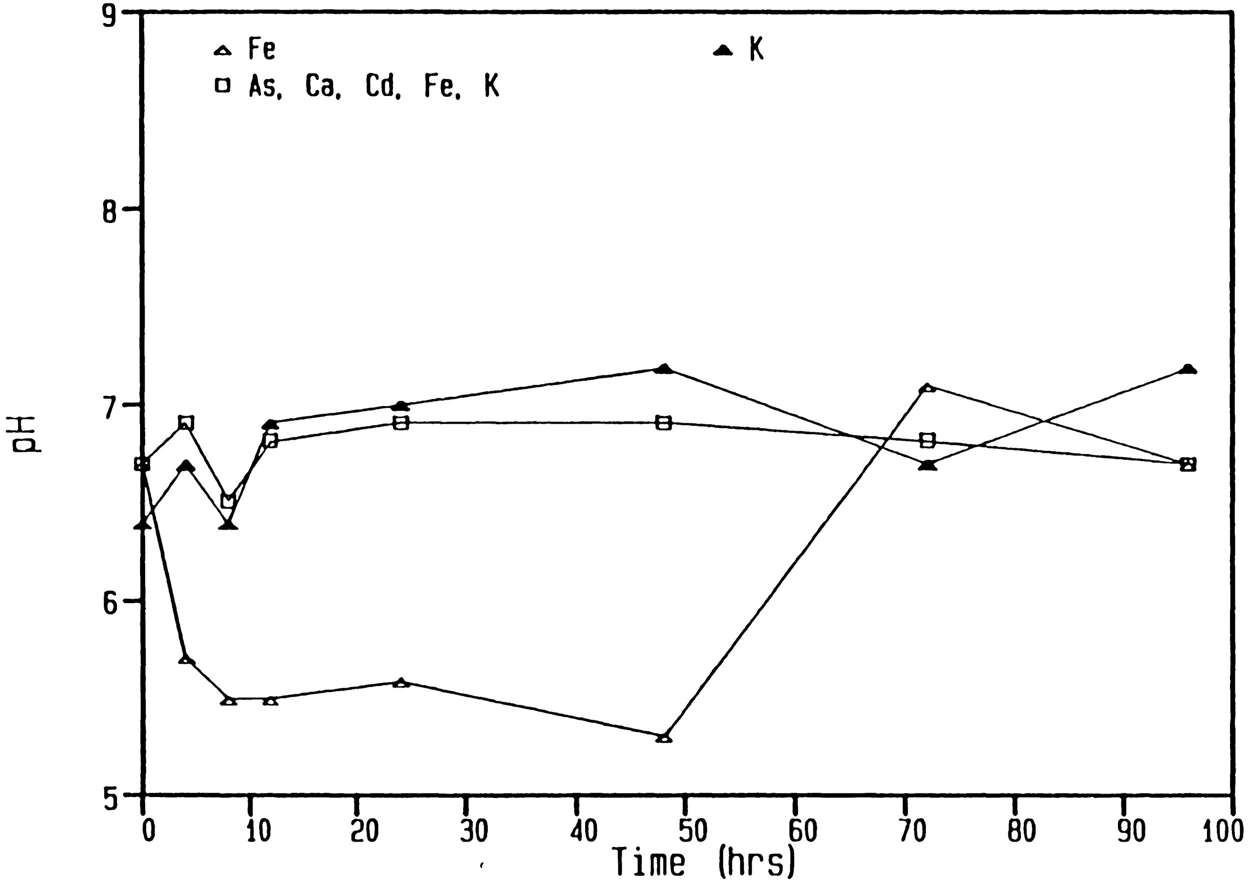

Figure D5. Variation of pH in control solution of cations (II)

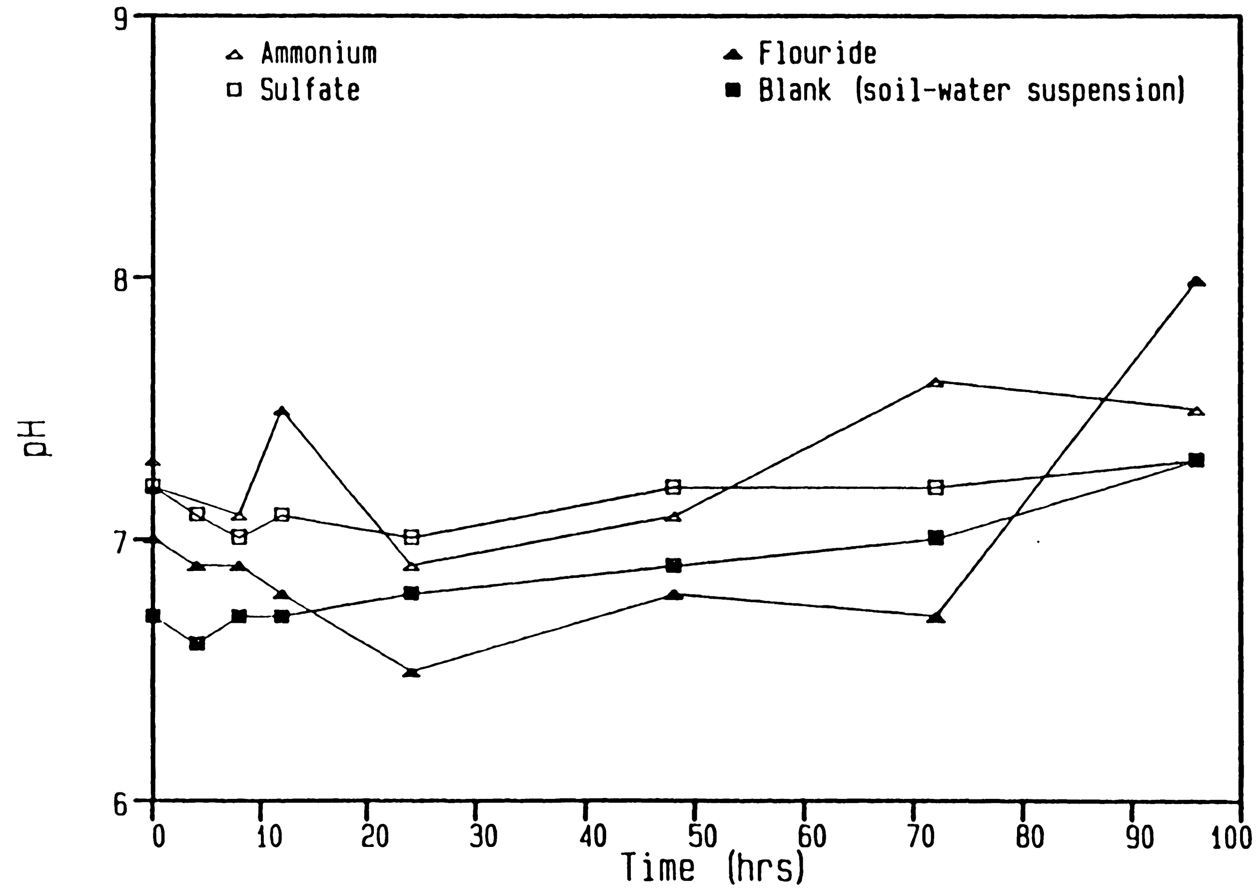

Figure D6. Variation of pH in control solution of NH_4, SO_4, and F

Appendix E. Variation of Conductivity in Batch Sorption of Inorganic Ions

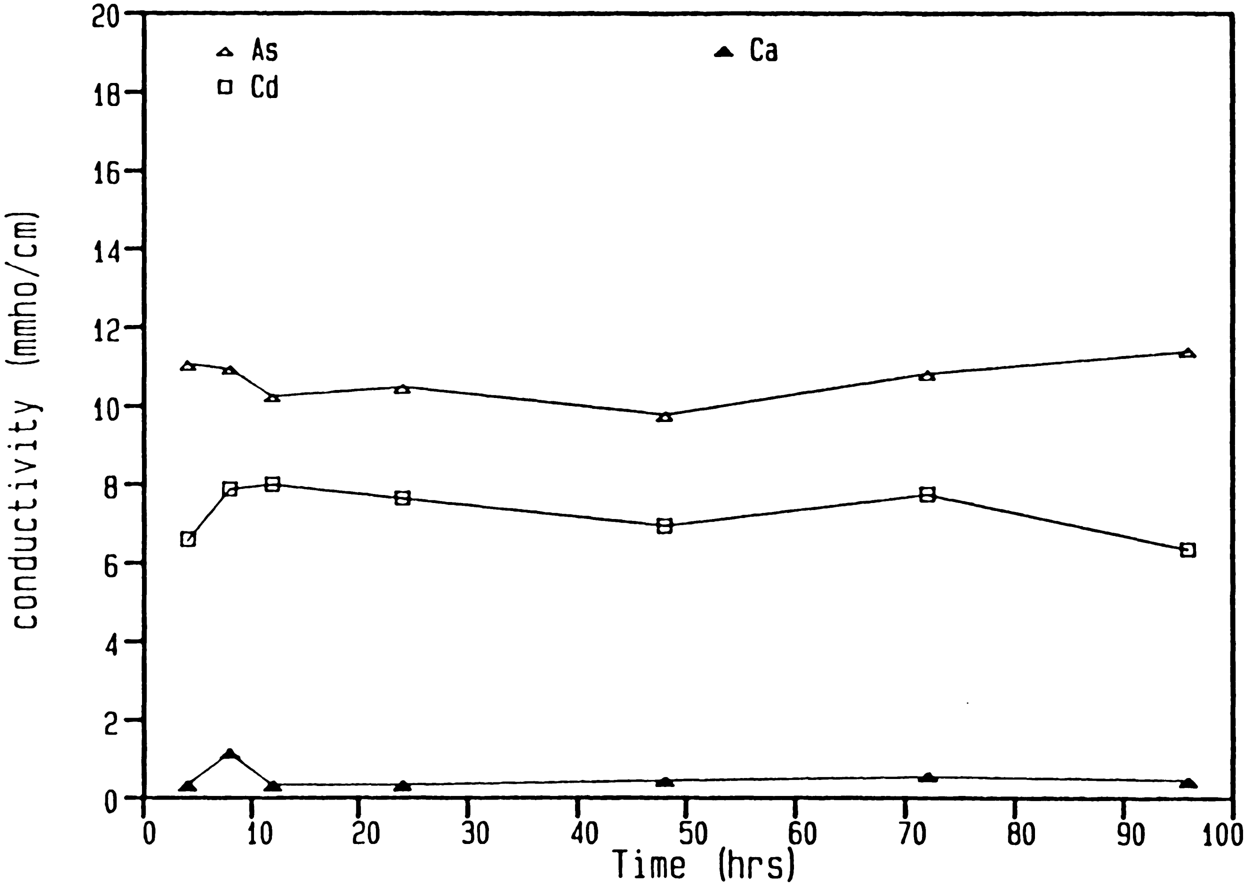

Figure E1. Variation of conductivity in sorption of cations (I)

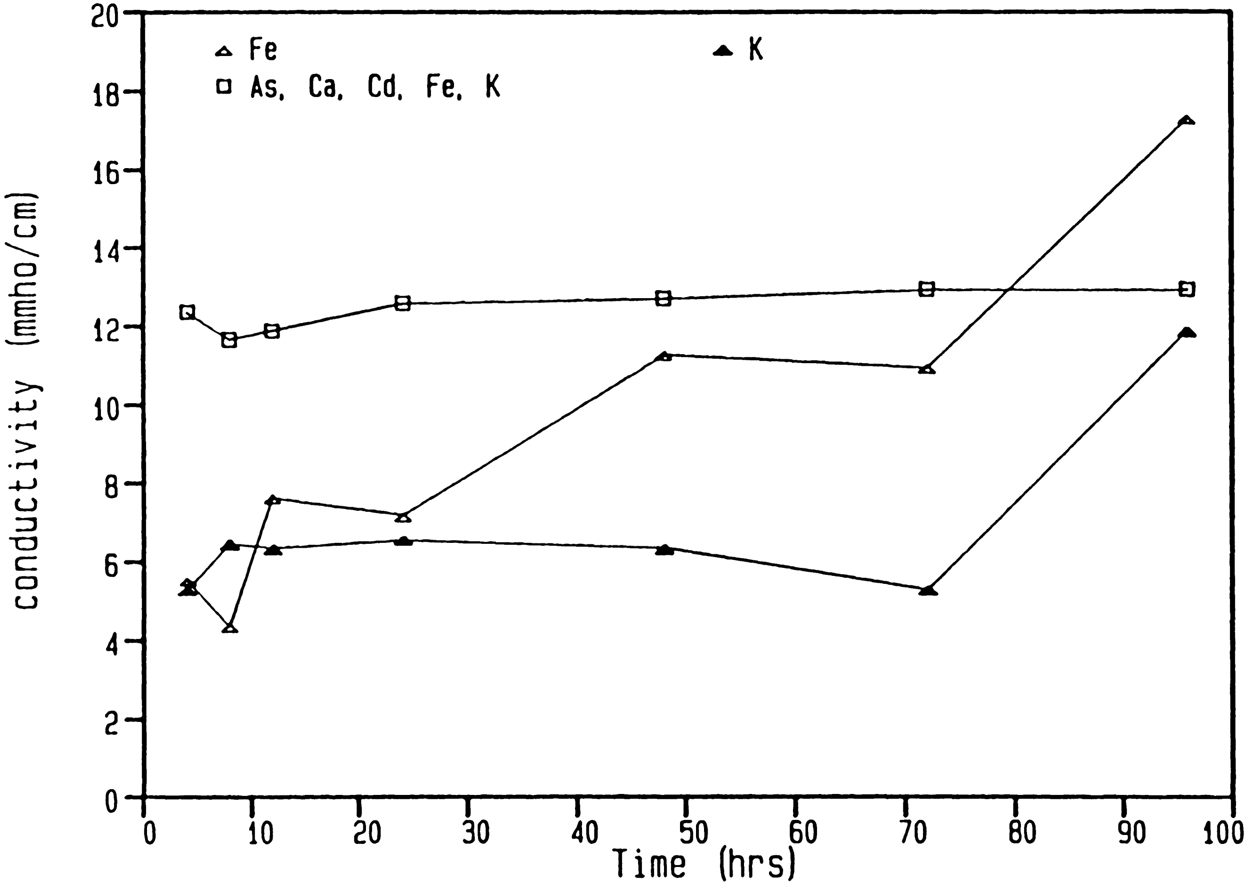

Figure E2. Variation of conductivity in sorption of cations (II)

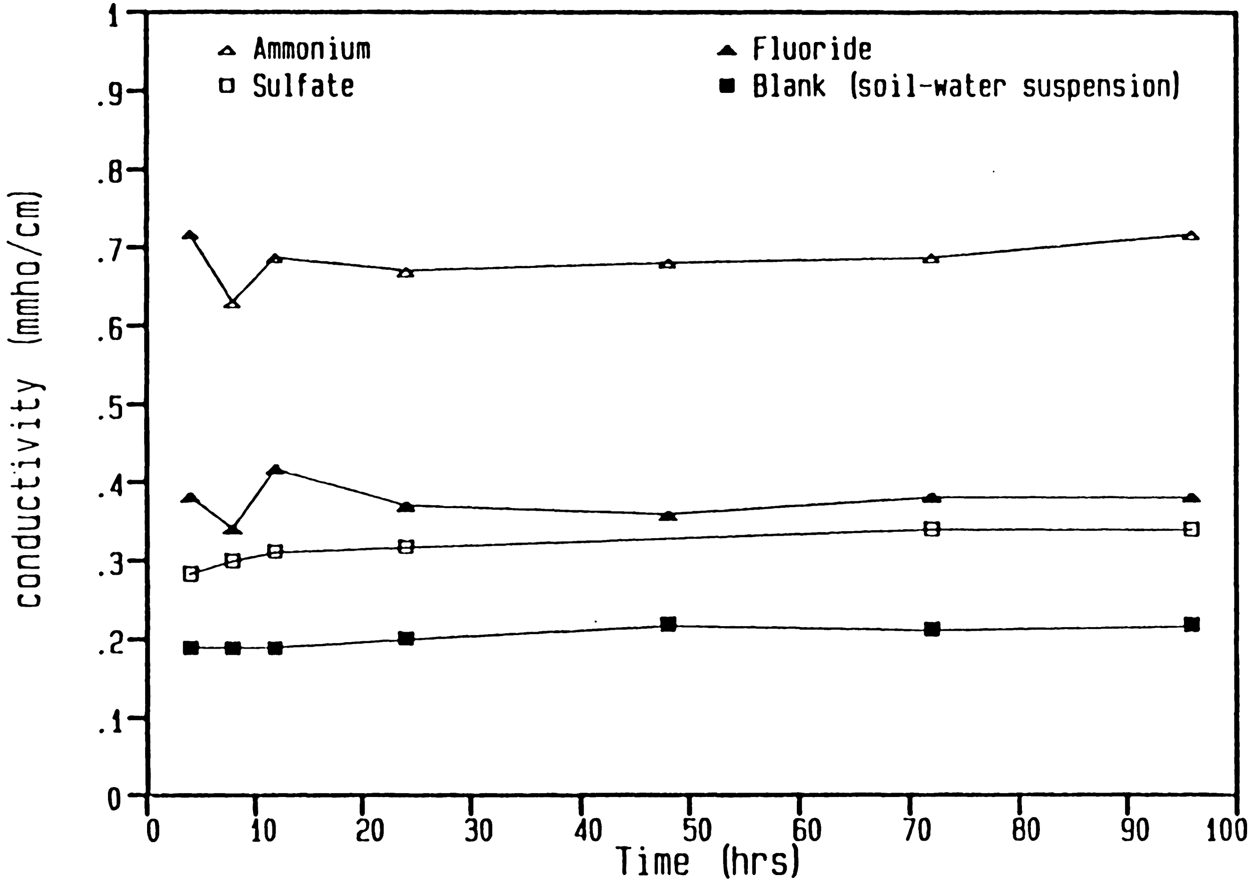

Figure E3. Variation of conductivity in sorption of NH_4, SO_4, and F

Appendix F. Variation of pH in Column Sorption of Organic Compounds

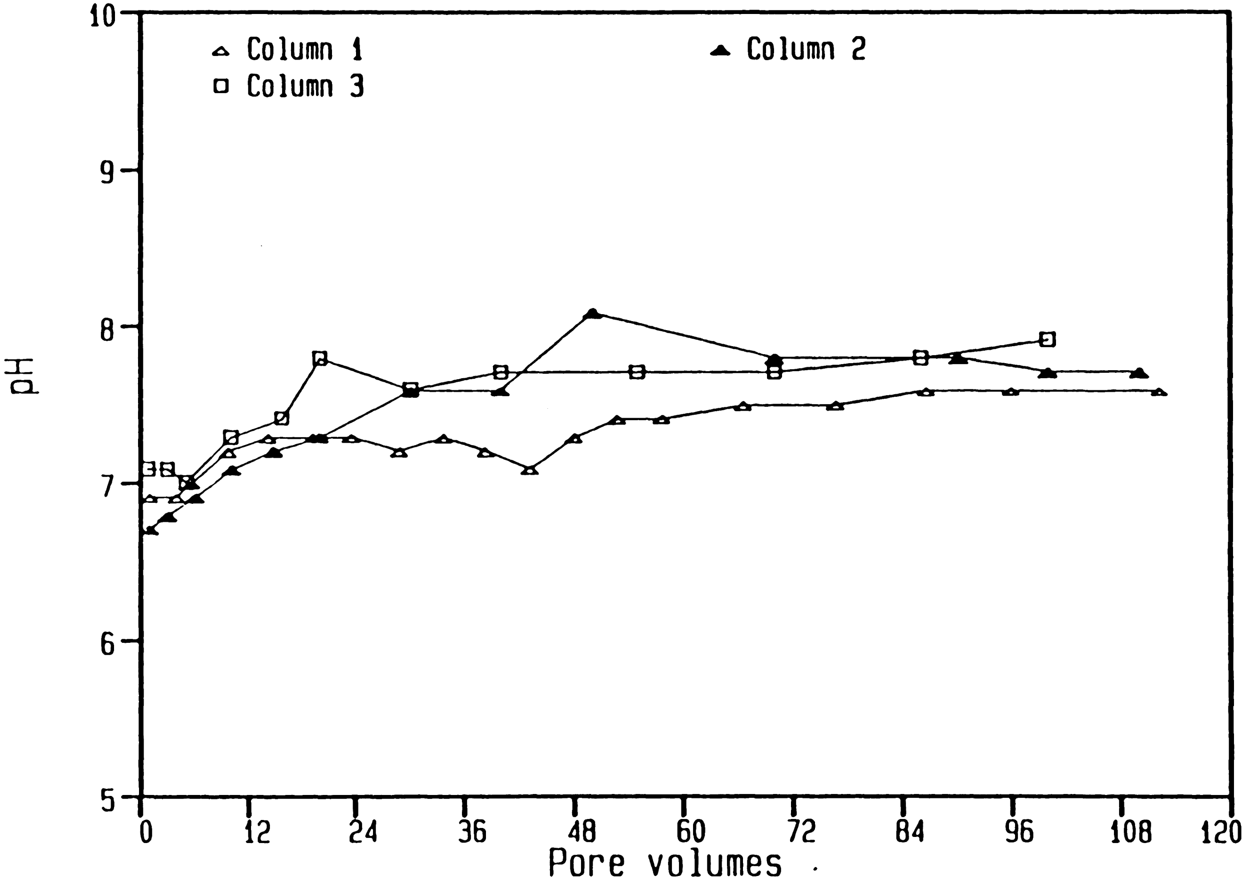

Figure F1. Variation of pH in sorption on Antrim shale

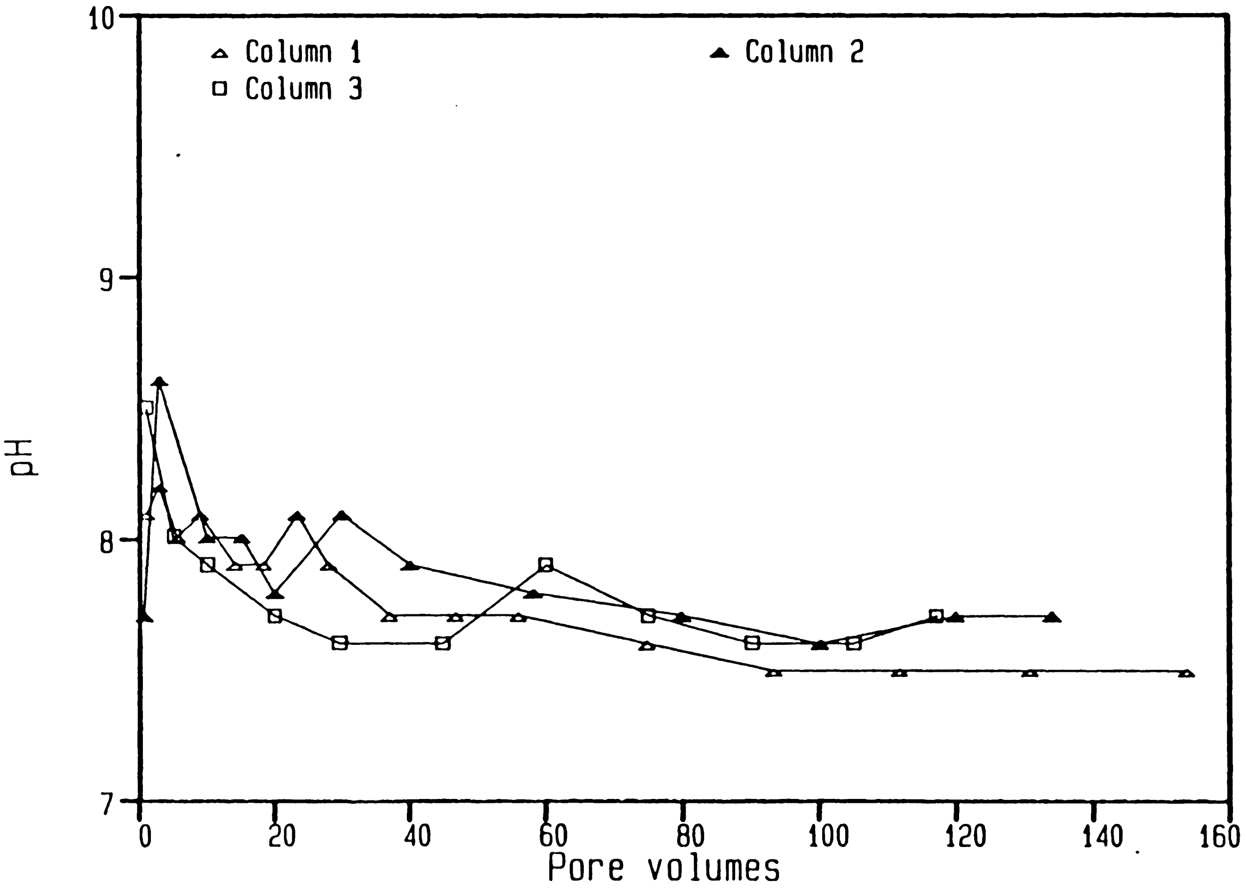

Figure F2. Variation of pH in sorption on Anvil Points shale

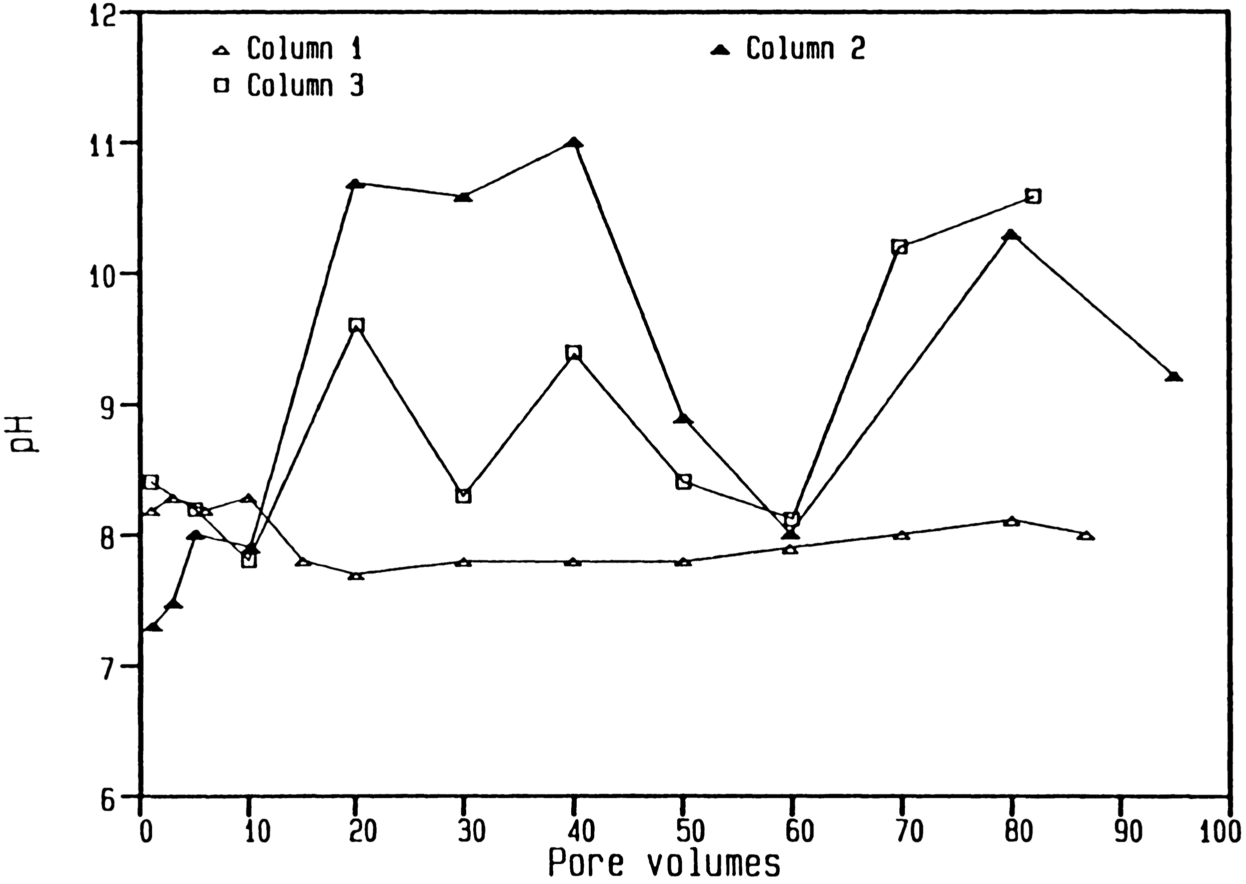

Figure F3. Variation of pH in sorption on Oxy 6 shale

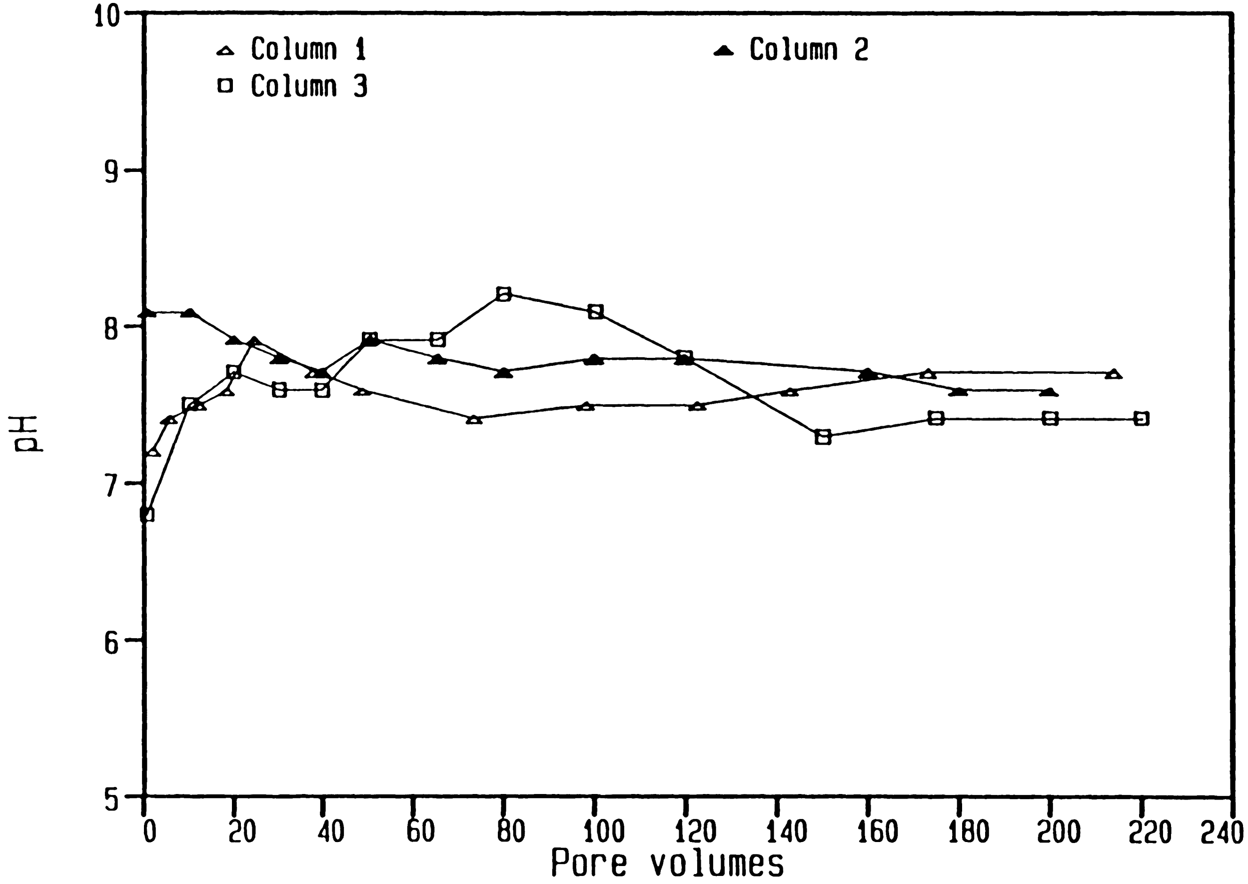

Figure F4. Variation of pH in sorption on Run 16 shale

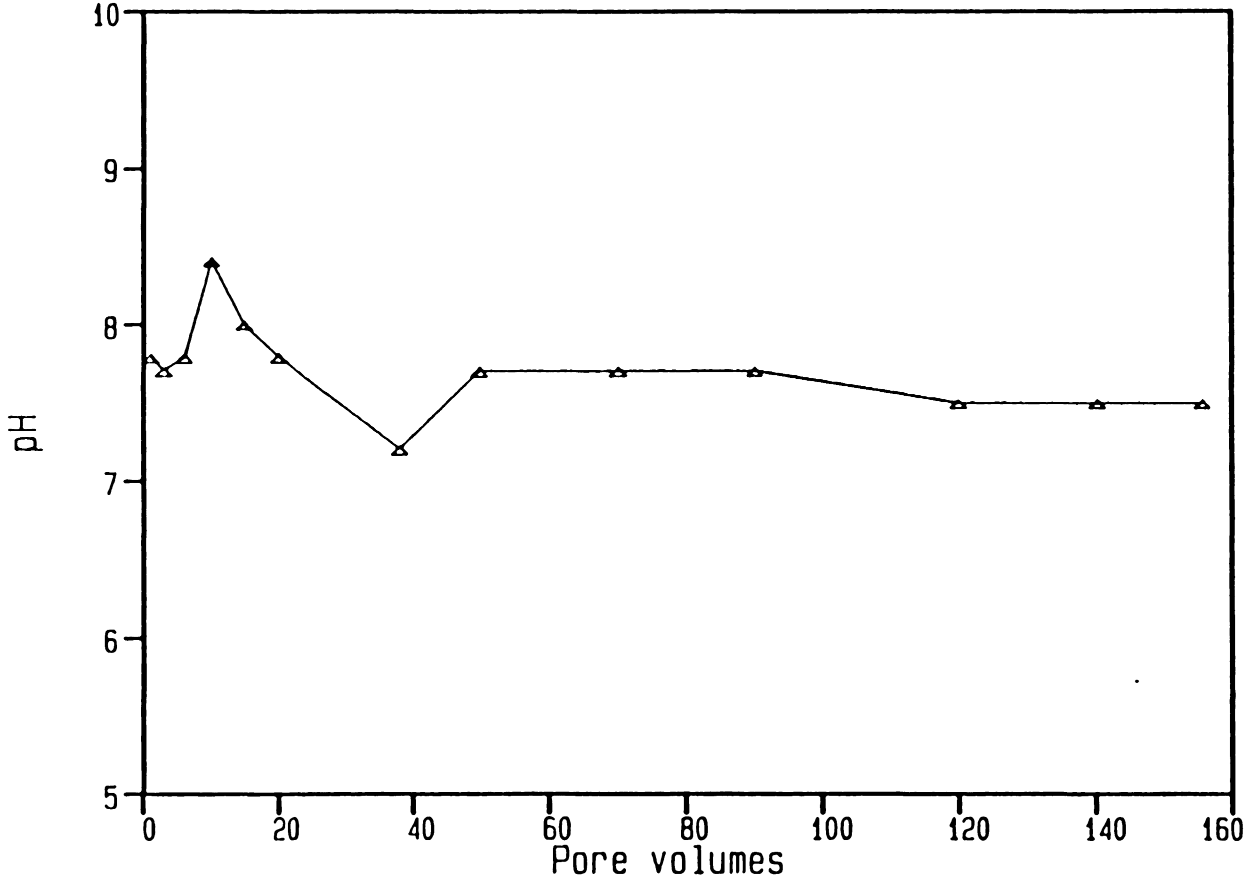

Figure F5. Variation of pH in sorption on the western soil

Appendix G. Sorption of Organic Compounds on the Oil Shales and the Western Soil

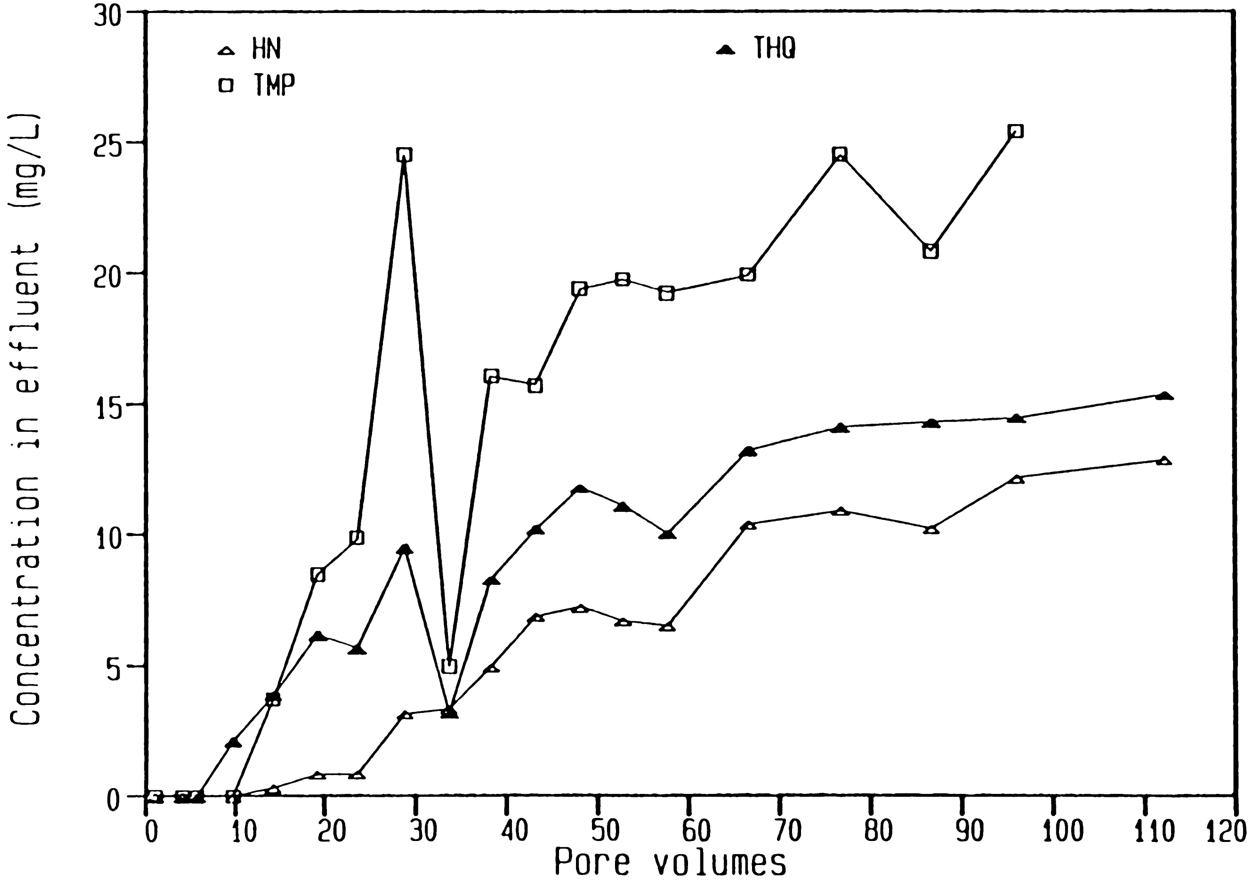

Figure G1. Sorption of HN, THQ, and TMP on Antrim shale (Trial 1): (C_0=25 mg/L)

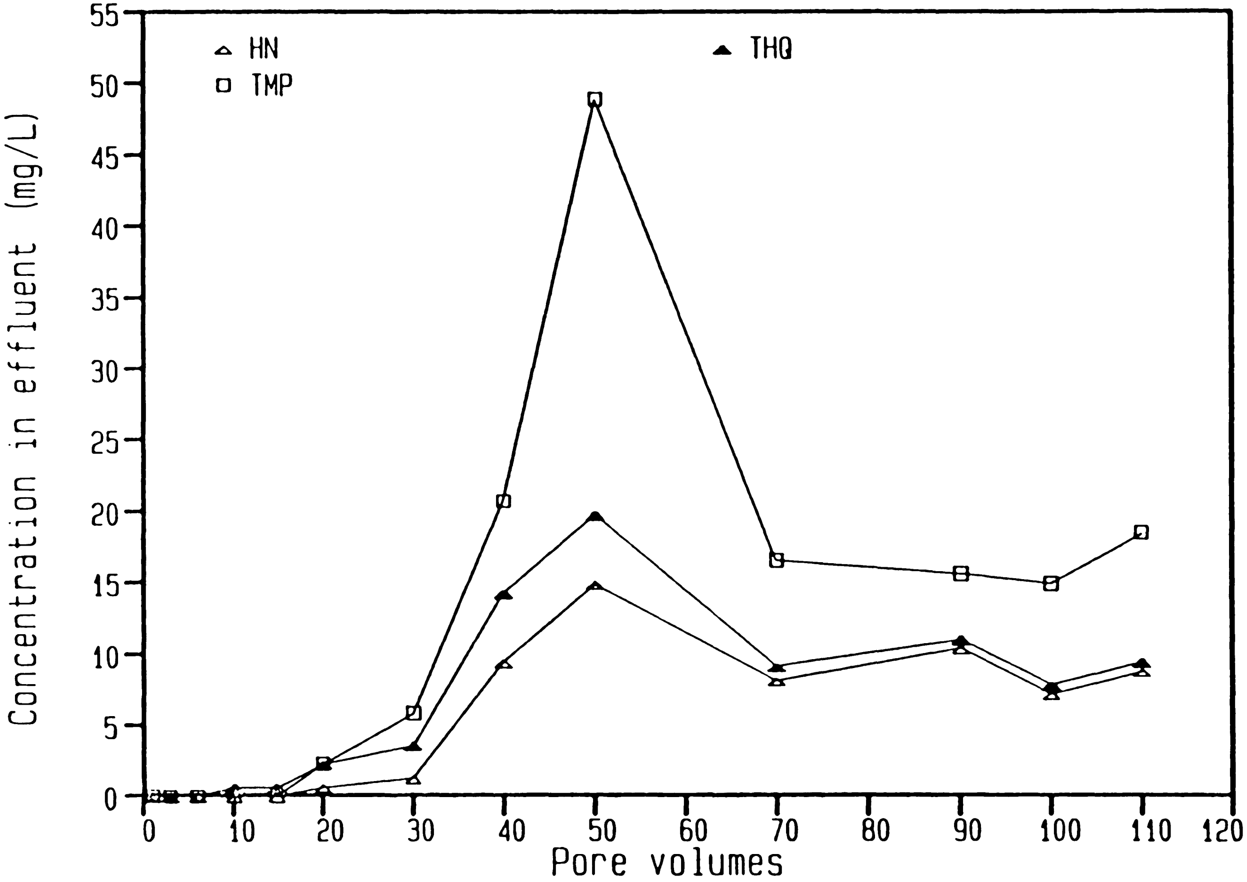

Figure G2. Sorption of HN, THQ, and TMP on Antrim shale (Trial 2): (C_0=25 mg/L)

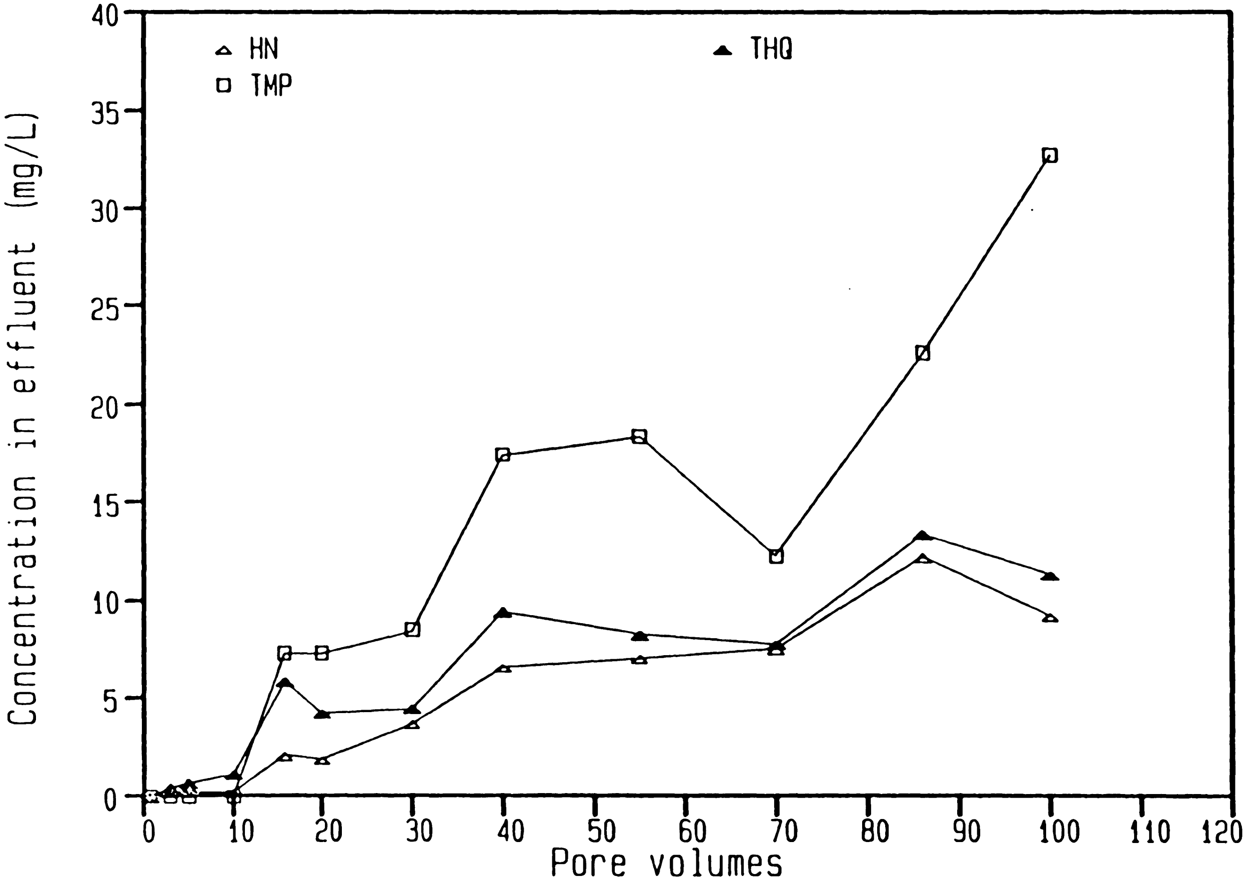

Figure G3. Sorption of HN, THQ, and TMP on Antrim shale (Trial 3): ($C_0 = 25$ mg/L)

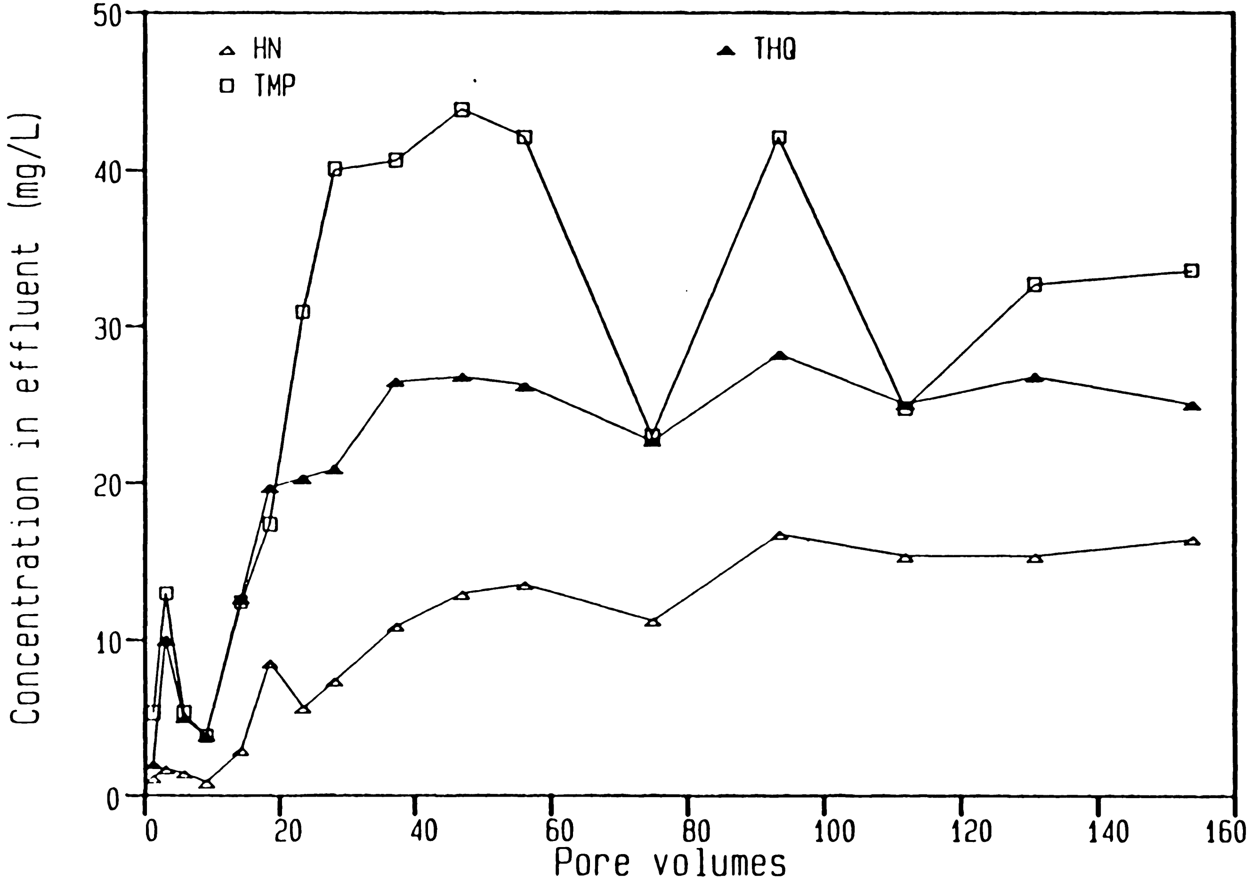

Figure G4. Sorption of HN, THQ, and TMP on Anvil Points shale (Trial 1): (C_0 = 25 mg/L)

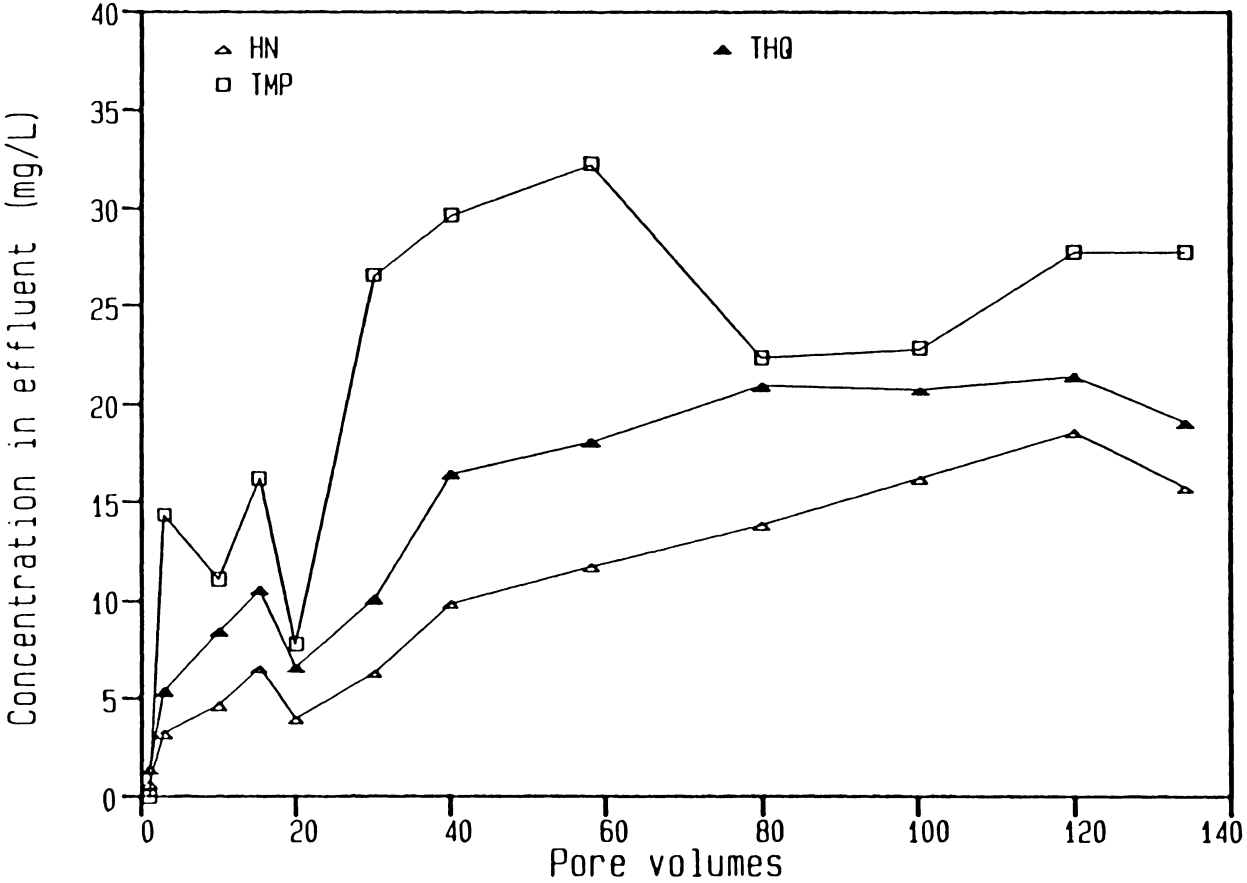

Figure G5. Sorption of HN, THQ, and TMP on Anvil Points shale (Trial 2): ($C_0 = 25$ mg/L)

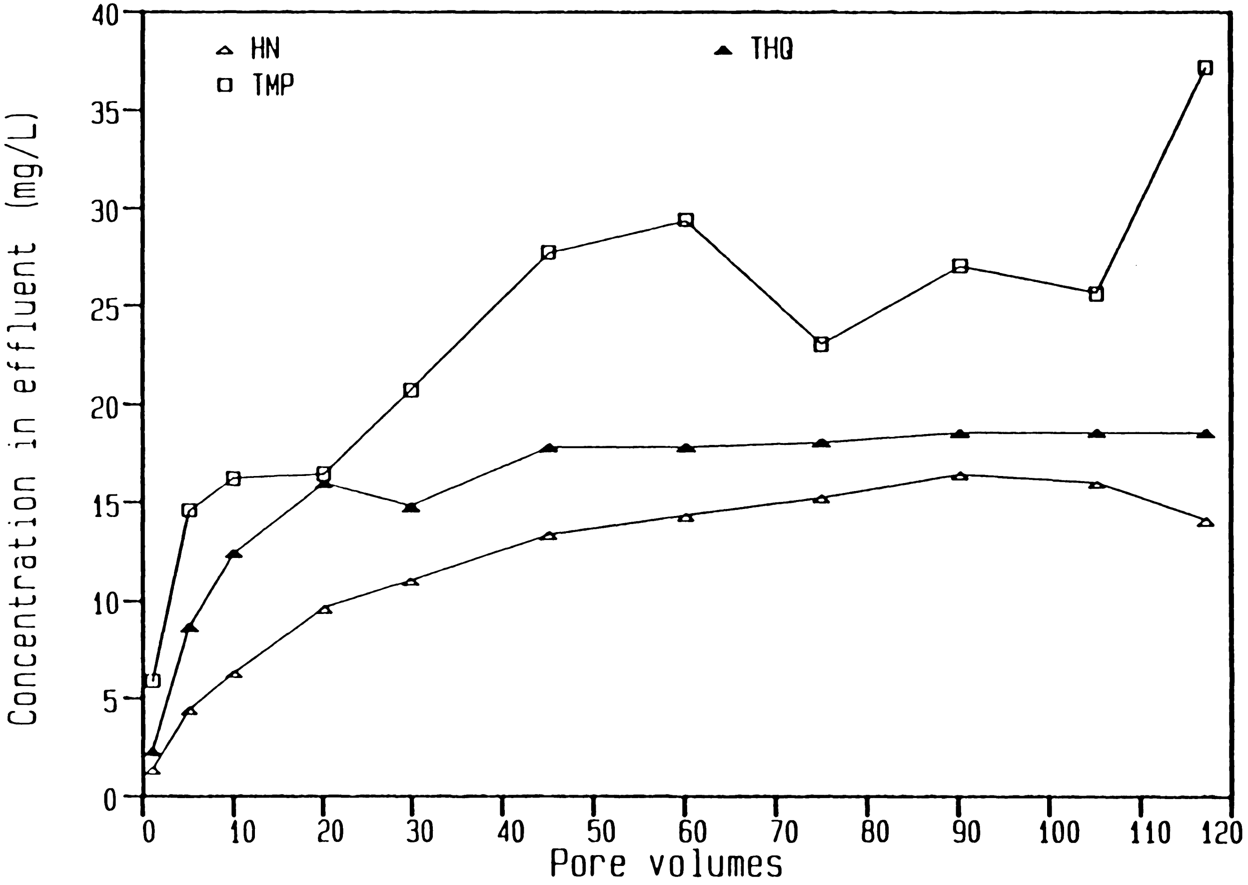

Figure G6. Sorption of HN, THQ, and TMP on Anvil Points shale (Trial 3): (C_0 = 25 mg/L)

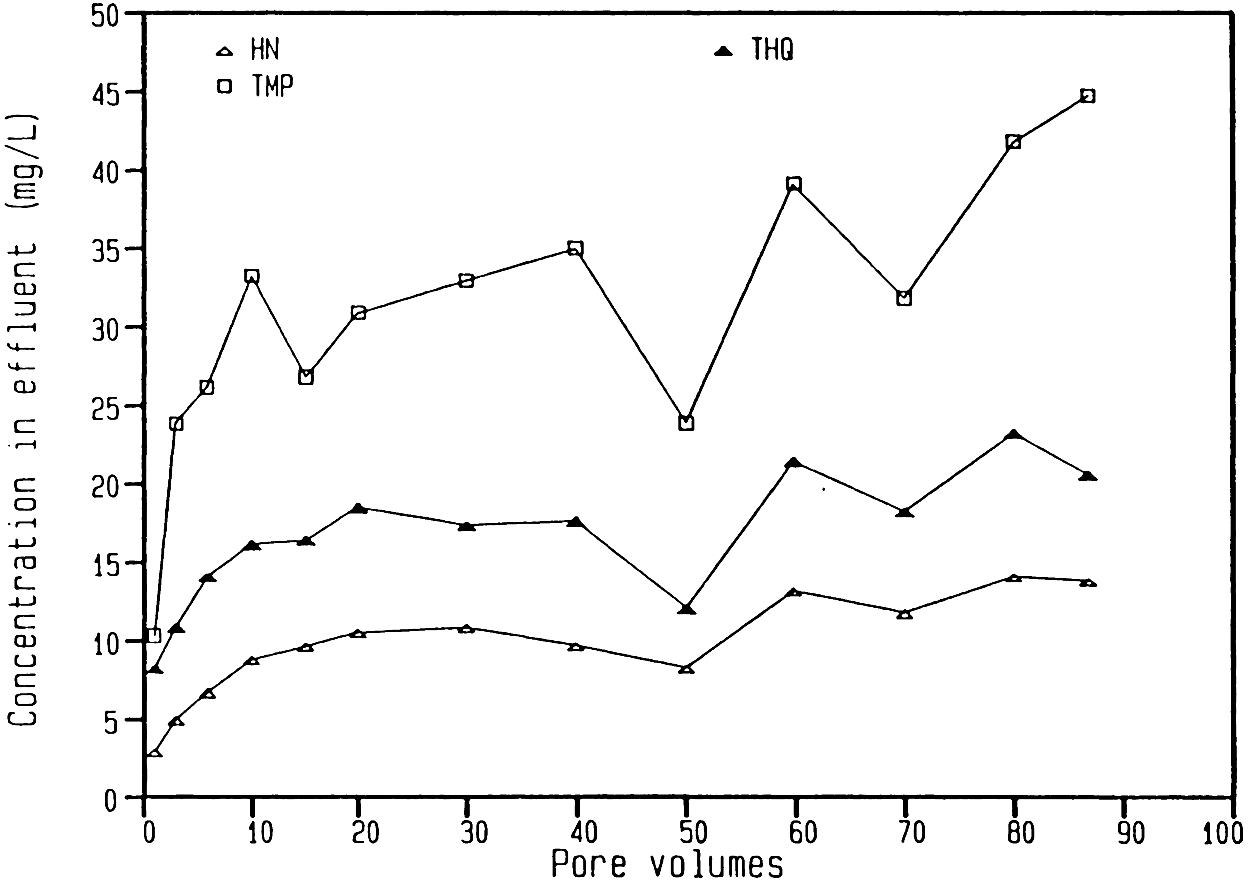

Figure G7. Sorption of HN, THQ, and TMP on Run 16 shale (Trial 1): (C_0 = 25 mg/L)

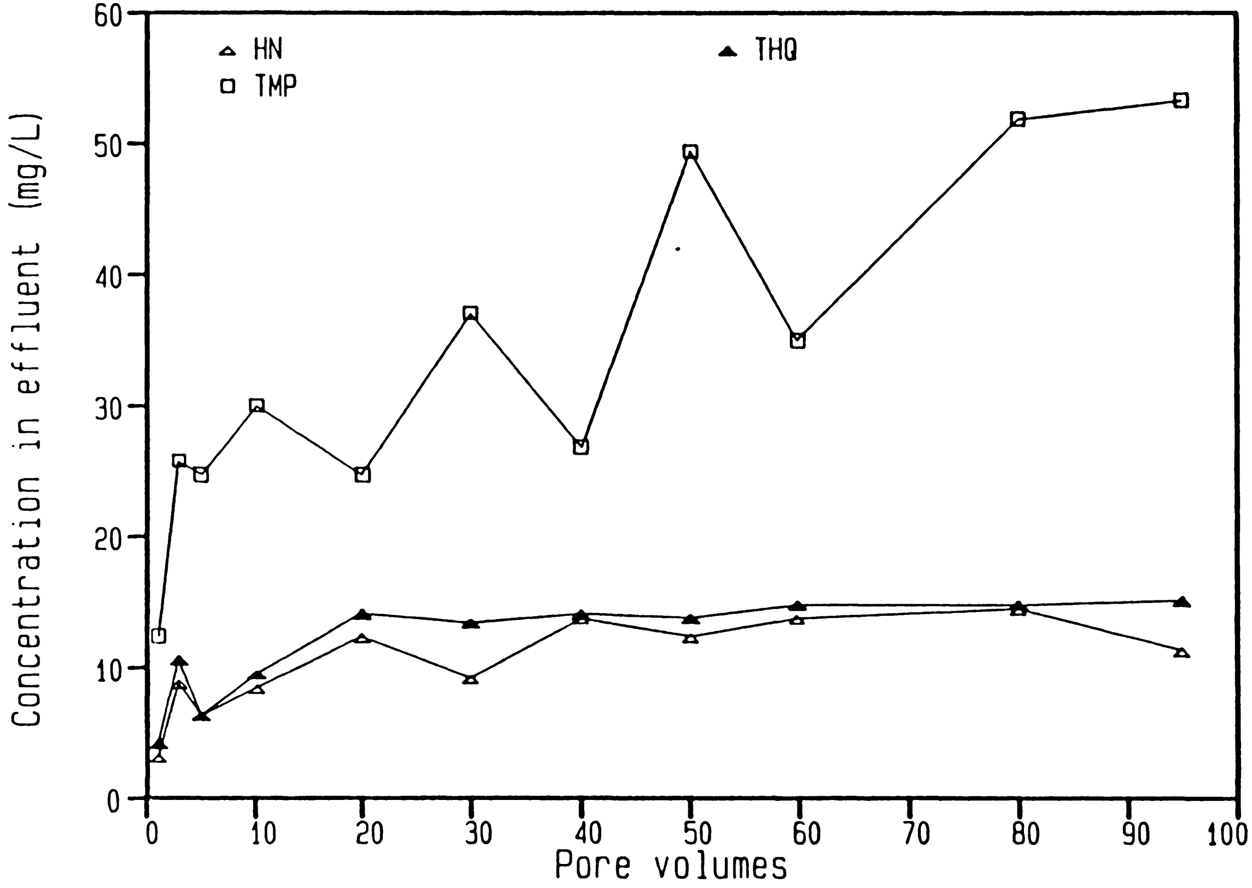

Figure G8. Sorption of HN, THQ, and TMP on Run 16 shale (Trial 2): ($C_0 = 25$ mg/L)

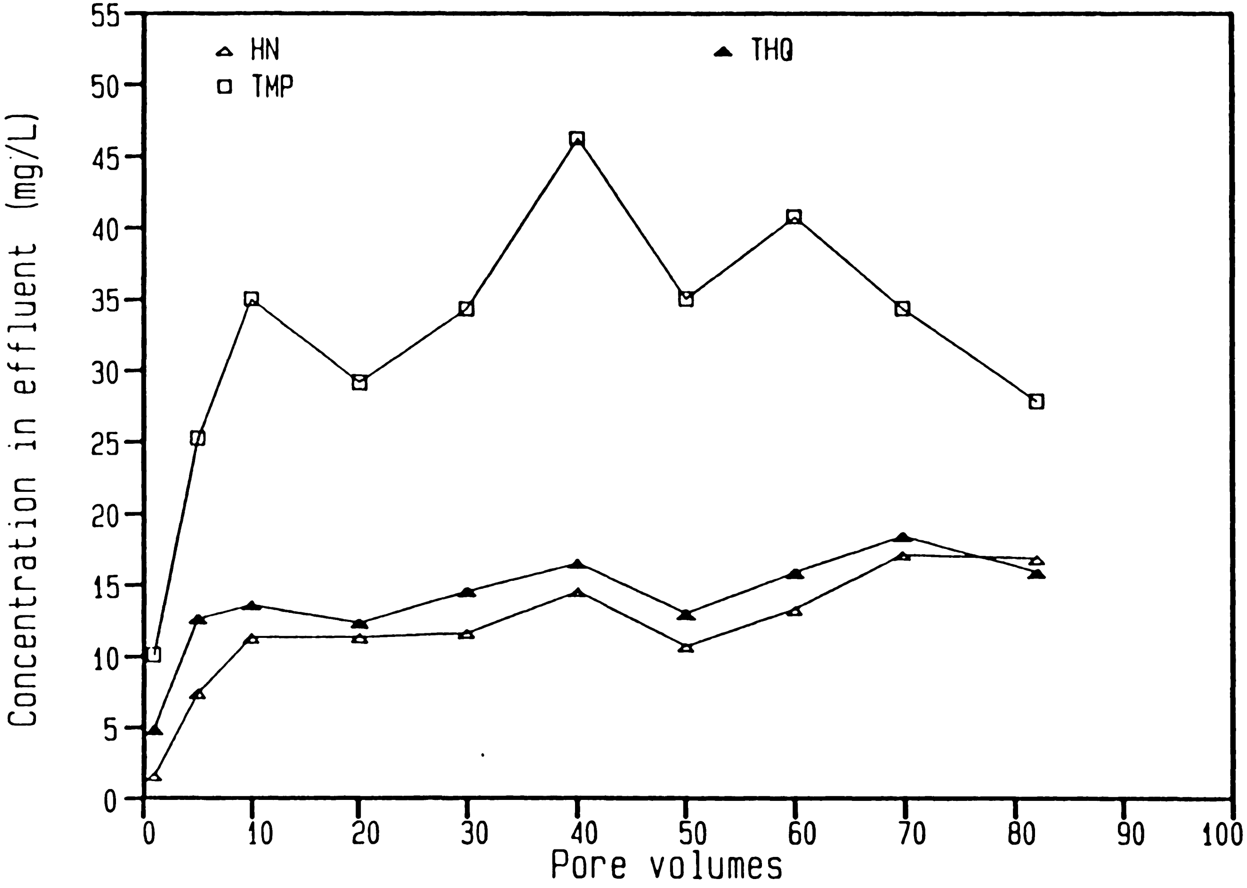

Figure G9. Sorption of HN, THQ, and TMP on Run 16 shale (Trial 3): (C_0=25 mg/L)

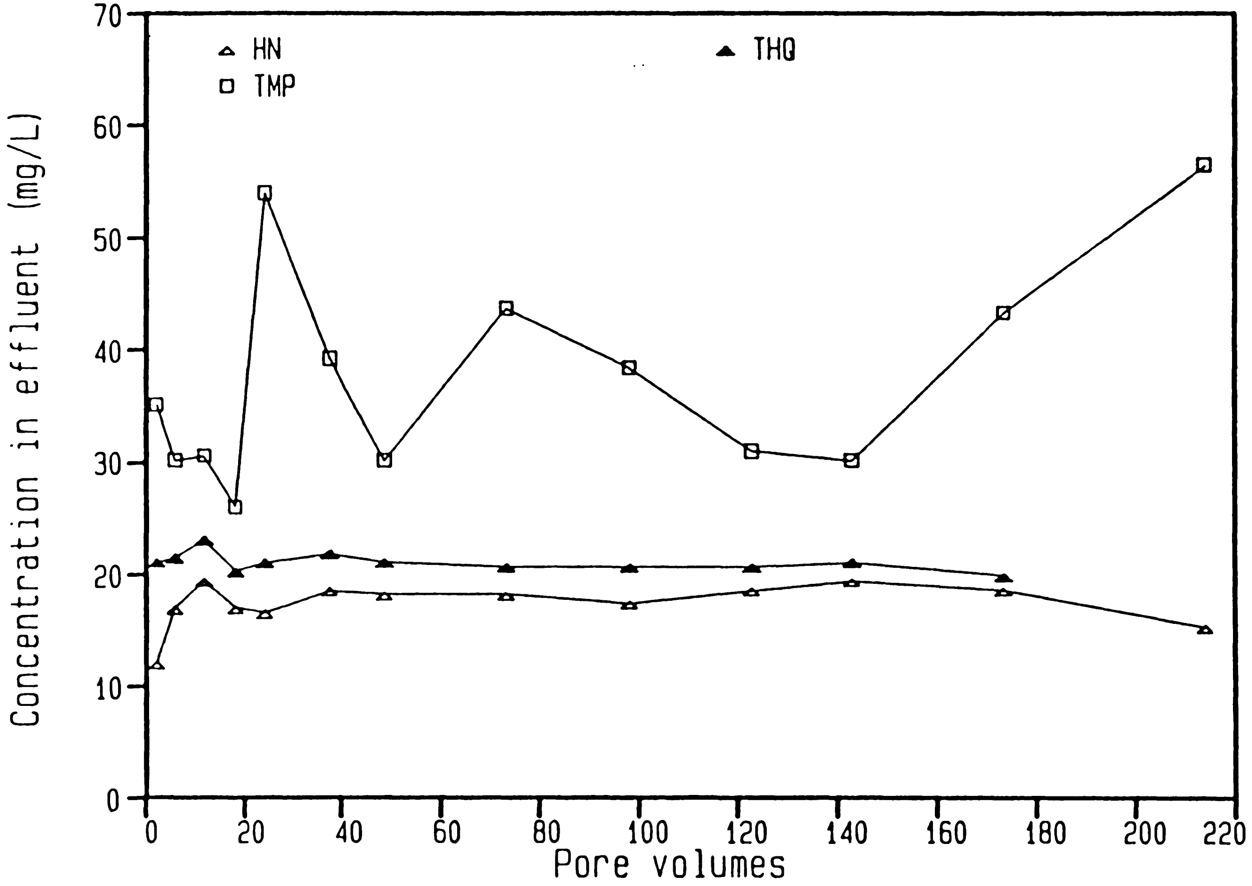

Figure G10. Sorption of HN, THQ, and TMP on the western soil shale (Trial 1): ($C_0 = 25$ mg/L)

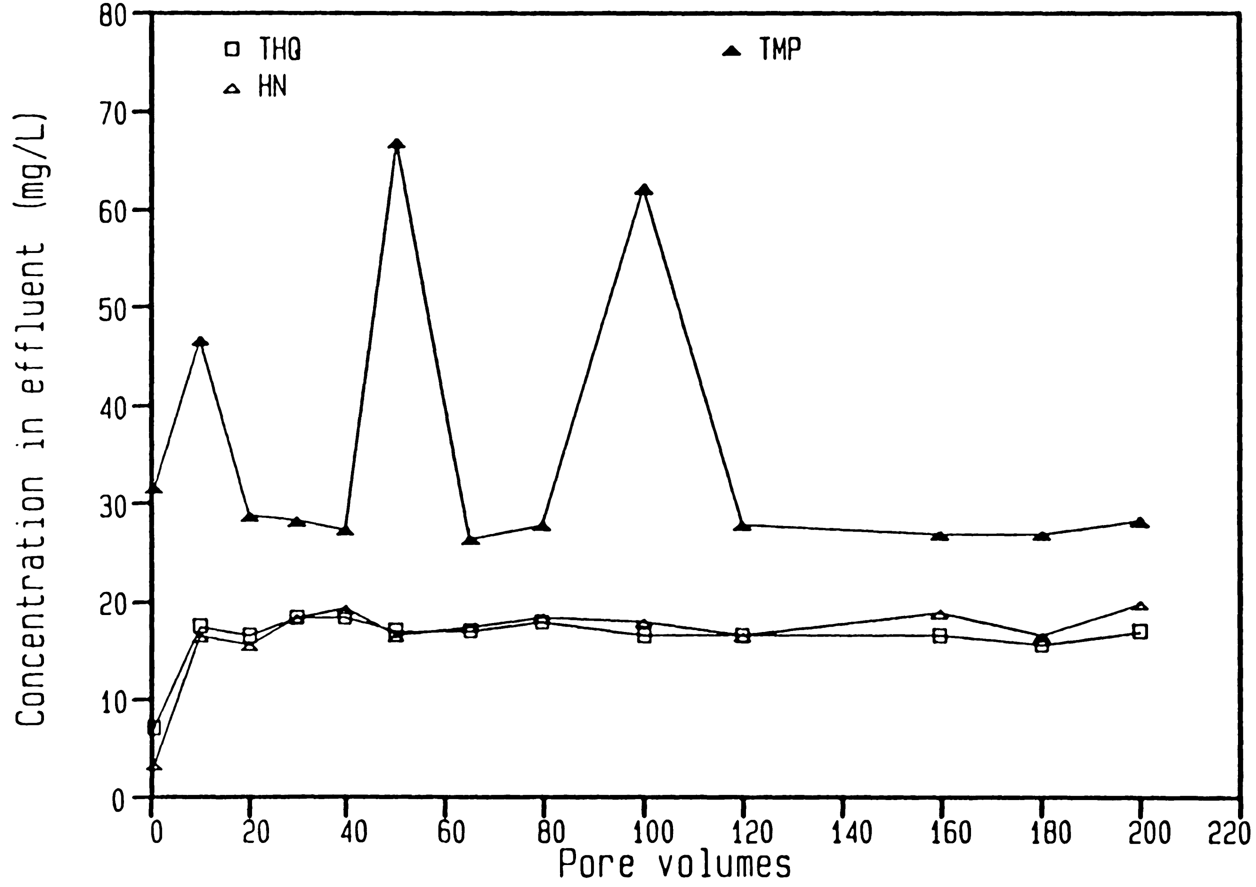

Figure G11. Sorption of HN, THQ, and TMP on the western soil shale (Trial 2): (C_0 = 25 mg/L)

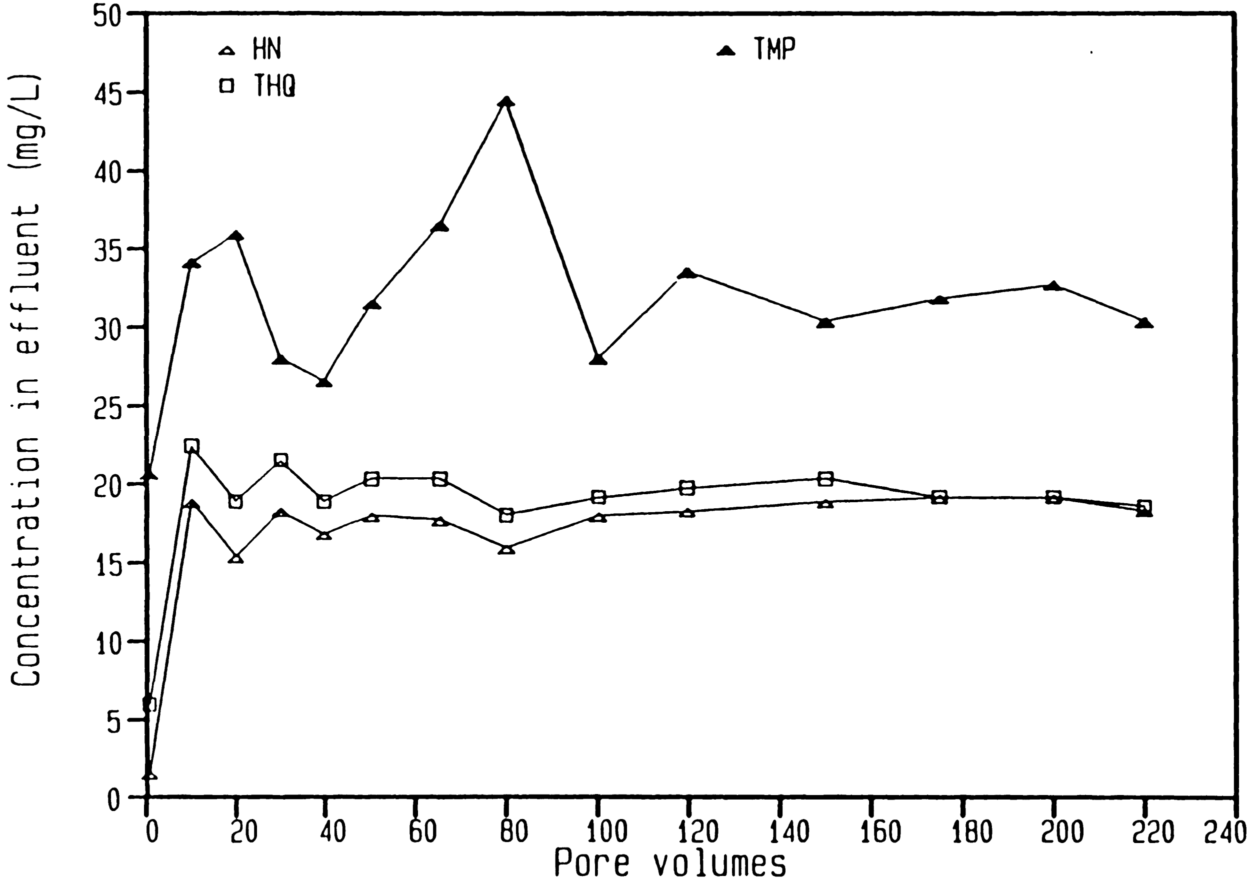

Figure G12. Sorption of HN, THQ, and TMP on the western soil shale (Trial 3): ($C_0 = 25$ mg/L)

Appendix H. Variation of Chemical Properties in Effluents from the Soil Columns

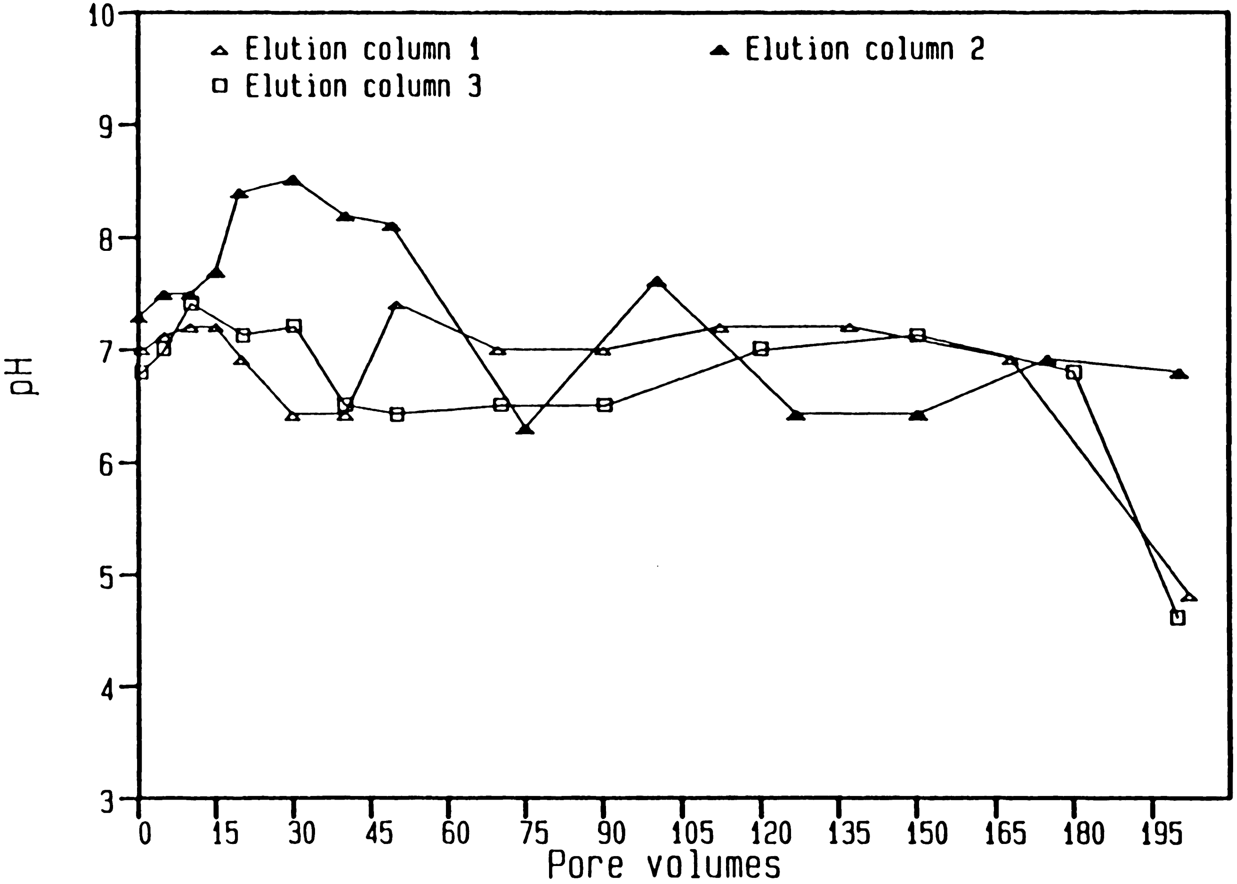

Figure H1. Variation in pH of soil column effluent

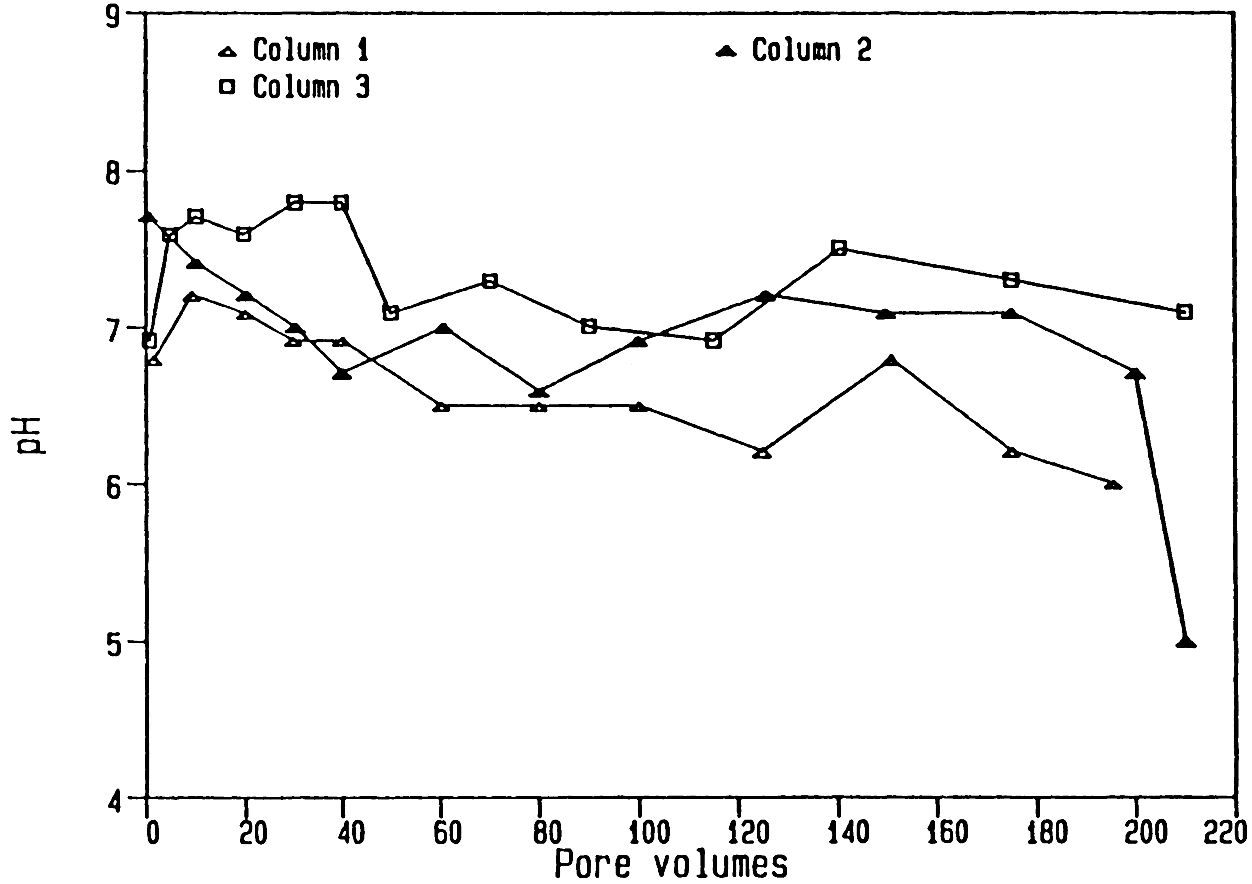

Figure H2. Variation in effluent pH of sorption of four cations on soil

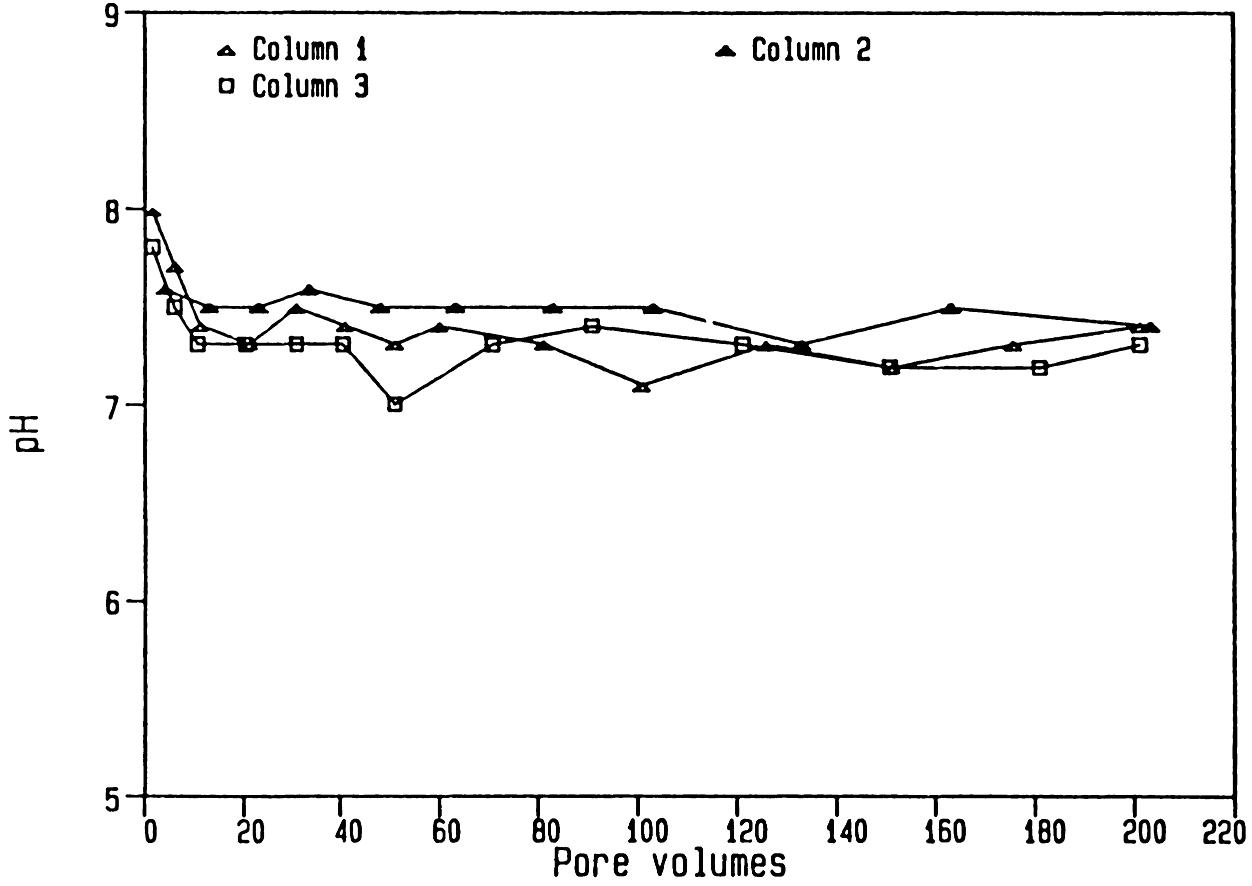

Figure H3. Variation in effluent pH of sorption of NH_4, SO_4, and F on soil

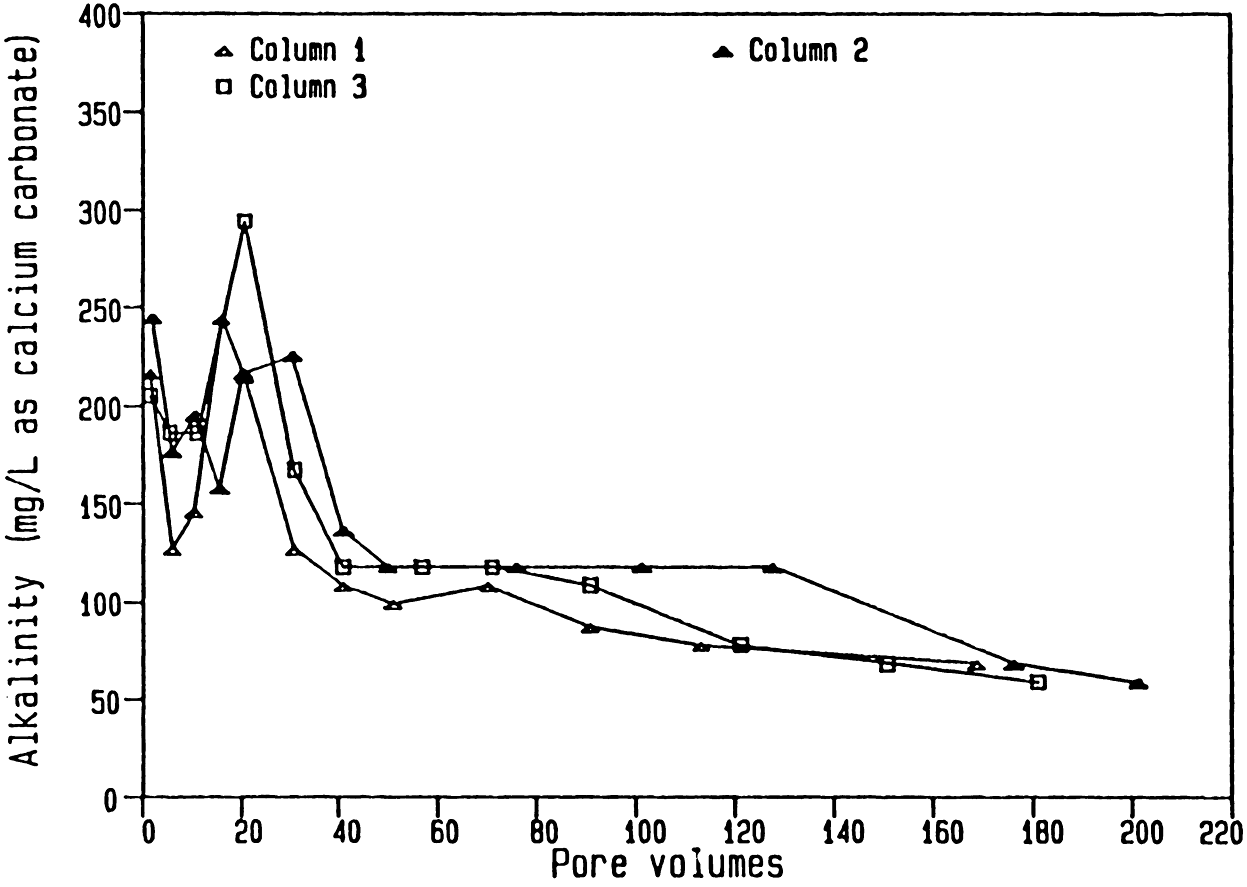

Figure H4. Variation in effluent alkalinity of sorption of eight ions

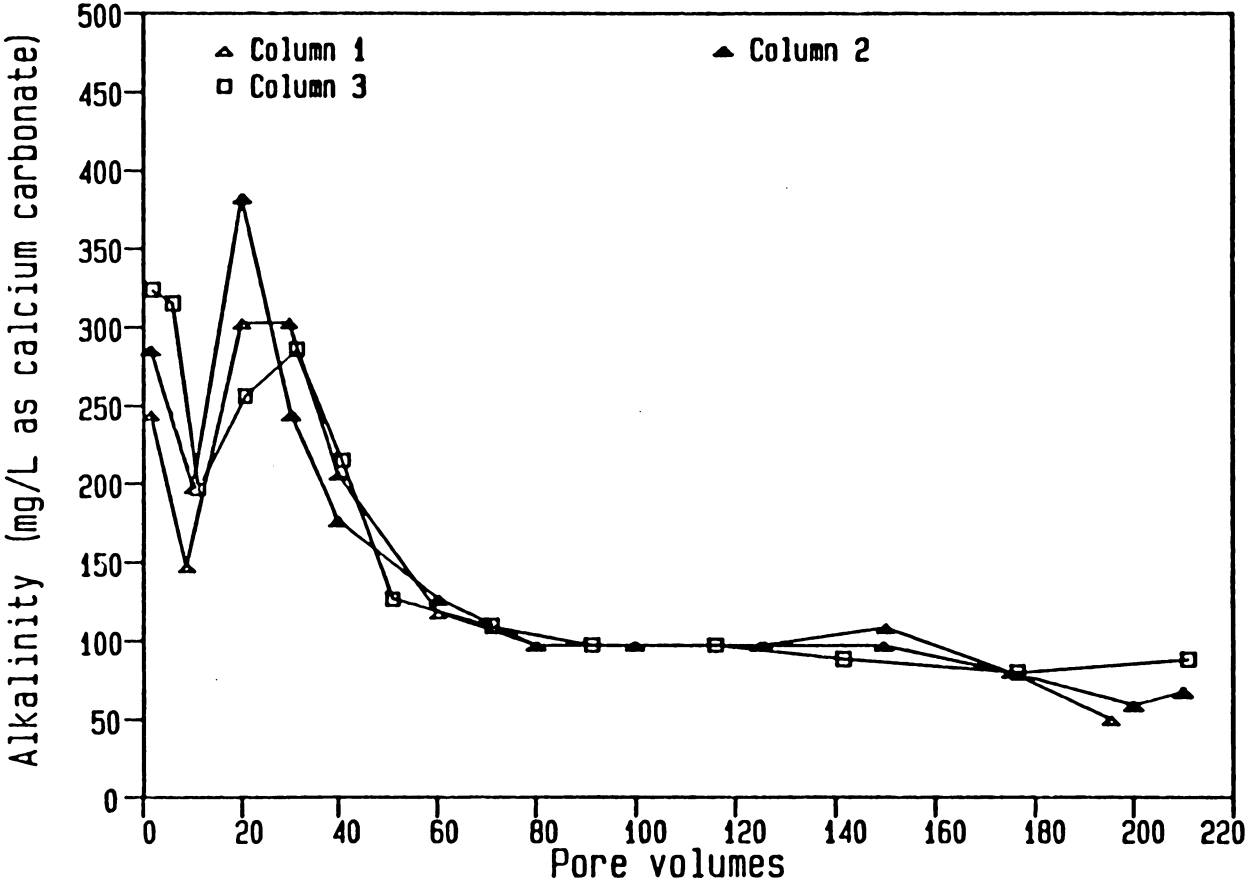

Figure H5. Variation in effluent alkalinity of sorption of four cations on soil

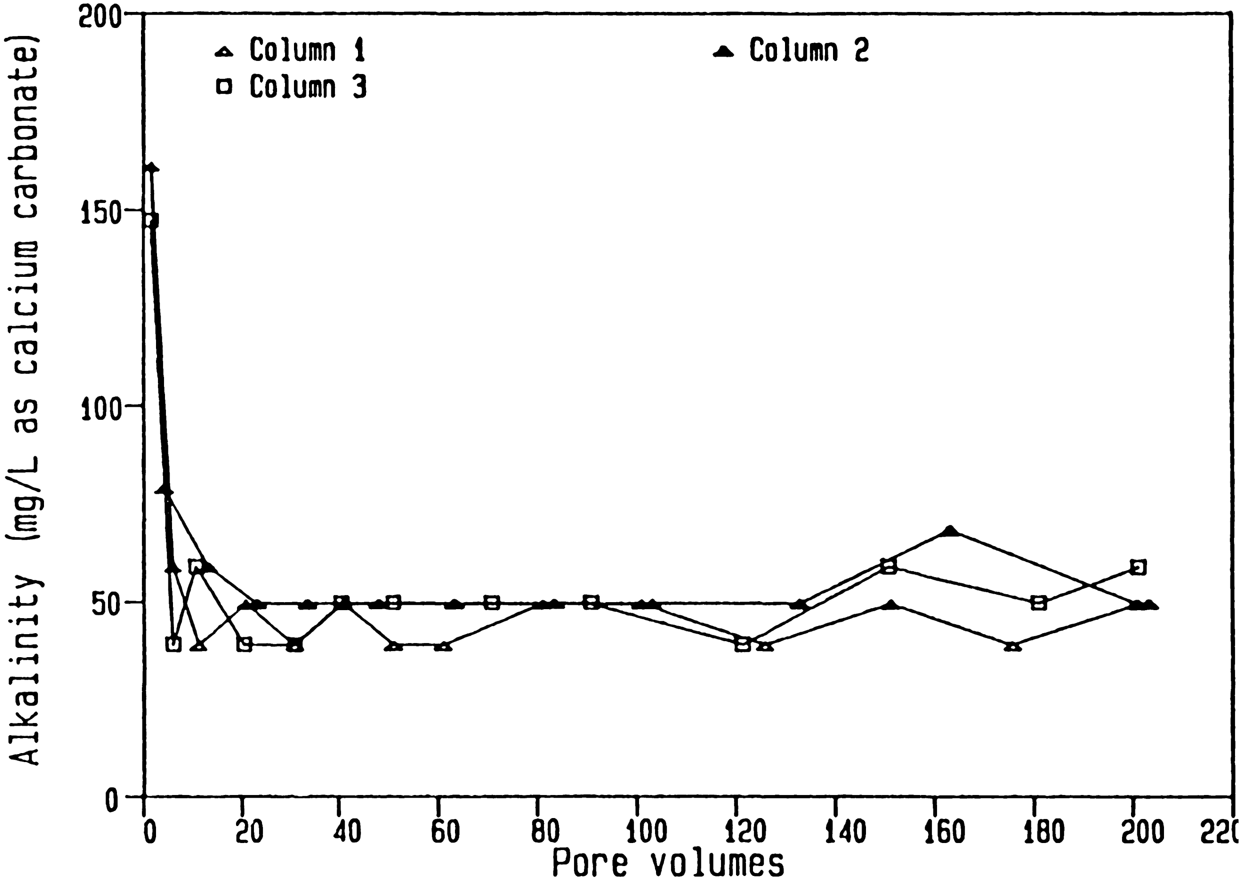

Figure H6. Variation in effluent alkalinity of sorption of NH_4, SO_4, and F on soil

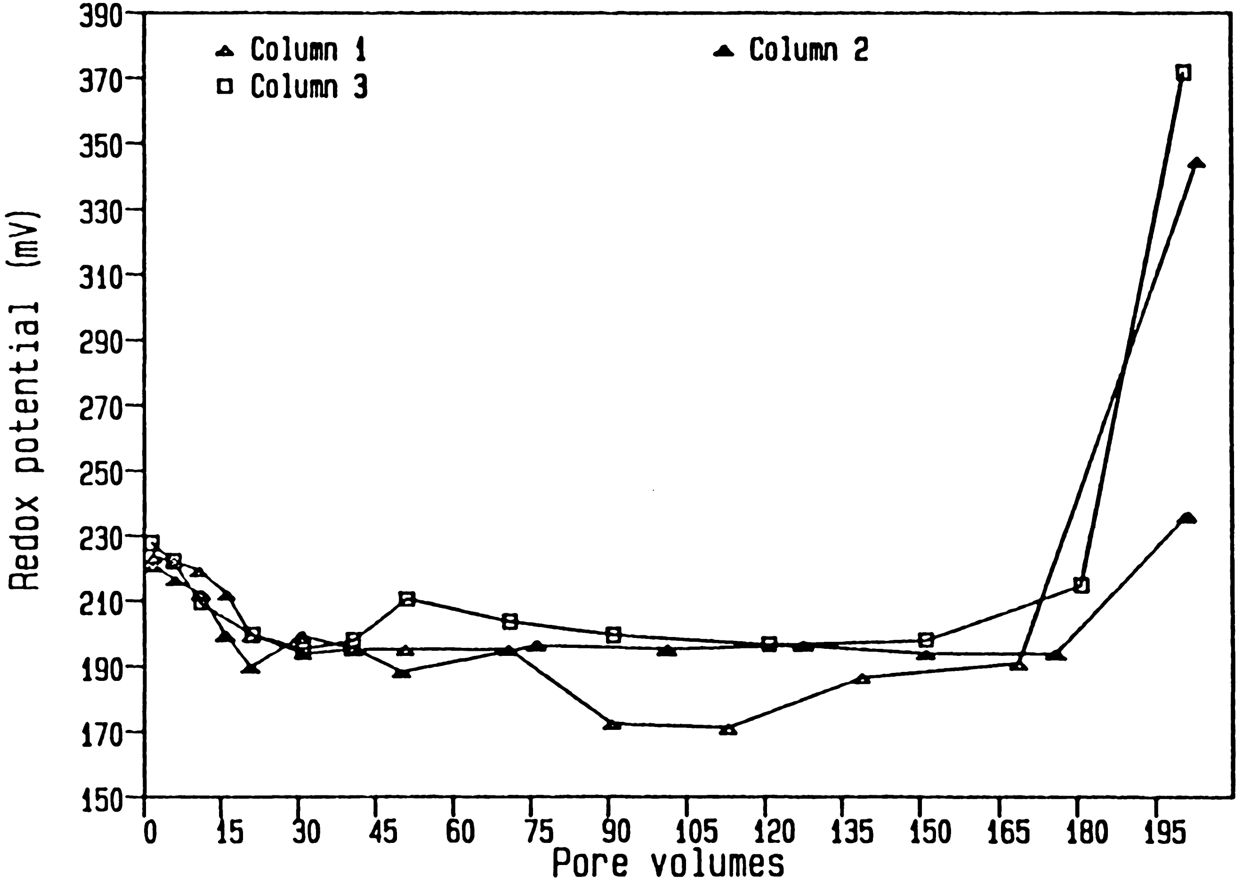

Figure H7. Variation in effluent redox potential of sorption of eight ions

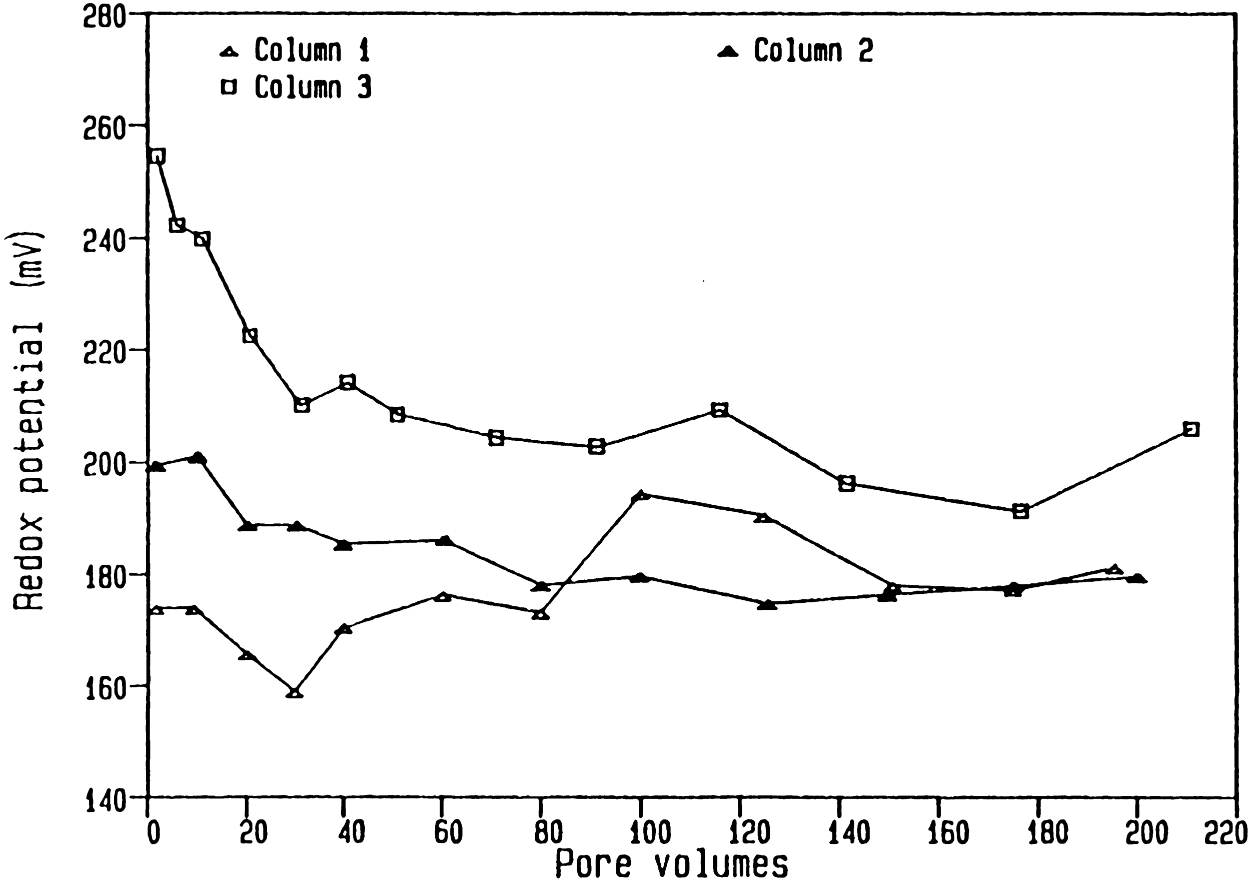

Figure H8. Variation in effluent redox potential of sorption of four cations on soil

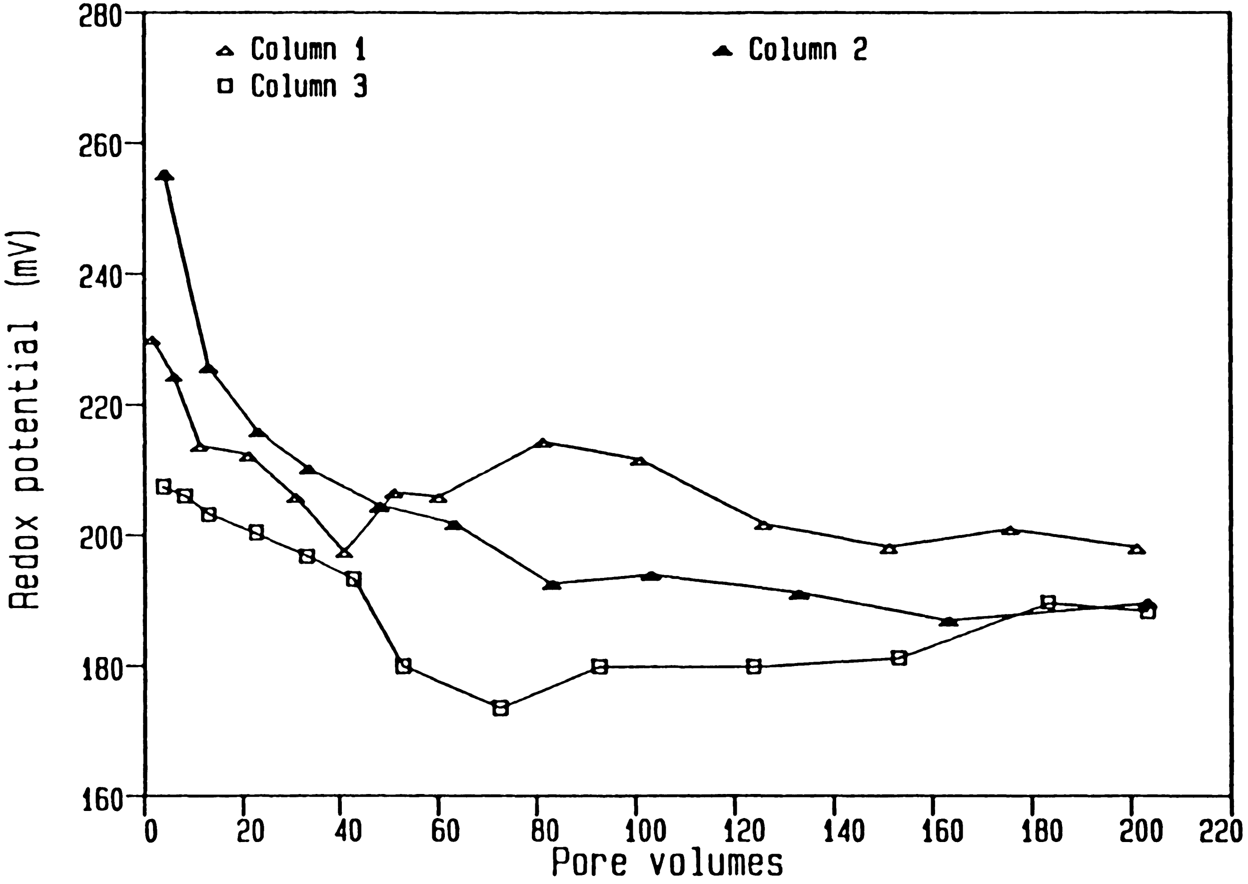

Figure H9. Variation in effluent redox potential of sorption of NH_4, SO_4, and F on soil

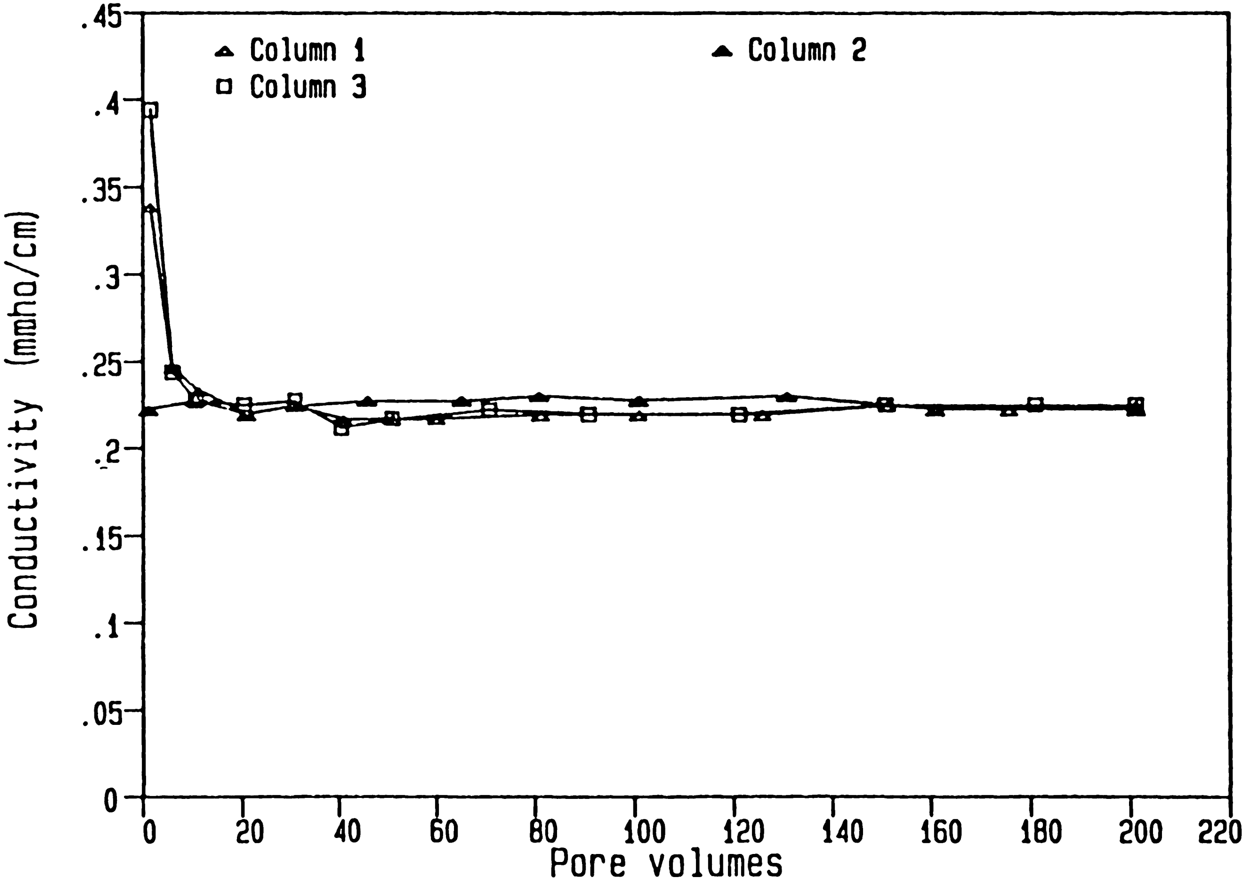

Figure H10. Variation in conductivity of soil column effluent