

**Monitoring and Remediation of Gasoline
Storage Facilities: Aqueous Leachability
of Gasoline in a Connecticut Sand**

by

**George Hoag, Assoc. Professor
David Ahlfeld, Asst. Professor
Amine Dahmani, Grad. Res. Asst.
Dennis Strother, Grad. Res. Asst.**

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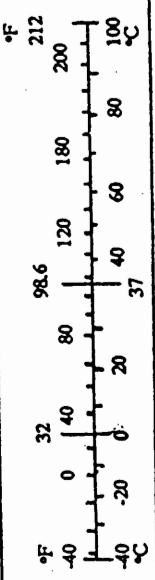
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16. Abstract A series of laboratory experiments are conducted to determine the chemical nature of natural leachate from gasoline contaminated soils. Soil columns are used and 7 compounds are analyzed, including methyl tert-butyl ether (MTBE). A major finding is that MTBE leaves the soil quickly (e.g. one year) while other major gasoline components will persist for many years or decades.					
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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS				APPROXIMATE CONVERSIONS TO SI UNITS			
Symbol	When You Know	Multiply By	To Find	Symbol	When You Know	Multiply By	To Find
<u>LENGTH</u>				<u>LENGTH</u>			
in	inches	25.4	millimetres	mm	mm	0.039	inches
ft	feet	0.305	metres	m	m	3.28	feet
yd	yards	0.914	metres	m	m	1.09	yards
mi	miles	1.61	kilometres	km	km	0.621	miles
<u>AREA</u>				<u>AREA</u>			
in ²	square inches	645.2	millimetres squared	mm ²	mm ²	0.0016	square inches
ft ²	square feet	0.093	metres squared	m ²	m ²	10.764	square feet
yd ²	square yards	0.836	metres squared	m ²	ha	2.47	acres
ac	acres	0.405	hectares	ha	km ²	0.386	square miles
mi ²	square miles	2.59	kilometres squared	km ²			
<u>VOLUME</u>				<u>VOLUME</u>			
fl oz	fluid ounces	29.57	millilitres	mL	mL	0.034	fluid ounces
gal	gallons	3.785	Litres	L	L	0.264	gallons
ft ³	cubic feet	0.028	metres cubed	m ³	m ³	35.315	cubic feet
yd ³	cubic yards	0.765	metres cubed	m ³	m ³	1.308	cubic yards
<u>MASS</u>				<u>MASS</u>			
oz	ounces	28.35	grams	g	g	0.035	ounces
lb	pounds	0.454	kilograms	kg	kg	2.205	pounds
T	short tons (2000 lb)	0.907	megagrams	Mg	Mg	1.102	short tons (2000 lb)
<u>TEMPERATURE (exact)</u>				<u>TEMPERATURE (exact)</u>			
°F	Fahrenheit temperature	5(F-32)/9	Celcius temperature	°C	°C	1.8C + 32	Fahrenheit temperature
NOTE: Volumes greater than 1000 L shall be shown in m ³ .				NOTE: Volumes greater than 1000 L shall be shown in m ³ .			



*SI is the symbol for the International System of Measurement

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INTRODUCTION

Groundwater resources in the United States have been estimated at as much as 100 quadrillion gallons and even the lowest estimates exceed by more than 20 fold the total quantity of water contained in all U.S. lakes, rivers and streams. Nearly 100 billion gallons of groundwater are withdrawn daily in the U.S. Over 77 percent of the water supply and more than one third of the largest cities rely on groundwater resources, including approximately 15,000,000 families who rely on individual wells for water supply.

A significant threat to this water resource is that an increasing percentage of this groundwater withdrawn is being contaminated by volatile and semi-volatile organic compounds associated with various petroleum-based hydrocarbon fuels. It is becoming increasingly recognized that it is not merely the presence of these hydrocarbons, but also their potential for mobility within the environment which should be the criterion for assessing future risk. Generally, the transport mechanism of greatest interest is the continued solubilization and subsequent transfer of a contaminant into the saturated groundwater zone. This concern leads to the following question: given a petroleum product in a particular soil matrix, what are the constituents, if any, which will exfiltrate, in a solubilized form, from this soil?; and, for how long?

The major objective of this study is, therefore, to assess the leaching potential of a contaminated soil. To achieve this goal, a column leaching procedure and an analytical method were developed and used to estimate the rate of solubilization of hydrocarbons in percolating water. The procedure simulates more closely the actual field situation.

LITERATURE SURVEY

Petroleum products leaking from underground storage tanks into the soil will tend to move downward to the water table of aquifers unless an impermeable bed is encountered or capillarity of the unsaturated zone prevents any further movement. Oil diverges from the fluid dynamics of water because of its different chemical and physical properties. Oil is immiscible with water; it has a smaller density and surface tension, and a higher viscosity. Its movement as well as its retention in porous media depend on the physical properties of the medium, such as porosity and permeability (itself dependent on grain size and grain size distribution); fluid statics such as moisture content, surface tension, capillarity and wettability characteristics of the soil; fluid dynamics such as the

behavior of the oil movement and its interaction with other substances. Hysteresis (saturation history) is also a major factor in retention. The hysteretic effect is due to the presence of different contact angles during wetting and drying, and to geometric restrictions of single pores. It has important effects on water and solute distributions during field conditions which involve alternate wetting and drying of the porous medium.

Oil retained by the soil is mainly in the form of blobs. These trapped oil blobs during water passage are mobilized in a sequence of decreasing size with subsequent increases in capillary number. The capillary number, which is the ratio of viscous forces to surface forces, can be expressed as:

$$N_{ca} = K * \Delta P / \sigma L$$

where,

- K = effective permeability, md
- ΔP = pressure drop across the distance L of the porous medium, psia
- L = length of porous medium, ft
- σ = interfacial tension between the wetting and non-wetting phases, dynes/cm.

The larger blobs, which extend over many adjacent pores, break up repeatedly upon mobilization and the resulting smaller blobs are reentrained. Usually, there is negligible oil displacement until the blob population has been reduced to single pore blobs. Thus, the capillary number needed to mobilize significant amounts of oil blobs is dependent on the conditions needed to displace the singlets rather than the original blob size population. The critical condition for mobilization of a single blob is that the Darcy pressure difference from one end of the blob to the other, in the direction of flow, exceed the maximum net difference in capillary pressure between upstream and downstream menisci. Mobilization usually starts at capillary numbers greater than $10E-3$.

Many mechanisms are believed to affect transport in the unsaturated zone. These include advection with air and water, dispersion in air and water, diffusion into immobile water, mass transfer resistances at the air-water and mobile-immobile water interfaces, and adsorption.

Solubilization of Hydrocarbons in Water

Groundwater contamination results from the solubilization of the alkane, alkene and more importantly, aromatic hydrocarbon components of gasoline. A simulation based on the composition of an actual gasoline revealed that aromatic constituents, although

constituting a fraction of the initial gasoline composition, completely defined the groundwater contamination potential (1). This potential will change with time as constituents are selectively removed from the unsaturated zone. It is important to note that very small concentrations of dissolved hydrocarbons make water unfit for domestic use. Benzene is a major concern because of its extremely low drinking water standard (0.5 ppb) and its carcinogenic properties. Toluene is also a concern at a proposed maximum recommended contaminant level of 2mg/l (2ppm). Concentrations as high as 14 ppm for benzene and more than 10 ppm for each of toluene, m- and p-xylene and o-xylene were reported for domestic water wells in Connecticut (2).

Solubility of a component controls its dissolution, reactivity or degradability. Solubility decreases as the molecular weight increases for each class of hydrocarbons in oil (e.g. alkane, cycloalkane, aromatics). Addition of one carbon atom to the hydrocarbon molecule (i.e. pentane vs hexane) will decrease solubility of normal alkanes by 75% and aromatics by 70%. Temperature, pressure and salinity also affect solubility. As temperature increases, so does solubility, and since solubility also increases with increasing pH, then the presence of salts influences rates of dissolution. Table 1 shows some solubility values (3) of petroleum hydrocarbons in water at 25 C.

Table 1: Some solubilities (mg/l) of petroleum hydrocarbons in water at 25 C.

Straight chain or branched paraffins		Olefins	Cycloparaffins +Cycloolefins	aromatics			
Methane	24	ethene	131	cyclopentane	156	benzene	1780
ethane	60	propene	200	cyclohexane	55	toluene	515
propane	62	1-butene	222	cyclooctane	8	o-xylene	175
n-butane	61	1-hexene	50	cyclopentene	535	iso-propyl-	
iso-butane	49	1-octene	3	cyclohexene	213	-benzene	50
n-pentane	39						
iso-pentane	48						
2,2-dimethyl							
-pentane	33						
n-hexane	10						
n-heptane	3						
n-octane	0.7						
n-decane	0.02						
n-dodecane	0.0009						
n-tetra-							
-decane	0.0006						
n-hexa-							
-decane	0.0005						

The solubility of a mixture of petroleum hydrocarbons is assumed to be some average of the individual hydrocarbon properties, weighted according to the amount of each hydrocarbon in the mixture. Gasoline and kerosene exhibit a higher total solubility than heavier products and crudes.

The rate at which water soluble compounds are leached is determined by the partition coefficient and water/oil ratio. The failure of general film theories to yield reliable predictive methods for estimating mass transfer is a result of the assumption that all mass transfers across the films occur as a result of diffusive transport. It is clear that for many multiphase systems, mass transfer near the interface of two phases is a result of both advective and diffusive processes, as well as chemical kinetics and density-driven flow (Rayleigh instability). It is generally believed that equilibrium between the non-aqueous phase liquid (NAPL) and aqueous phase is attained over length scales (4) and contact periods (5) in porous media of the order of respectively 20 cm and 15 minutes for the soluble hydrocarbon components of a gasoline, a kerosene and a gas oil. This assumes that only diffusive transport occurs across the oil/water interface. Additional fundamental understanding of phase interactions is necessary before determining the conditions under which equilibrium assumptions are valid, if any.

Mass transfer rate coefficients are also dependent on interfacial surface area. They are therefore influenced by the NAPL saturation-interfacial surface area relationship. The surface area of a NAPL contaminating a given volume of porous medium is a function of head and neck menisci. Head menisci will be in contact with the flowing aqueous phase, whereas the neck menisci will be in contact only with the mostly immobile aqueous phase film between the solid surface and the NAPL neck as shown on Figure 1.

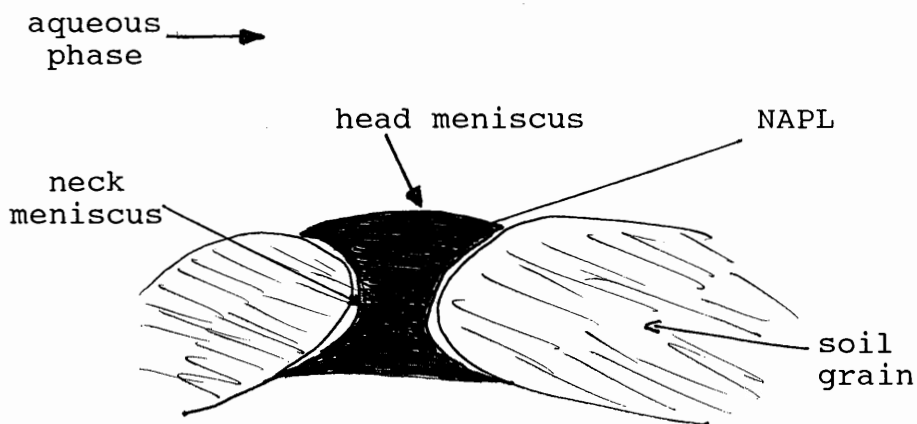


Figure 1: NAPL in a pore space.

One would expect to see higher rates of mass exchange at the head menisci than at the neck menisci, therefore an effective interfacial area, which accounts for the variations in accessibility to the NAPL, may be a more appropriate term to describe the NAPL-aqueous phase interfacial area involved in the mass transfer process. Experiments have shown that as NAPL saturation increases, mass transfer rate coefficients increase which suggests that oil/water interfacial area becomes larger with higher NAPL saturations. It is important to note that in the case of multicomponent NAPL's, resistance to mass transfer occurs within the NAPL as well as the aqueous phase and also that no relationship was established between the rate coefficients and particle size.

Ganglia Dissolution

The dissolution flux of ganglia can be expressed as:

$$F = K_l * (C_s - C)$$

where,

K_l = mass transfer coefficient

C_s = water solubility

C = average concentration dissolved in water at that location.

For ganglia diameters orders of magnitude greater than grain size, K_l can be expressed as (7):

$$K_l = 1.09 * U/n * (U * D_p/D) ** -2/3$$

where,

U = water velocity

n = porosity

D_p = particle diameter

D = molecular diffusivity of the chemical in water

The percentage of solubility of ganglia decreases with increases in flow velocity because the dissolution flux is proportional to $U^{1/3}$. Groundwater flow velocities are usually high enough that concentrations in groundwater samples are below solubility limits even when soil concentration data indicate the presence of a separate phase. The above analysis is only valid during the initial flow of groundwater through an aquifer containing trapped ganglia (plug flow). As the ganglia dissolve, their size and surface area will decrease and lower dissolution rates are expected. Ganglion lifetimes are weakly dependent on flow velocity such that to decrease the lifetime from 100 years to 10 years requires a 3 order of magnitude increase in flow velocity(8).

The extraction process of gasoline constituents into the water phase can be described if the following assumptions are used (9):

1. The transfer of components in the oil phase may be described as a single stage extraction process.

2. The low solubility of hydrocarbons causes concentrations in the extracts which decrease very slowly.

3. The extraction of the whole variety of components can (if the hydrocarbon concentration in drainwater is $>1\text{mg/l}$) be described by one partition coefficient.

4. The volume of the oil phase is equal to a constant taken as 50% of the initial amount present.

5. The oil phase is dispersed to an extent that it exposed a sufficiently large surface area to trickling water such that equilibrium concentrations in the latter phase are readily reached.

6. Adsorption is assumed negligible.

then,

$$C_w(t) = p * C_o \exp(-p*n*t/a)$$

where,

$C_w(t)$ = hydrocarbon concentration in drain water at time t (mg/l).

p = partition coefficient (w/v)

C_o = extractable concentration in oil phase at $t = 0$ (mg/l)

n = rate of water supply (L/h)

t = time (h)

a = oil phase (L)

Sorption Processes

Adsorption by the porous medium may reduce the total amount of oil transport to groundwater, reduce concentrations and delay transport. Lime, clay or organic matter will enhance adsorption. Limestone is a very weak adsorbent and organic matter has the highest adsorption potential. This physical process can usually be detected by persistent smells in the porous medium especially when oil components in the boiling range of 175 - 350 C (gas oil) are involved.

Experiments have shown (9) that in the case of dune sand which has a low adsorptive affinity, the delay in breakthrough of the various oil compounds is very obvious and chromatographic in nature. Many compounds of environmental interest do exhibit linear sorption isotherms; examples include several halogenated aliphatic hydrocarbons, polynuclear aromatic hydrocarbons and benzene. Some of the dissolved constituents may be adsorbed by some types of soil in the saturated aquifer zone, but they will be desorbed by

relatively cleaner recharge water. Therefore, adsorption and desorption must both be considered.

Biodegradation of Hydrocarbons

Microbial organisms in the soil will degrade hydrocarbons which serve as energy and carbon sources. Oxygen is required for significant microbial degradation of hydrocarbons which is carried out largely by aerobic bacteria. The optimum conditions of aeration, moisture content and nutrient availability hardly exist in nature. Very often, oxygen rather than the supply of hydrocarbons is limiting in such environment (10). 3.5 lbs of O₂ are required on the average to degrade 1.0 lb of gasoline hydrocarbon. This precludes rapid biodegradation of hydrocarbons without supplementing the oxygen which may replenish the contaminated subsurface environment under natural conditions. For a particular soil, other nutrients and minerals required by the microbes may also be limiting. However, the upper limit on degradation imposed by the O₂ storage is universal. Field and laboratory data have shown that after contamination, there is microbial degradation of petroleum products and there is an associated reduction zone surrounding the plume where free oxygen is no longer available. Very often, the hydrocarbon concentration of a contaminated soil is too high and therefore too toxic for microbial degradation to be effective.

Biodegradation is also sensitive to the diffusive properties of the soil. The larger the effective diffusion constant for the soil, the more oxygen recharge permitted, allowing for larger estimates of the upper bound for aerobic degradation. Normal alkanes and aromatics are the compounds most subject to microbial degradation.

Evaporation of Hydrocarbons

The vapor pressure of a component controls its evaporation potential. The vapor pressure of a hydrocarbon mixture is presumably some average of the individual hydrocarbon properties, weighted according to the amount of each hydrocarbon in the mixture. Gasoline range hydrocarbons exhibit a range of vapor pressures that would be considered intermediate. The vapor phase diffusion coefficients for most gasoline range hydrocarbons are in the range of 10⁴ times greater than aqueous phase diffusion coefficients, therefore vapor phase diffusion can be considered to be the primary transport mechanism of gasoline range hydrocarbons within the vadose zone and from the vadose zone to the atmosphere. Benzene, for example, is highly mobile. Experiments have shown that a pulse of benzene is quickly dispersed by leaching water. Therefore, one must consider both the high convective and diffusive mobilities of the compound. Soil cover, however, can prevent escape through the soil surface.

The liquid-vapor partition is generally represented through Henry's law:

$$C_g = H * C_l$$

where,

C_g = concentration of solute in the vapor phase
 C_l = concentration of solute in the liquid phase
 H = Henry's law constant.

Henry's law constant values, H , for the major constituents of gasoline are shown in table 2.

Hydrocarbon Mixture Analysis

The environmental behavior of fuel mixtures can best be characterized, interpreted and predicted by breaking the fuel down into a number of groups of hydrocarbons of similar structure and properties, and assigning properties such as vapor pressure, solubility and degradability to each group. Grouping must be done with assurance that the members have similar evaporation, dissolution and degradation properties.

Fuel mixtures have conservatively been estimated to consist of about 1000 components. It may be necessary for the hydrocarbons to be grouped into more than 70 classes. However, the most environmentally significant because of their relatively higher water solubility and toxicity are the aromatics which range from alkylated benzenes to naphthalenes and higher polycyclic aromatic hydrocarbons (PAH's). Table 2 shows the major constituents of environmental interest and some of their properties.

Table 2: Some properties of major constituents of gasoline (1).

Constituents	Molecular Weight g/mole	Aqueous Solubility g/cc*10**3	Henry's Constant
Benzene (C6 aromatic)	78	1.78	5.88
Toluene (C7 aromatic)	92	0.515	3.85
C8 aromatics	106	0.156	3.57
C9-C11 aromatic	132	0.040	2.94
C5 alkenes	70	0.203	0.12
C5-C6 alkanes	83	0.021	0.03
C6 naphthenes	84	0.055	0.10
C7-C11 alkanes	113	0.002	0.008
C6-C11 alkenes	103	0.030	0.23

C7-C11 naphthenes	98	0.030	0.030
Cyclohexane	84	0.055	0.15
1-hexene	84	0.050	0.067
n-hexane	86	0.0095	0.015
o-xylene	106	0.152	4.68
n-octane	114	0.00066	0.0079

EXPERIMENTAL APPROACH

The potential for mobility of hydrocarbons in the environment is the main criterion for assessing future risk. Unfortunately, there is no general reliable predictive tool for assessing this risk. However, experimental data can be obtained to determine the mobility of different hydrocarbon constituents in a given soil, thereby providing valuable data for assessing the risk for prolonged contamination of groundwater by percolating gasoline-contaminated water in a given area. The data obtained is usually site-specific. For the present study, it was decided to use a soil which is commonly exposed to gasoline contamination in Connecticut. By developing a reliable soil preparation and leaching procedure along with an appropriate analytical method that produces good resolution of the gasoline-contaminated water samples, it is possible to generate very useful data.

EXPERIMENTAL PROCEDURE

Column leaching experiments were conducted in a glass column as shown in figure 2. The soil used in these experiments was a Hinckley soil taken from the C-horizon, the unconsolidated material underlying the solum or true soil. The C-horizon was chosen because petroleum leaching is generally located within this horizon.

The Hinckley soil is a coarse sand and is classified as a sandy skeletal, mixed, mesic Typic Udorthent. It is considered excessively drained. The soil was collected from a quarry bank in Putnam, Connecticut. The quarry is located in a wooded area in a glacial outwash deposit (ice contact stratified drift). The parent material is stratified sandy gravelly and cobbly glaciofluvium derived principally from granite, gneiss and schist. The sampled horizon was described as follows: Whitish yellow (10YR 8/4) medium

sand, 5% cobble, single grained, loose, nonsticky, nonplastic, clear wavy boundary. Soil characteristics are shown in tables 3 and 4. Organic matter and clay contents are very small, therefore adsorption should be very minimal.

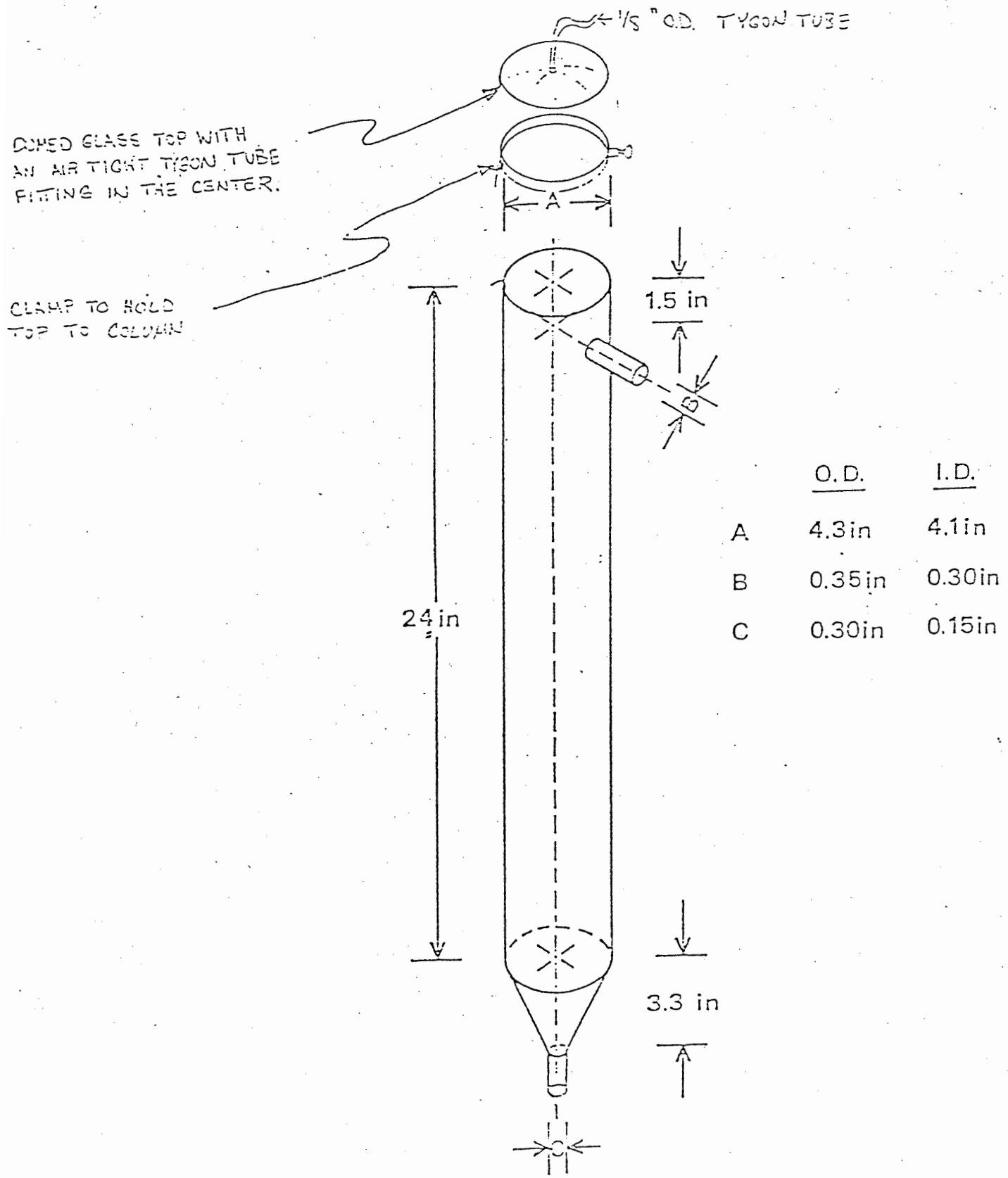


Figure 2: GLASS COLUMN

Table 3: Soil Characteristics

Characteristic	Hinckley Soil
pH	5.2
% organic matter	0.08
Cation exchange capacity (meq NH ₄ per 100 g of soil)	0.79
% free iron	0.01
% sand	99.0
% silt	0.7
% clay	0.3

Table 4: Particle size analysis

Range (mm)	Hinckley soil (%)
2 - 1	22.2
1 - .5	47.0
.5 - .25	21.7
.25 - .1	7.0
.1 - .05	1.1
.05 - .002	0.7
<.002	0.3

The Hinckley soil was sieved through 2mm mesh sieves, air dried and stored in sealed plastic bags at room temperature until used. The Soil Conservation Service (U.S. Department of Agriculture, 1983) lists in-situ bulk density and saturated hydraulic conductivity for the Hinckley soil (at depths collected) as 1.3-1.5 g/cc and >50.8 cm/hr, respectively. Particles larger than 2mm but smaller than 0.635cm were used as a gravel pack for

the bottom of the soil column.

Soil Column Preparation

To avoid stratification and air entrapment during the packing procedure, the soil was slowly but continuously poured in a water-containing glass column. Precaution was taken to keep the deionized distilled water level above the soil level. The column was gently shaken during the procedure to obtain a closer packing. Measurements of water, soil and column volumes were taken to determine the porosity of the soil:

$$\phi = \frac{V_w}{V_c}$$

where,

V_w = Volume of water in the soil column, cc
 V_c = Volume of column, cc = Bulk volume of soil

Reproducibility studies showed that the average porosity of the soil was $40.1 \pm 0.7\%$; coefficient of variation, C.V = 1.3%. The average bulk density was 1.58 ± 0.03 g/cc; C.V = 0.3%. This value compared well with the above-listed in-situ value of 1.3-1.5 g/cc.

After water drainage, the soil was saturated with the gasoline by injecting from the bottom inlet of the column. This prevents fluid fingering from occurring by having a gravity stable injection. Fuel and air saturations in the soil were determined by measuring the amount of fuel that entered the column.

$$F_s = \frac{F_v}{P_v}$$

where,

F_s = fuel saturation in the soil
 F_v = fuel volume in the soil
 P_v = pore volume of the soil

also,

$$A_s = \frac{A_v}{P_v}$$

where,

A_s = air saturation in the soil
 A_v = air volume in the soil
 P_v = pore volume of the soil

24 hours after the saturation process, the soil was allowed to desaturate by letting the fuel drain freely from the column for two days. Measurements of fuel and water amounts that drained out were taken. Final average water, fuel and air saturations in the column were calculated using the abovementioned equations.

The water saturation in the column should have the profile shown in Figure 3. Long column packs (>25cm) are usually chosen to avoid the end effect of the sample core. The end effect is analogous to the capillary fringe of a soil profile. At the sample bottom or effluent end the net upward component of capillary forces is greater than the net downward component. Gravity is somewhat overcome, so retention and saturation values are greater in this section than in the higher portions of the pack where capillary forces are balanced. Fluid saturation would be 100% if a free fluid body existed at the base. The end effect is minimum when capillarity is weak, i.e., when porosity and permeability are high. The packs used in the present experiments were 31 cm long and fairly permeable. Therefore, the end effect was not significant.

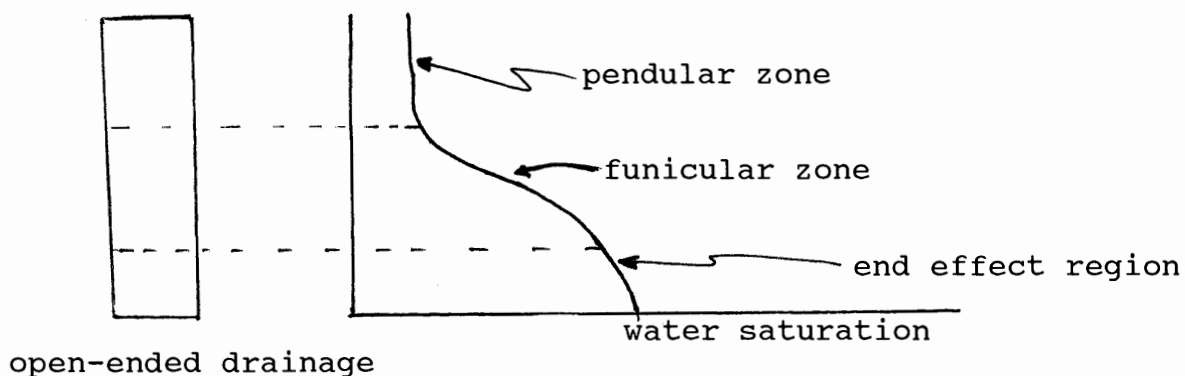


Figure 3: Water retention in an open-ended drainage.

The absolute permeability of the soil was measured by measuring the quantity of water flowing out of the column within a given time interval. The soil column was kept fully saturated during the test. The following Darcy's law equation for a fully saturated medium containing a single fluid was used:

$$k = \frac{0.002364 * Q * \mu}{- A [\Delta P / \Delta L - 0.433 * \rho * \cos \theta]}$$

where,

- k = absolute permeability, darcy
- Q = water flowrate, cc/mn
- μ = water viscosity, cp
- A = cross-sectional area of the soil column, ft
- ΔP = pressure drop across soil column, cm
- ΔL = length of soil column, cm
- ρ = specific gravity of water, g/cc
- θ = angle between the soil column axis and vertical axis

Reproducibility studies showed that the average value of absolute permeability obtained was 16.5 + 0.8 darcy. The average saturated hydraulic conductivity value was 55.4 + 1.1 cm/hr (C.V = 3.8%) and compared well with the U.S. Department of Agriculture data for Hinckley soil at the depths collected (>50.8 cm/hr).

After water saturation the soil column was allowed to achieve a stabilized water-wet condition (24 hours). The soil was then desaturated by allowing water to flow freely out of the column for a period of 48 hours. An average residual water saturation in the soil was calculated by measuring the amount of water that drained out of the column.

$$Rws = \frac{Wv}{Pv}$$

where,

- Rws = residual water saturation in the soil
- Wv = water volume left in the soil after drainage
- Pv = pore volume of soil

The average residual water saturation obtained was 25.4 + 0.3%; C.V = 1.1%.

The soil column was then saturated with SUNOCO gasoline by injecting the fluid from the bottom of the column to allow for a gravity stable saturation. The column was left undisturbed for two days so that soil/water/gasoline equilibrium could be reached. The gasoline was then allowed to drain freely out of the column. The average residual gasoline saturation obtained after four days of drainage was 11.6 + 0.4%; C.V = 0.7%.

The porous medium was kept unaerated to decrease O₂ availability that would enhance biodegradation. This also helped minimize volatilization of the more volatile hydrocarbon components

of the gasoline.

Leaching and Sampling Procedure

The equivalent of five inches of Milli-Q deionized distilled water (approximately one pore volume or 1100 cc) was percolated daily through the soil column. A total of 285 inches of water was injected. Assuming an average Connecticut yearly rainfall of 50 inches, the amount injected corresponds to 5.7 years of rainfall. Samples of effluent water were taken regularly for analysis of the most environmentally significant water soluble contaminants, namely benzene, toluene, ethylbenzene, m- and p- and o- xylenes, as well as methyl tert-butyl ether (MTBE).

Fuel Characterization

The SUNOCO gasoline was characterized using a GC/FID purge and trap method. Table 5 and Figure 4 show the data and corresponding chromatogram of the gasoline. It can be concluded from looking at the excellent resolution from the chromatogram that the SUNOCO gasoline contains high amounts of aromatics and olefins. The concentrations of the water soluble contaminants of interest are the following:

Benzene: 3.46%
Toluene: 11.13%
Ethylbenzene: 2.68%
m- and p- Xylene: 10.12%
o-xylene: 4.18%

Experimental Procedure for Hydrocarbon Detection in Water

All water samples and spiked standard solutions were prepared on a Tekmar 4000 purge and trap device. A 5-ml aliquat of water was purged for 8 minutes with a stream of nitrogen with a flowrate of 40ml/min. The purged hydrocarbons were adsorbed on a Carbotrap 300 trap (Supelco 2-0321) and then dry-purged for 4 minutes to remove excess water from the trap. The hydrocarbons were then desorbed at 240 °C for 1 minute with a stream of helium with a flowrate of 3ml/min. The desorbed flow was introduced via a heated transfer line at 180 °C into the split/splitless injection port at 200 °C of a HP5890A gas chromatograph. After the 1 minute desorb time, the purge valve was turned on, sweeping the remainder to vent. The Carbotrap was then baked for 8 minutes at a temperature of 280 °C under a 40ml/min stream of nitrogen.

Analytes were separated on a 30-meter, 0.32-mm i.d., fused silica capillary column (J & W 123-1035) having a 5 m DB-1 thin film coating. The helium carrier gas was maintained at a 20 psi head pressure, which delivered an approximate 3 ml/min flowrate through the column. Eluted molecules were detected by a flame

ionization detector, maintained at 200°C. A hydrogen fuel source was supplied at 30 ml/min, and the air oxidant was supplied at 350 ml/min.

Data acquisition, peak integration, and report generation were accomplished by using a HP-300 Pascal Chemstation. Report results were stored on 3.5 in. diskettes for storage and transferred to a MS-DOS PC-compatible computer via a RS-232 linkage for data presentation and final report integration.

ANALYSIS OF RESULTS

The reproducibility of the results obtained from Column 1 was checked by conducting a second column leaching experiment. Similar results were obtained proving that the results were reproducible. The values obtained from Column 2 were on the average 5% lower than the ones from Column 1, as can be seen from figures 5 and 6. A 5-point smoothing technique was used to smooth the raw data of figures 7 and 8. The differences observed between column 1 and 2 can be attributed to slight differences in porosity, permeability and gasoline saturations between the two columns (see table 6).

Table 6: Column Characteristics

	Column 1	Column 2
Porosity,	40.1	40.9
Permeability, K in Darcy	16.3	17.1
Residual water saturation,% of pore volume	25.6	25.2
Residual oil saturation,% of pore volume.	11.3	12.1

The data from figures 5 through 20 show that the solubility is an important factor in the rate of solubilization of hydrocarbons in water. MTBE, which is the most soluble component of gasoline reached concentrations <1 mg/l after 7 pore volumes of water (35 inches) were injected. This means that within a year of rainfall MTBE can be dissolved completely out of the gasoline in the porous medium. Benzene, which is the second most soluble component of the

gasoline attained the 1mg/l (1ppm) level after 24 pore volumes of water (120 inches) were injected. After 220 inches of percolation, the concentration was around 0.06 mg/l or approximately 6 ppb, still above the recommended maximum level of 0.5 ppb. This means that close to 5 years of rainfall may not be sufficient to solubilize all the benzene available in the NAPL. Toluene, the next most soluble component of gasoline reached a concentration <2mg/l (2ppm) which is the proposed maximum concentration level, after 47 pore volumes (235 inches of water) were injected, suggesting that it may take 5 years of rainfall to deplete the toluene from the residual NAPL. The remaining four components of gasoline analyzed (ethylbenzene, m- and p- and o- xylene) have much lower solubilities. The lowest concentration obtained after 57 pore volumes of water were injected were 4.53, 19.95 and 7.92 mg/l for respectively ethylbenzene, m- and p- xylene, and o-xylene. Therefore, the equivalent of 6 years of rainfall did not significantly drop the levels of the contaminants in the water. Decades may be necessary to bring down these levels to the recommended ppb level.

From Figures 5 and 6, one can notice that when the concentration of benzene sharply declined, the concentration of the other soluble components increased. Likewise, when the concentration of toluene declined sharply, a slight increase in the concentration of the xylenes and ethylbenzene was noticed. These observations suggest that there is indeed a synergistic co-solute effect between soluble gasoline components; The more soluble hydrocarbons will tend to solubilize faster in the flowing water phase, thereby affecting the concentration of less soluble hydrocarbons in the water stream. As the concentration of the more soluble hydrocarbons decreases, less competition for solubilization of the hydrocarbons in the water makes it possible for the less soluble hydrocarbons to reach higher concentrations in the water. This suggests that even though the more soluble aromatics will dissolve faster and present an urgent contamination problem, an underlying problem may exist due to increased concentrations of the less soluble hydrocarbons in years to follow.

It should be noted that the concentrations of the contaminants in the water were, as expected, below solubility levels. In the case of benzene, concentration levels were at best 5% of the maximum benzene solubility in water. For toluene the percentage was 20%. For xylenes, the percentage was about 12%. This indicates that, even though some equilibrium may have been reached in the water at the effluent end due to the length of the porous medium and the residence time of the water during percolation, the co-solute effect plays an important part in the rate of solubilization of the different hydrocarbon components of the gasoline.

Adsorption of gasoline is believed to have been negligible due to the low organic matter and clay content of the soil used. To further verify this fact, no retention of chromatographic nature of solubilized hydrocarbons was noticed since the first water samples collected had high concentrations of soluble hydrocarbon

contaminants similar to the samples that followed.

Biodegradation of the contaminants was not apparent. No algae formed in and around the porous medium. The initial presence of the hydrocarbon pure phase before the oil desaturation process created a medium that was probably too toxic for microorganisms to be effective. More dilute conditions later on may have led to some biodegradation. It was kept to a minimum by allowing no aeration of the medium, depriving the microorganisms of a sufficient supply of oxygen necessary for metabolizing the hydrocarbons.

CONCLUSIONS

The following conclusions can be drawn from the data presently available:

- The higher the solubility of the hydrocarbon, the faster it will be depleted from the NAPL.

- MTBE was the fastest component of the gasoline to reach very low concentrations in the water, and therefore it was the first to be depleted from the NAPL. Its solubilization into percolating rainwater may last for a year in a Hinckley soil.

- Years and even decades may pass during which the other soluble hydrocarbons (benzene, toluene, m- and p- and o- xylene, ethylbenzene) will continue to solubilize into the percolating rainwater and migrate to the underlying aquifers.

- The co-solute effect between hydrocarbons plays an important role in the rate of solubilization of hydrocarbons in water.

- Even though the more soluble aromatics will dissolve faster and present an urgent contamination problem, an underlying problem may be the increased concentrations of less soluble hydrocarbons in the following years.

- The soil preparation procedure developed for the experiments yielded excellent reproducibility thereby proving its adequacy.

- The GC/FID purge and trap method developed produced excellent resolution and proved to be very valuable and reliable.

RECOMMENDATIONS

- The leaching experiments should be continued to complete the data acquired.

- More hydrocarbons of environmental interest should be characterized and analyzed from the data presently available thanks to the excellent resolution obtained.

- Other types of porous media and gasolines should be used to confirm the above-mentioned conclusions.

- The use of longer porous media should be investigated to obtain more information on equilibrium conditions.

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FIGURES

Column 2 Elution Plots

BTEX 5-Point Smoothing

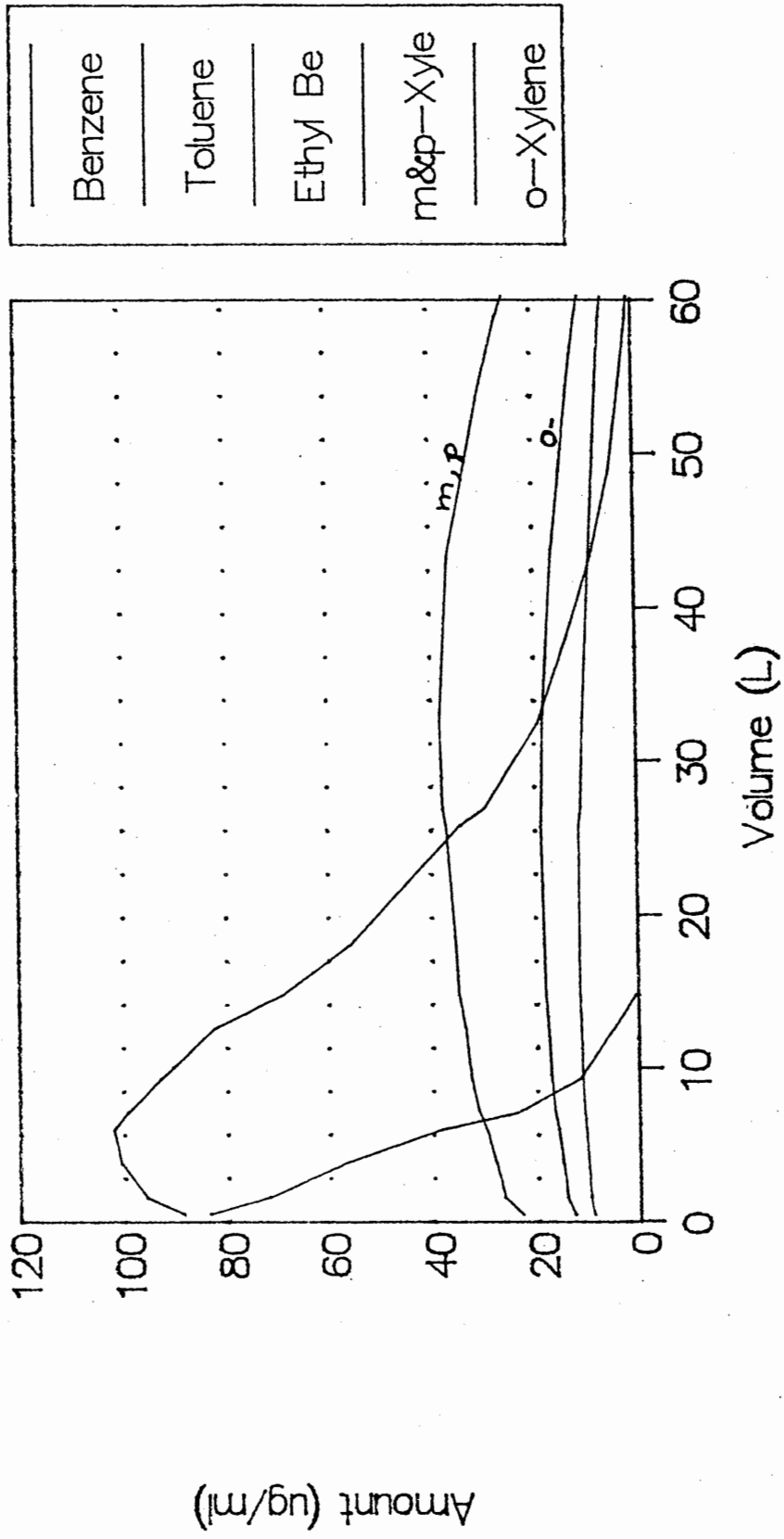


Figure 5: Concentration of BTEX in effluent water (smoothed data)

Column 1 Elution Plots 5-Point Smoothing

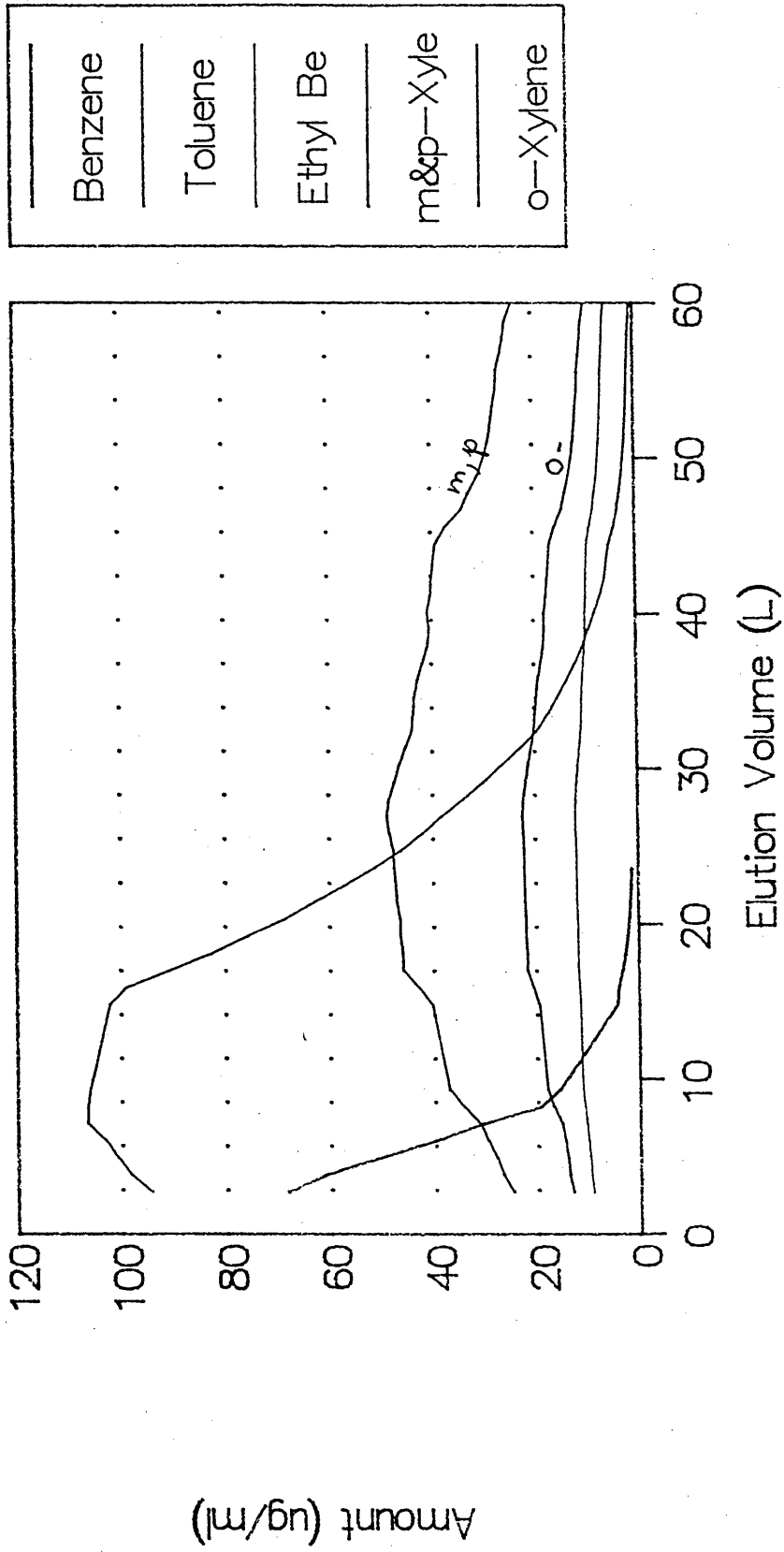


Figure 6: Concentration of BTEX in effluent water

Column 2 Elution Plot

BTEX Raw Data

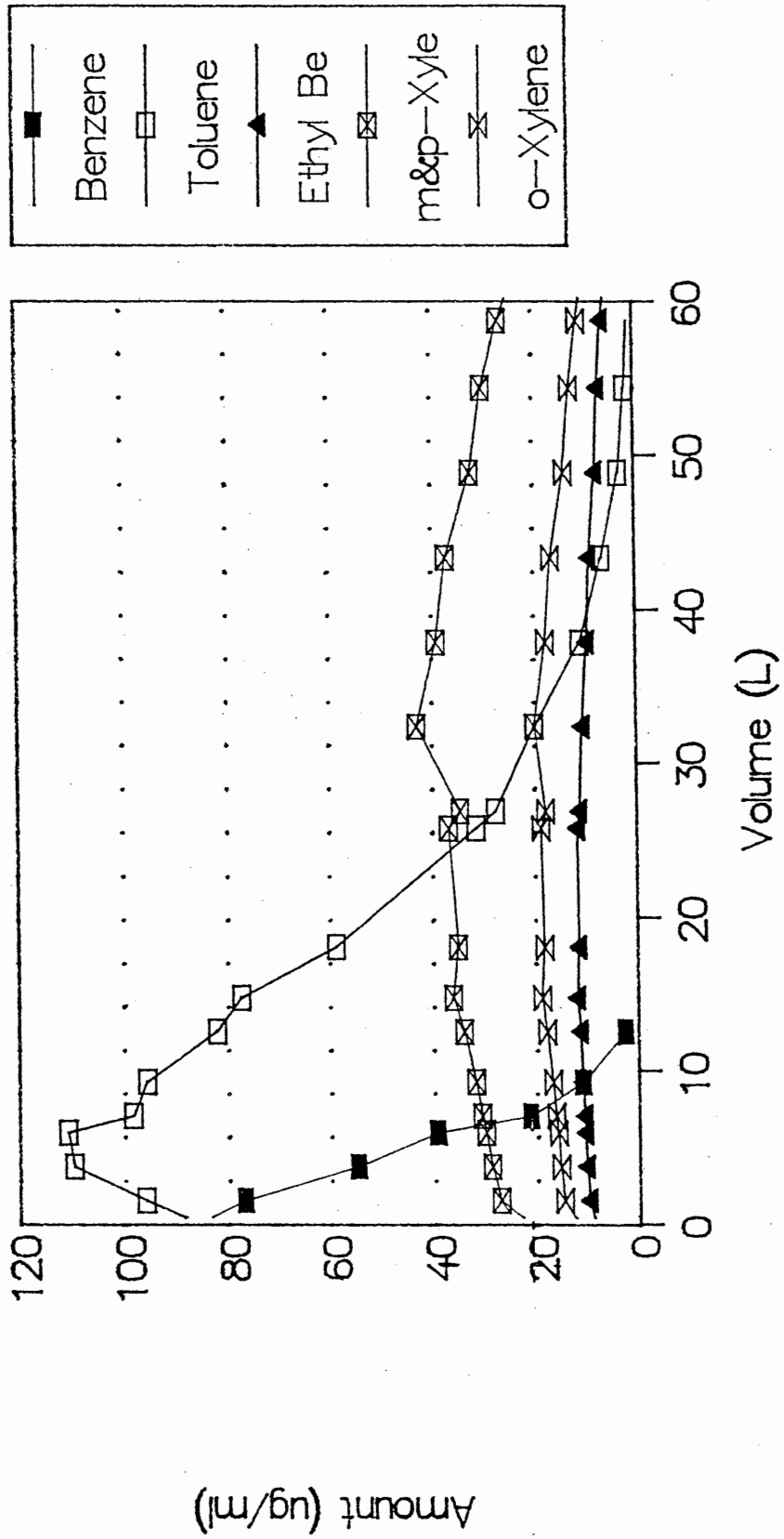


Figure 7: Concentration of BTEX in effluent water

Column 1 Elution Plots BTEX Raw Data

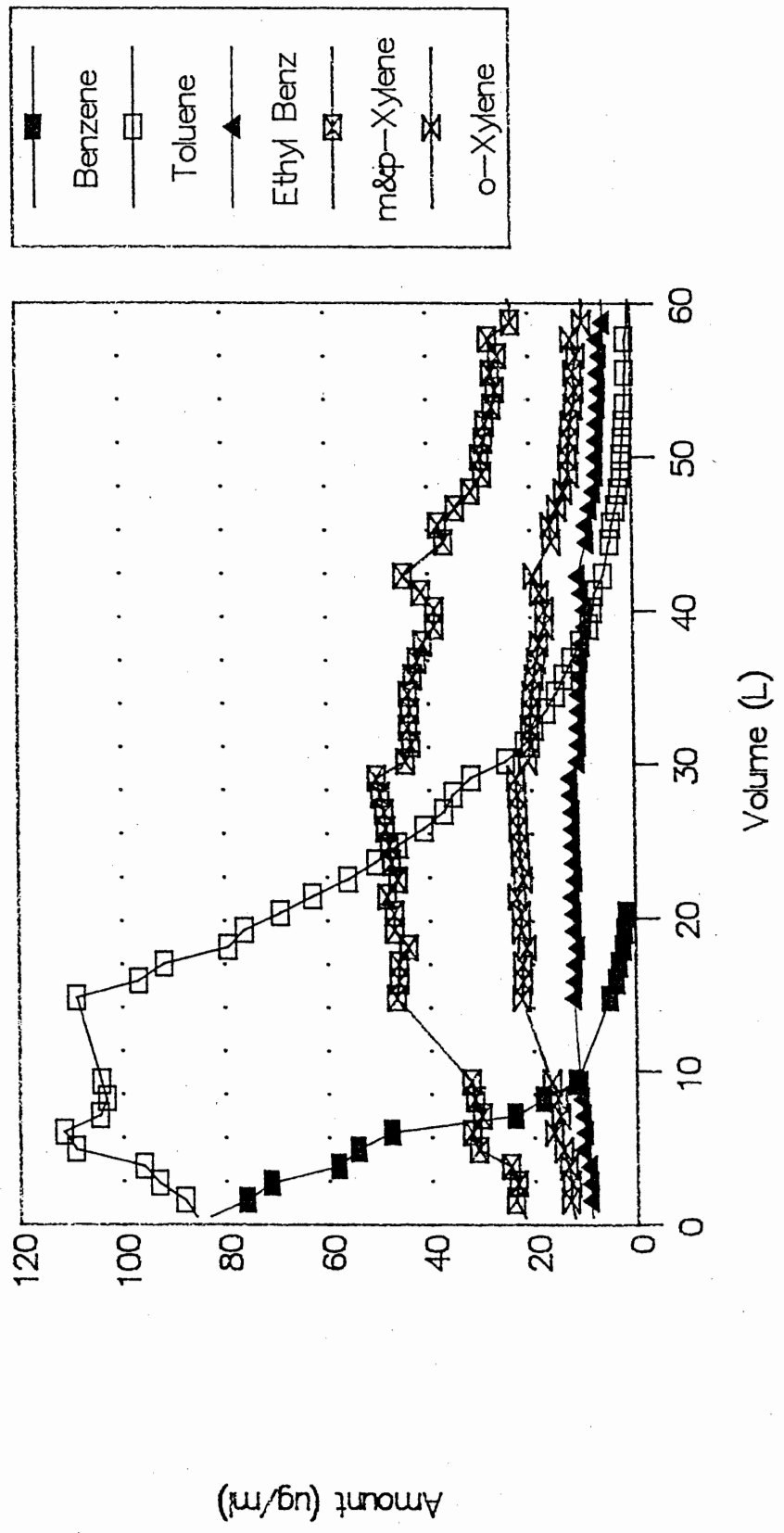


Figure 8: Concentration of BTEX in effluent water

Column 2 Elution Plot

Methyl t-Butyl Ether

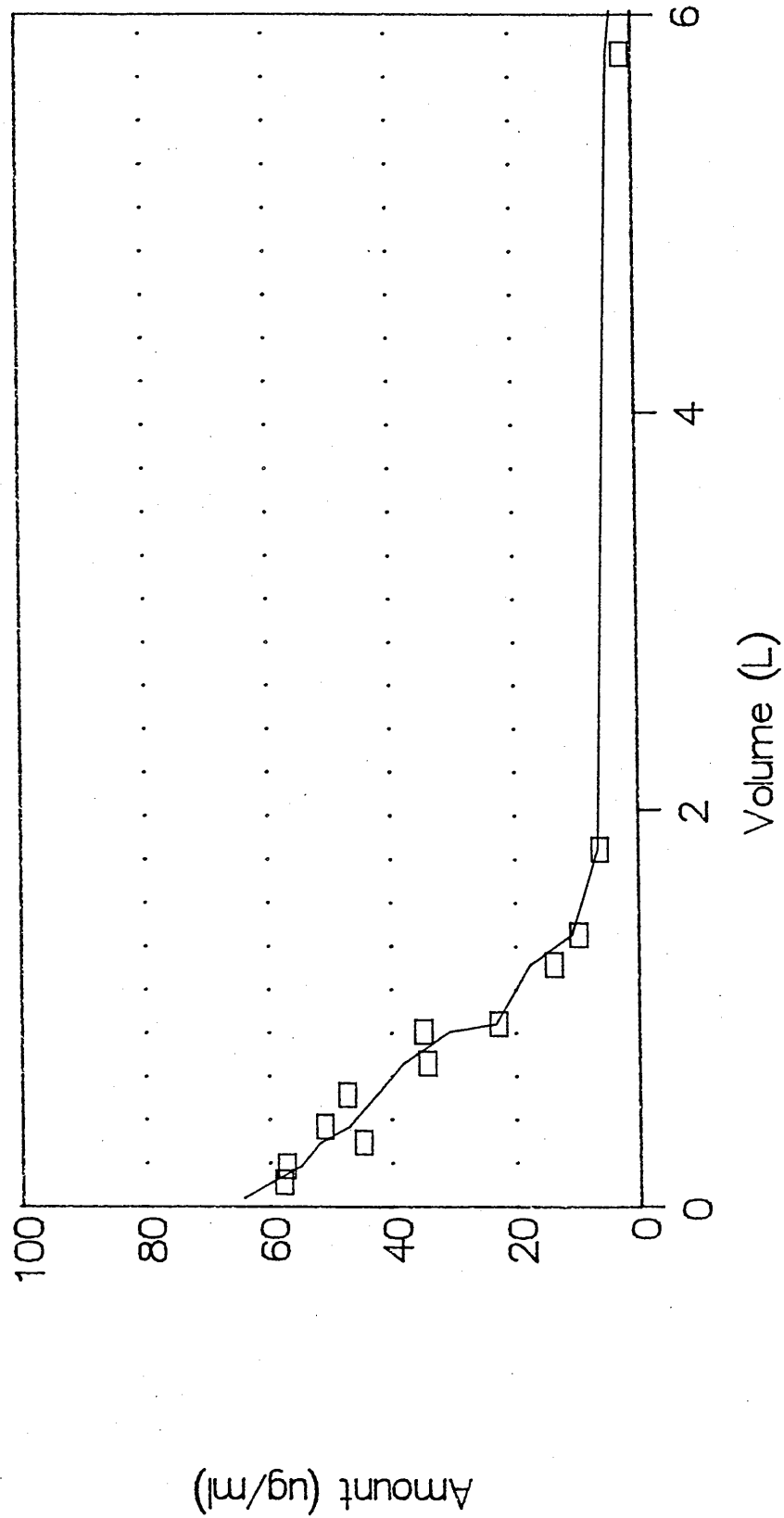


Figure 9: Concentration of MTBE in effluent water

Column 1 Elution Plot
Methyl t-Butyl Benzene

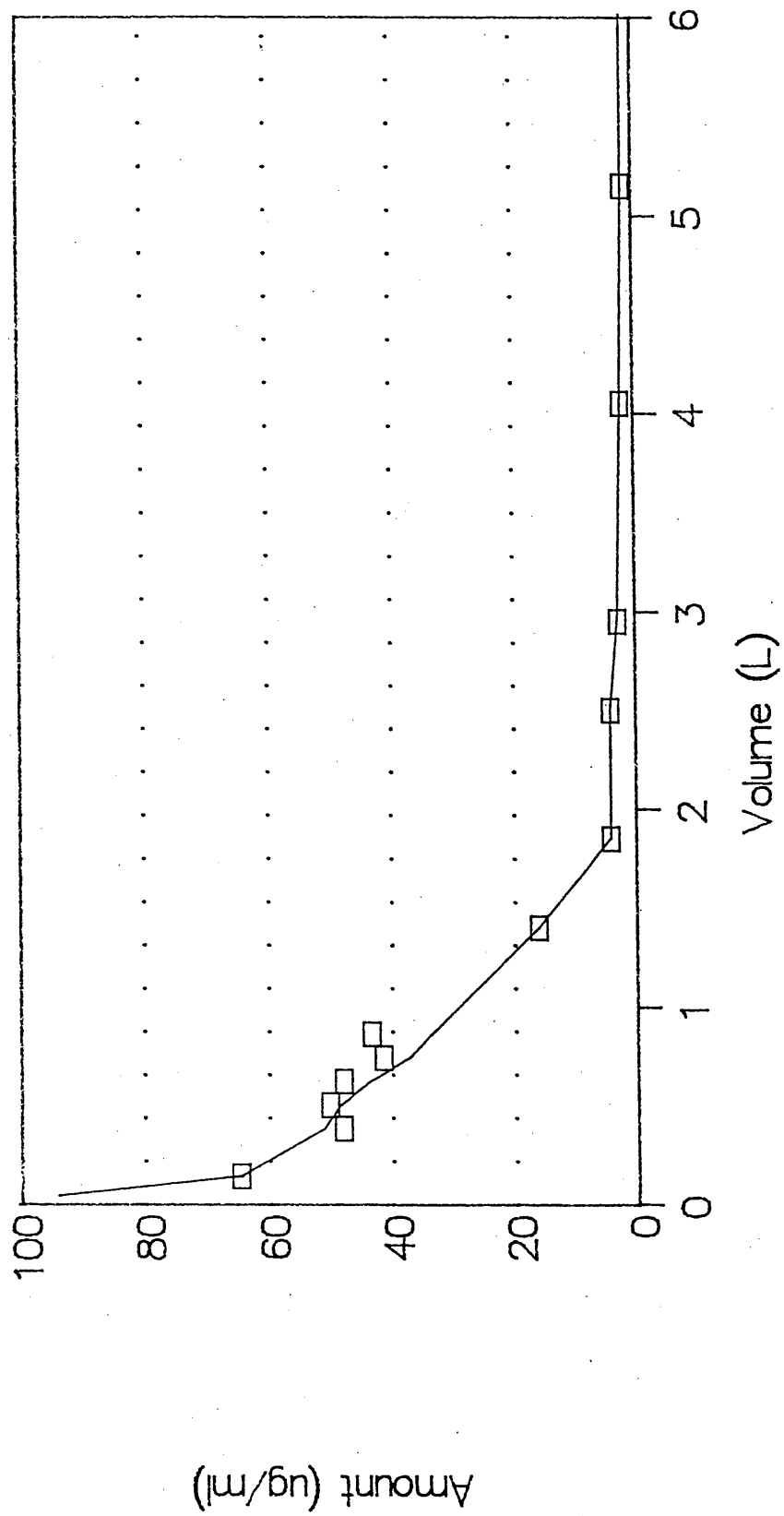


Figure 10: Concentration of MTBE in effluent water

Column 2 Elution Plot

Benzene

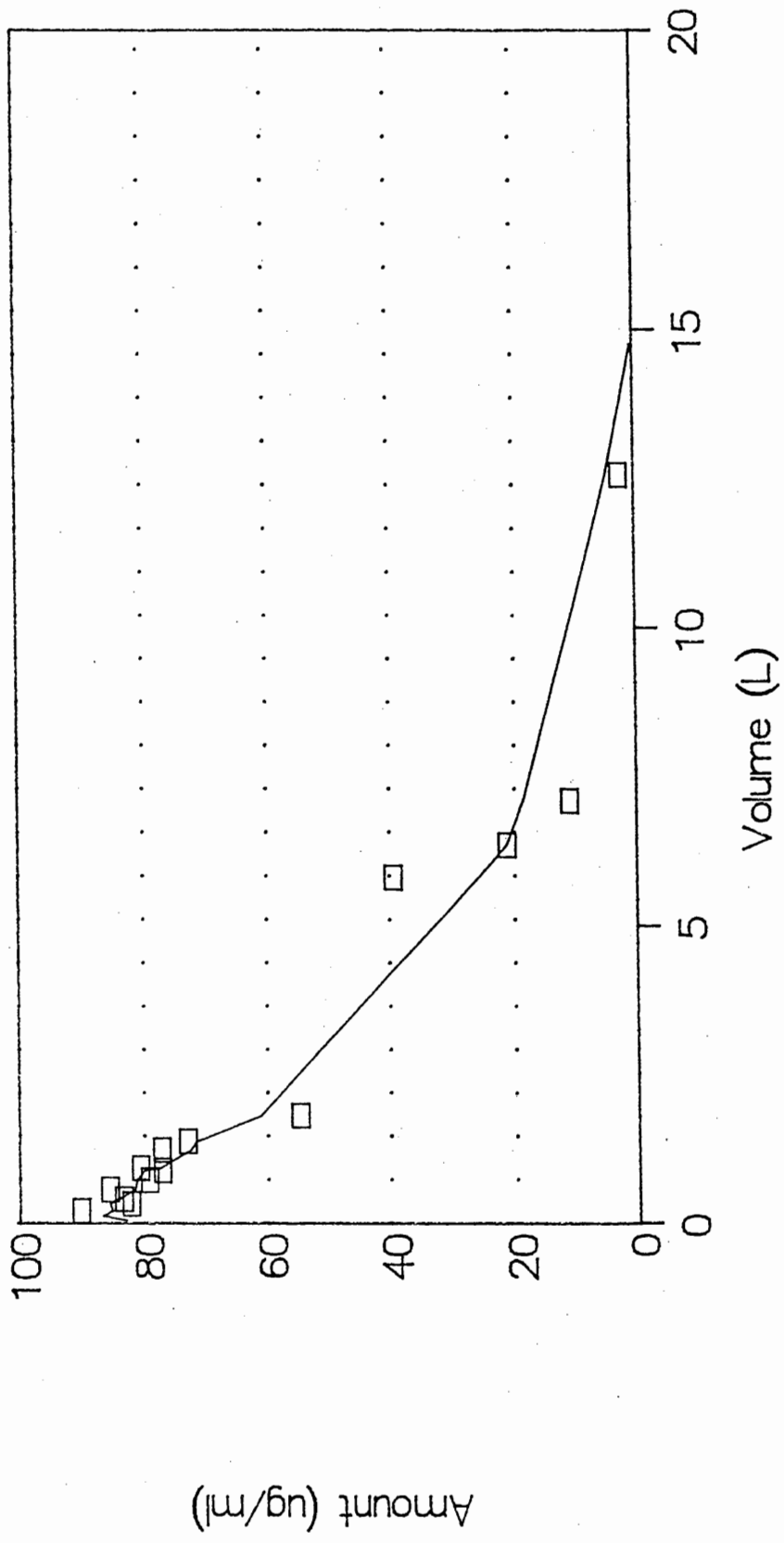


Figure 11: Concentration of benzene in effluent water

Column 1 Elution Plot

Benzene

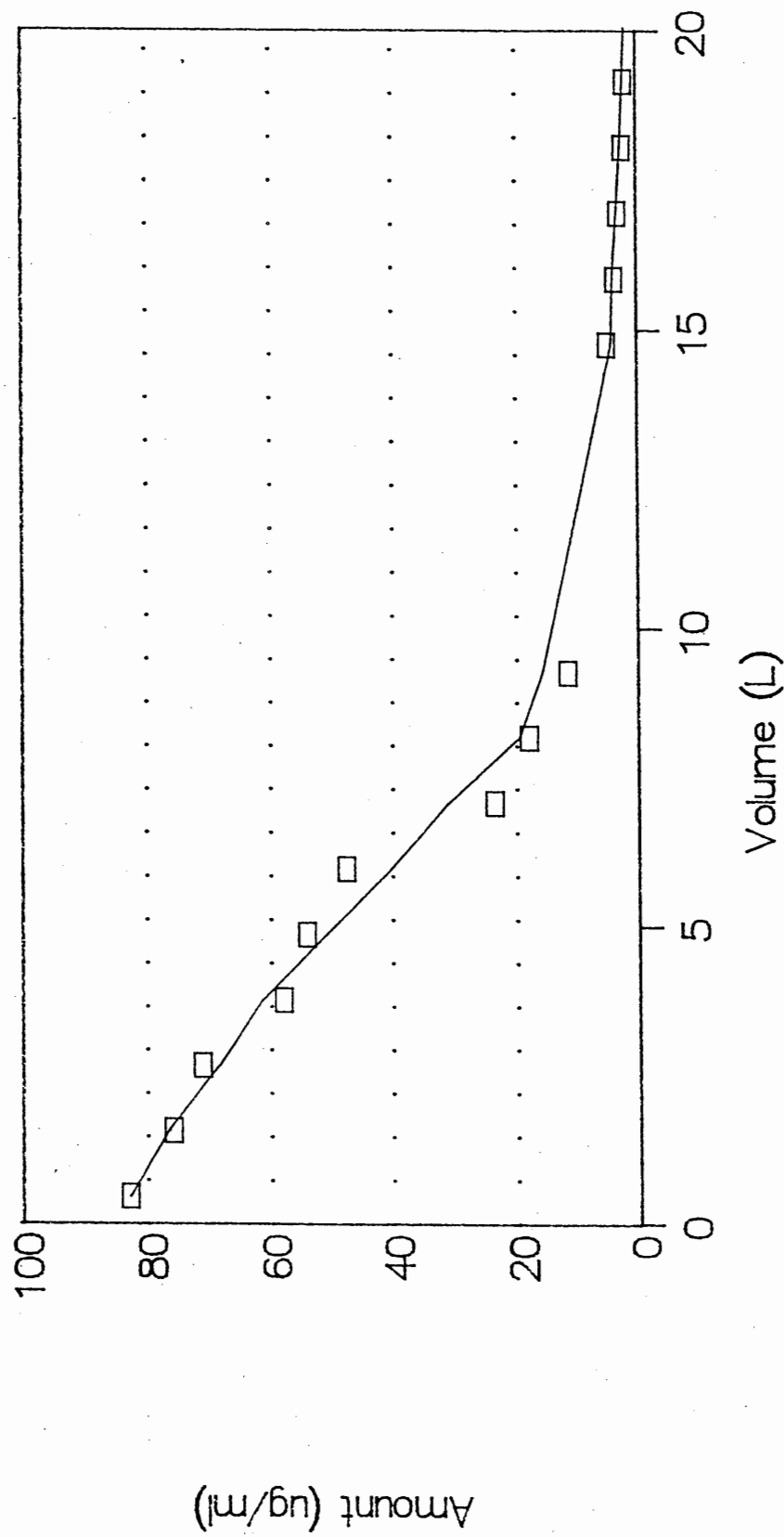


Figure 12: Concentration of benzene in effluent water

Column 2 Elution Plot

Toluene

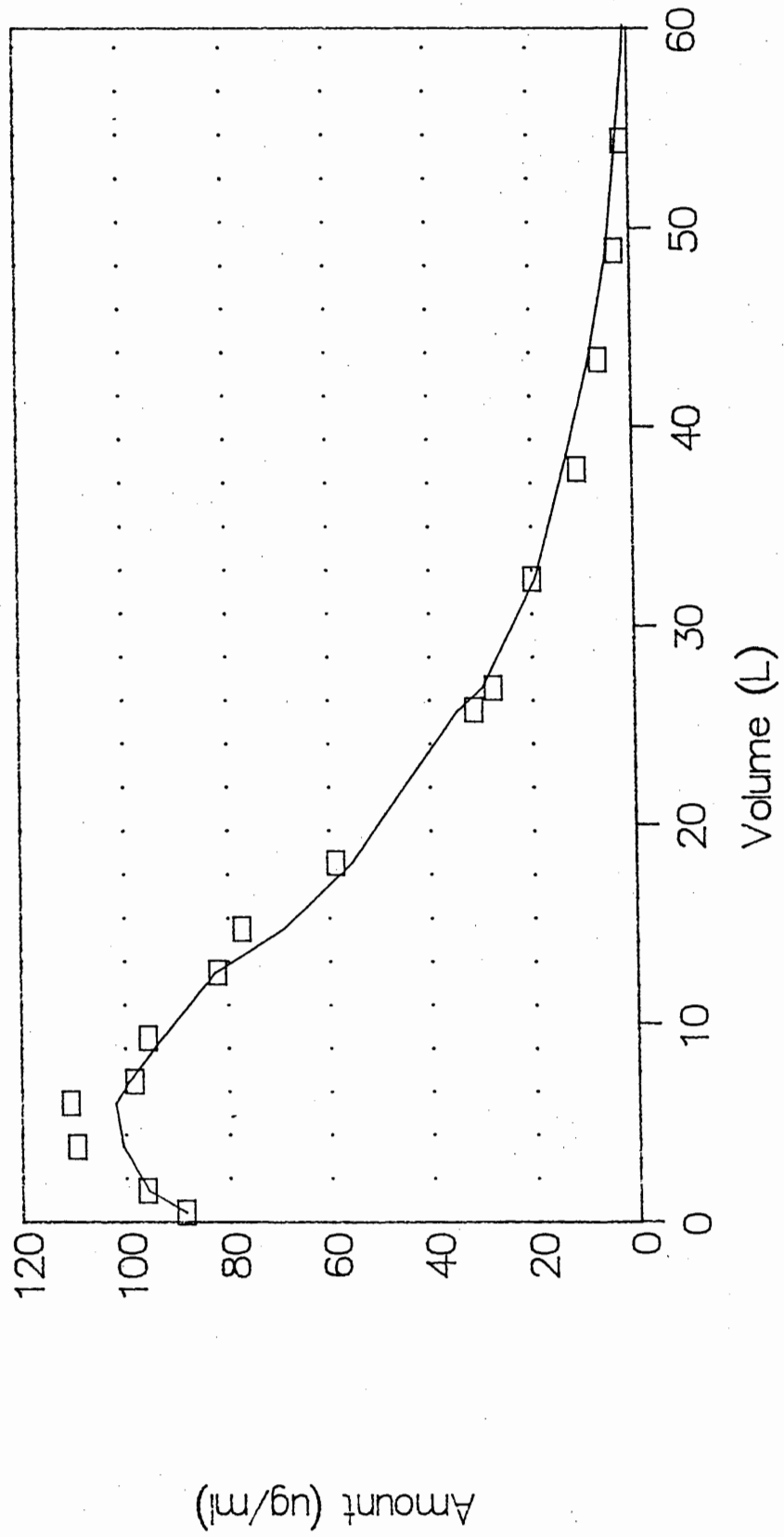


Figure 13: Concentration of toluene in effluent water

Column 1 Elution Plot

Toluene

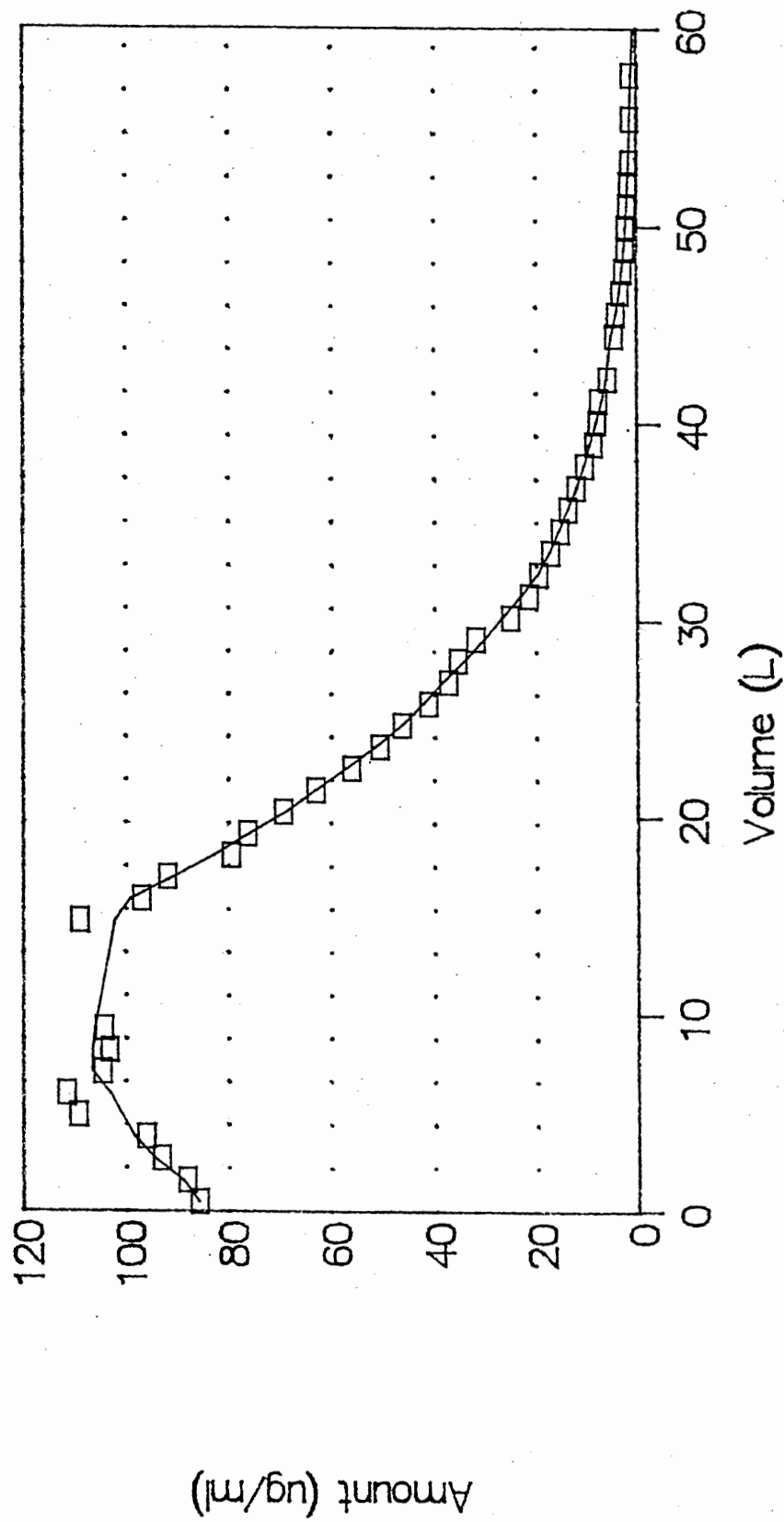


Figure 14: Concentration of toluene in effluent water

Column 2 Elution Plot

Ethyl Benzene

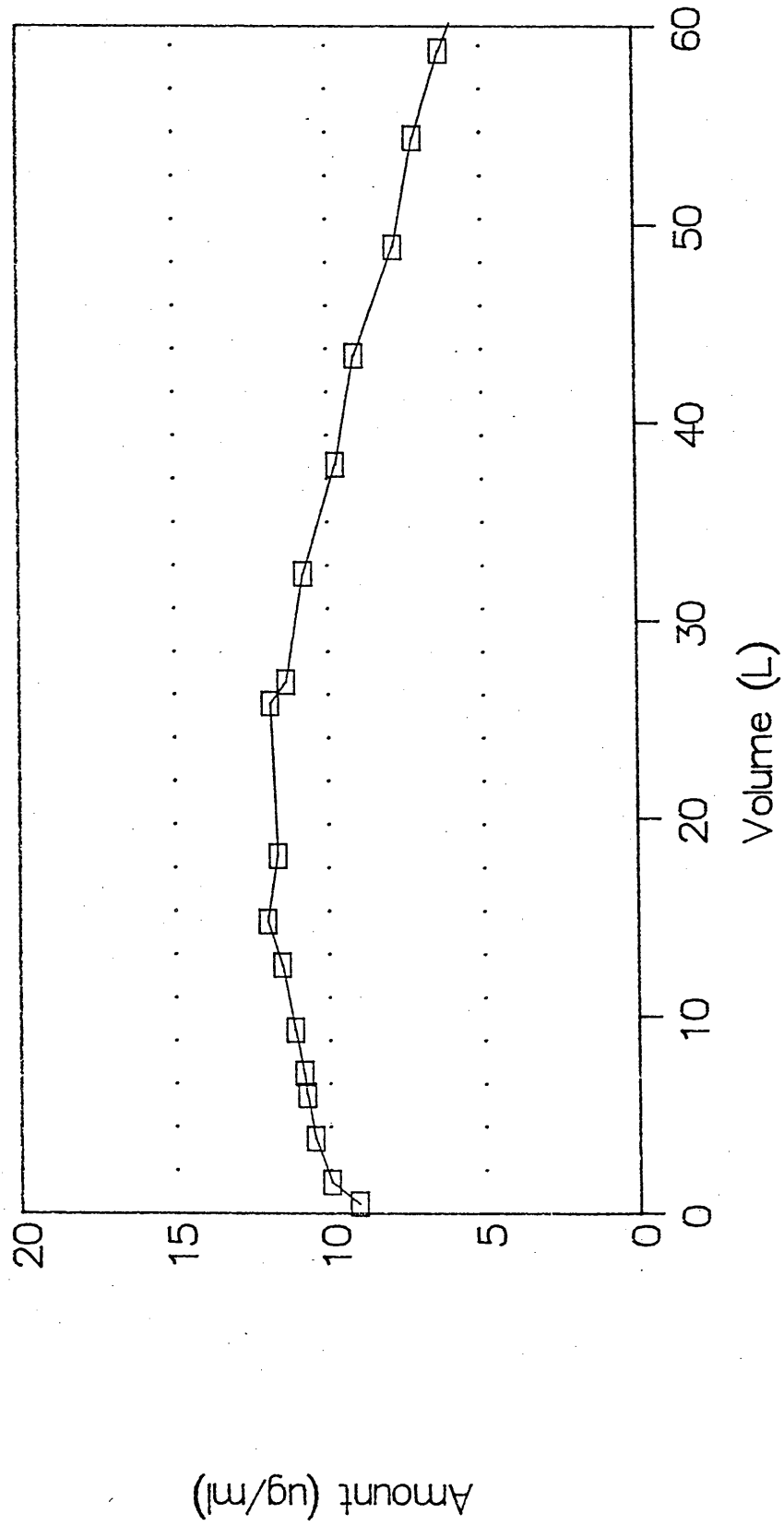


Figure 15: Concentration of ethylbenzene in effluent water

Column 1 Elution Plot

Ethyl Benzene

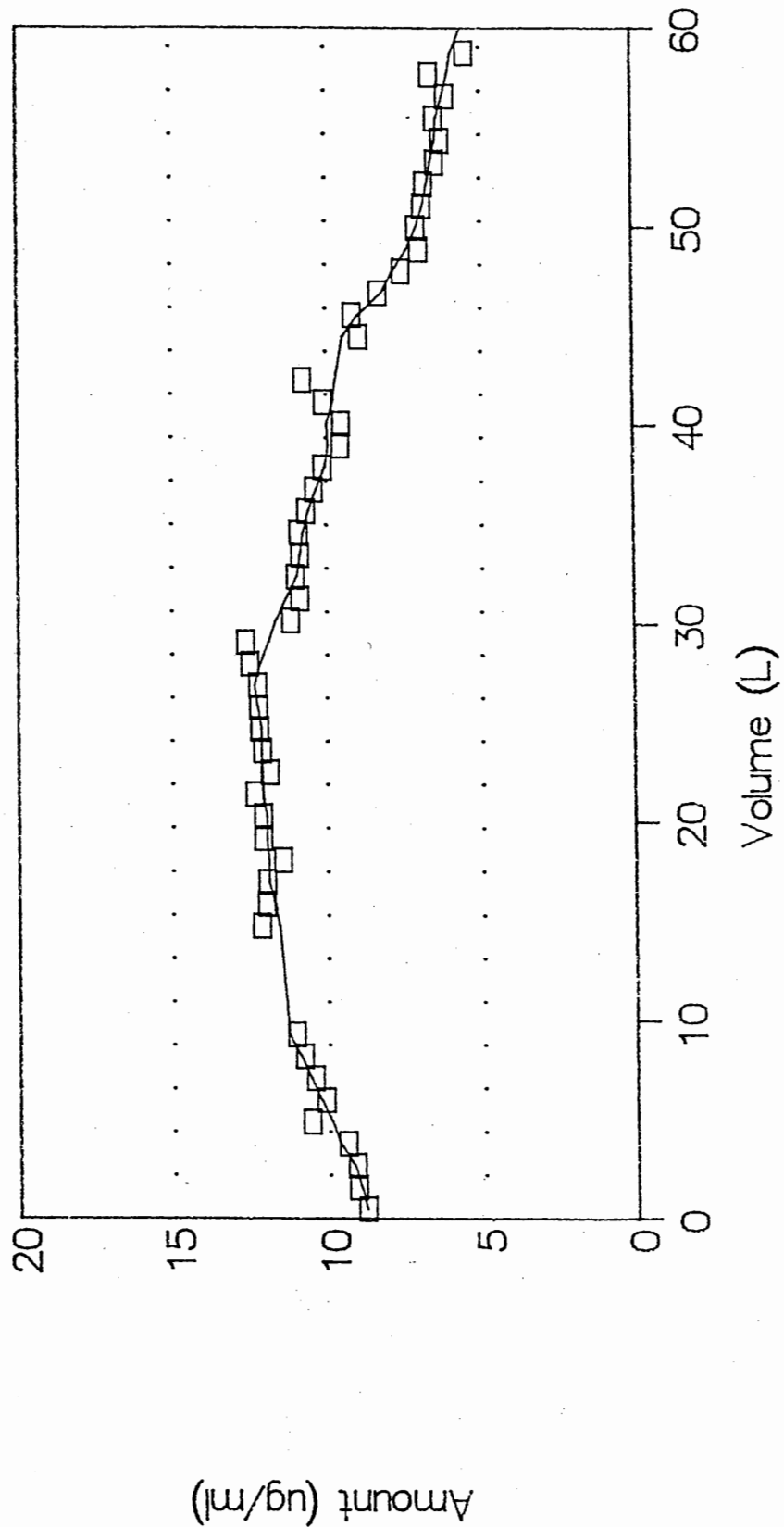


Figure 16: Concentration of ethylbenzene in effluent water

Column 2 Elution Plot

o-Xylene

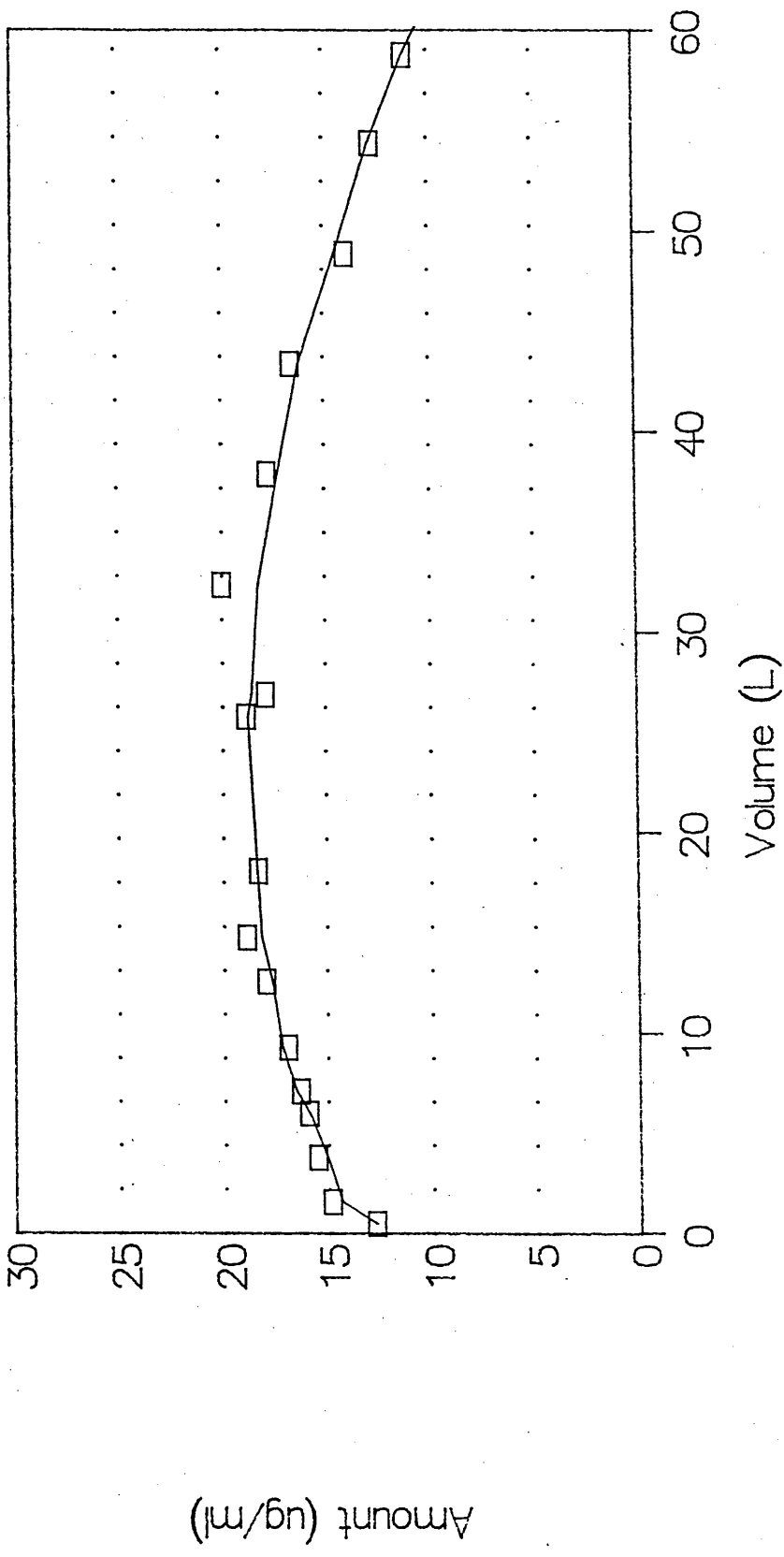


Figure 17: Concentration of o-xylene in effluent water

Column 1 Elution Plot

o-Xylene

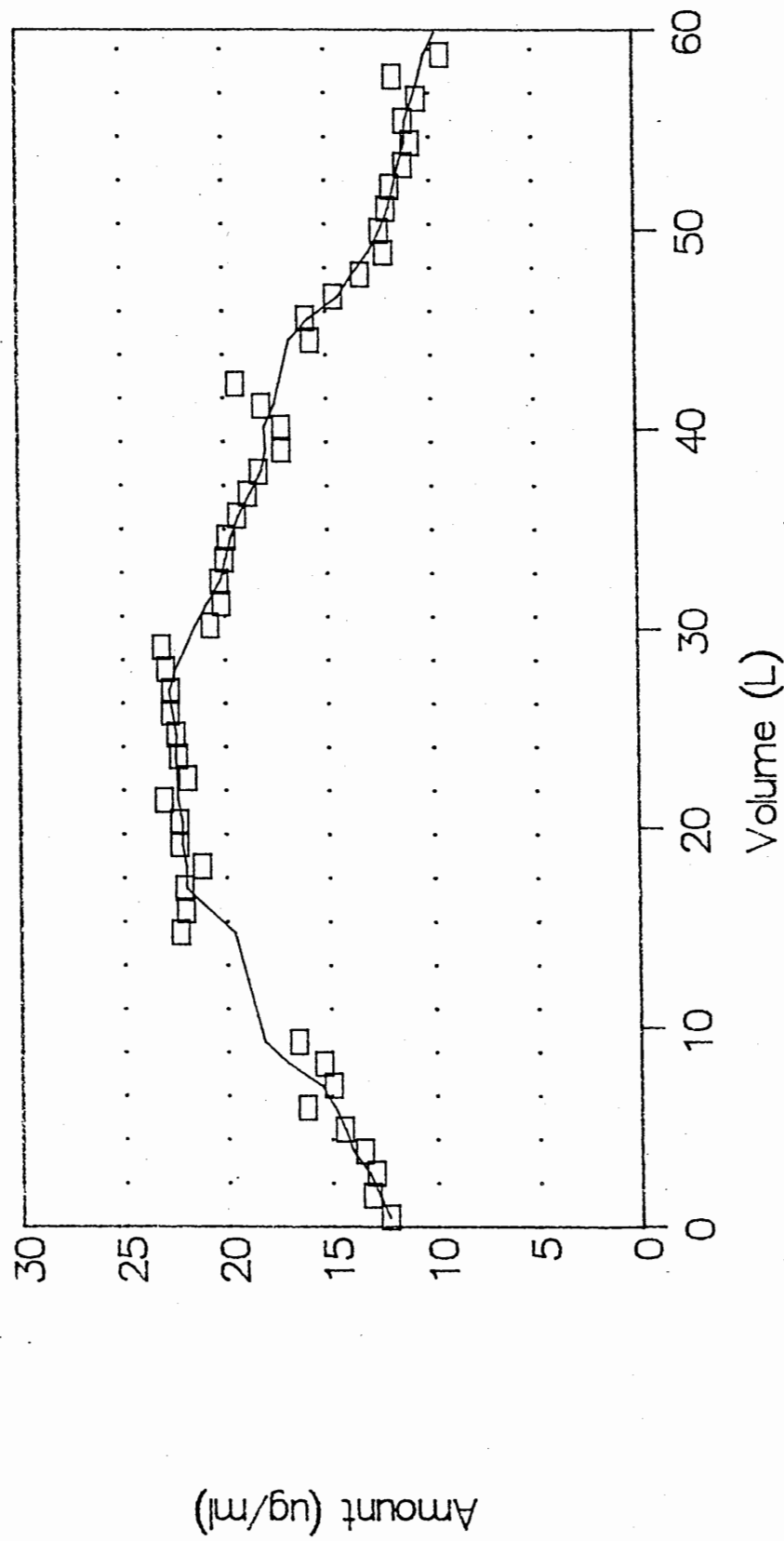


Figure 18: Concentration of o-xylene in effluent water

Column 2 Elution Plot

m&p-Xylene

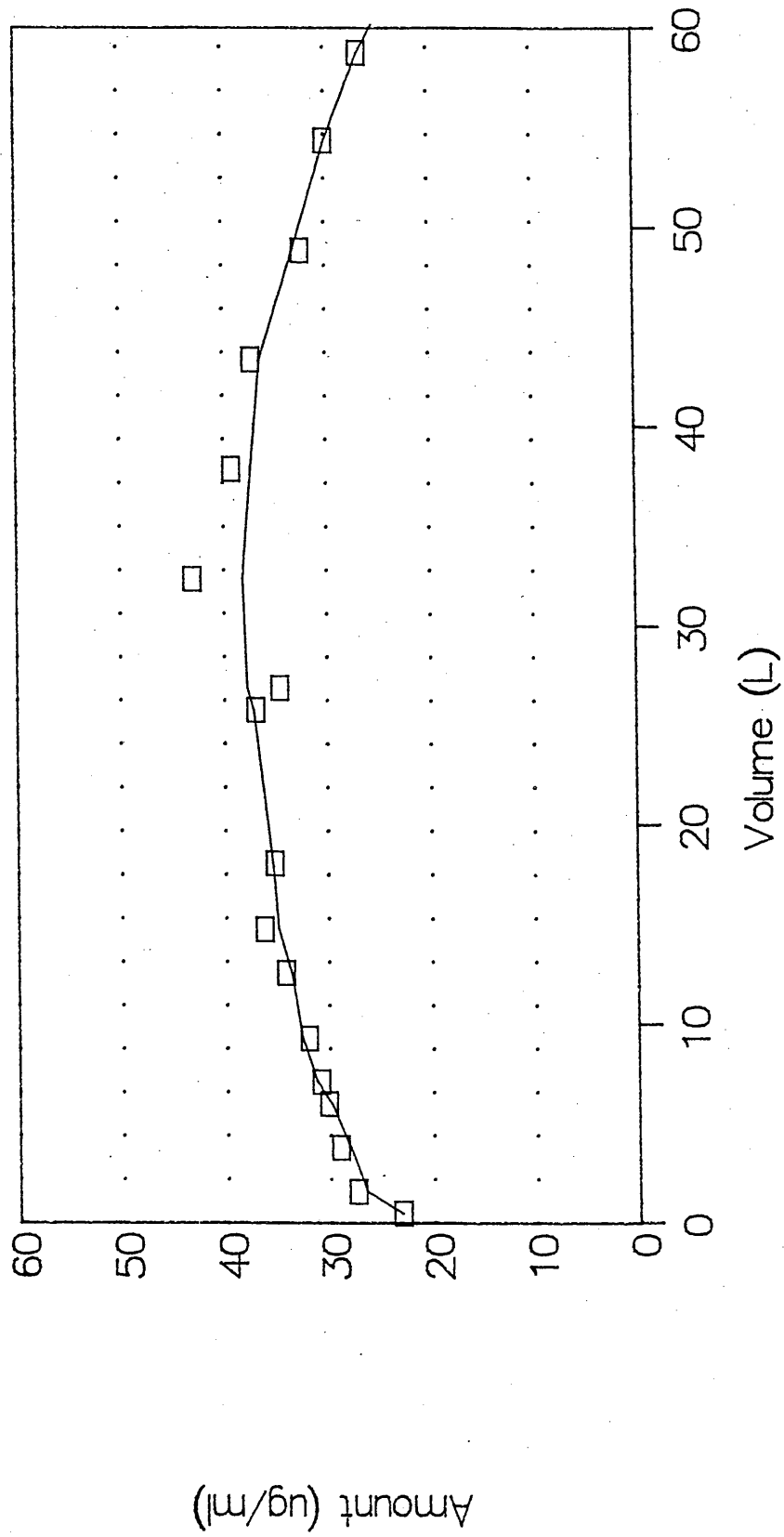


Figure 19: Concentration of m&p-xylene in effluent water

Column 1 Elution Plot
m- & p-Xylenes

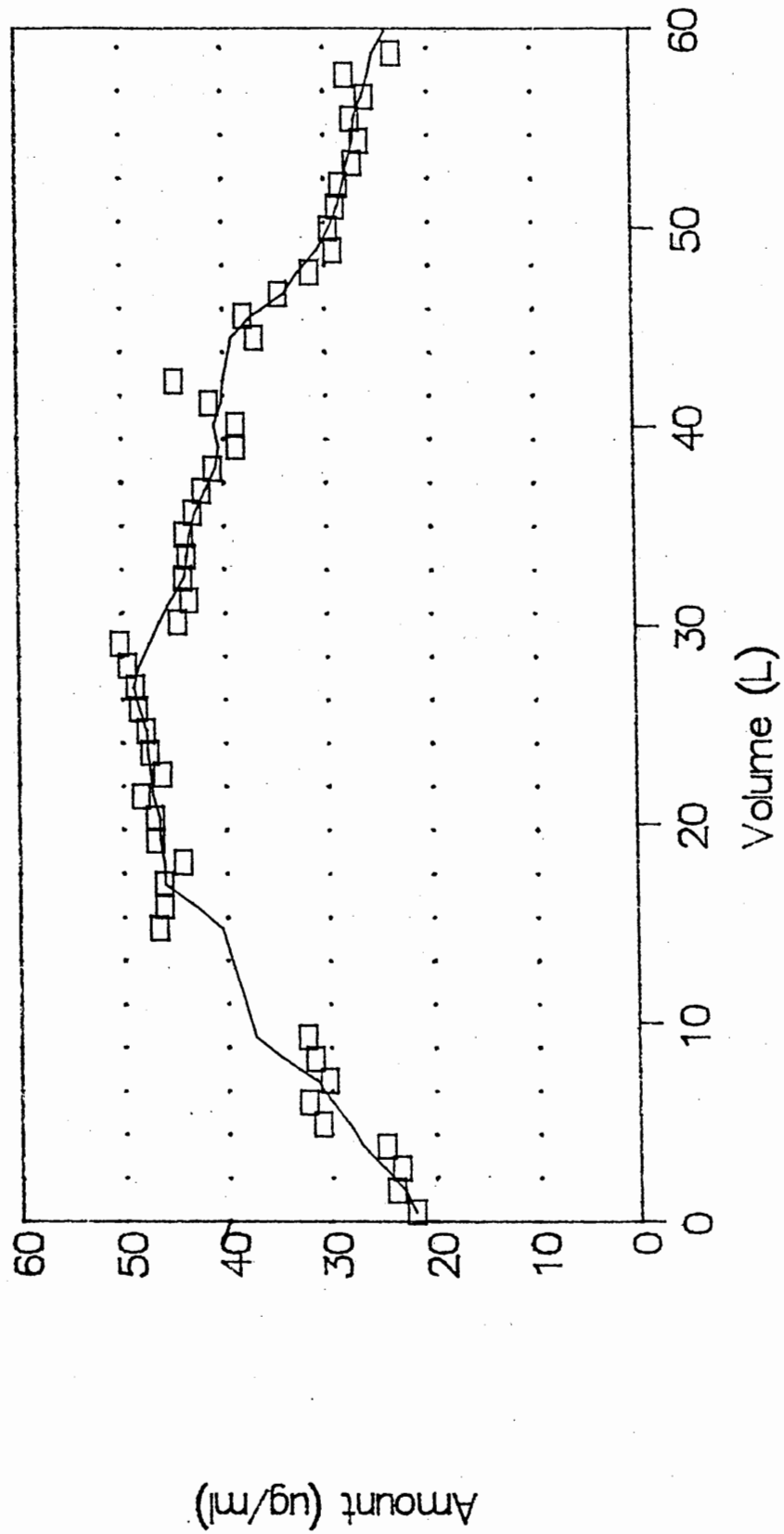


Figure 20: Concentration of m&p-xylene in effluent water

Appendix A

BTEX and MTBE Raw Data and Smoothed Data for Columns 1 and 2

Day	Accum. Volume (L)	Column 1 Raw Data (ug/ml)				
		Benzene	Toluene	Ethyl	p-Xylene	o-Xylene
1	0.45	82.77	85.62	8.77	21.90	12.23
2	1.55	75.76	87.95	9.07	23.75	13.08
3	2.65	71.06	92.93	9.11	23.25	12.87
4	3.75	57.89	95.98	9.39	24.66	13.42
5	4.85	54.03	109.23	10.55	30.83	14.39
6	5.95	47.49	111.51	10.10	32.14	16.17
7	7.05	23.52	104.52	10.43	30.17	14.90
8	8.15	17.97	103.20	10.78	31.49	15.34
9	9.25	11.63	104.24	11.03	32.18	16.54
14	14.75	4.97	108.94	12.14	46.60	22.25
15	15.85	3.68	96.81	11.97	46.08	21.97
16	16.95	3.11	91.75	11.95	46.10	22.04
17	18.05	2.32	79.36	11.43	44.22	21.17
18	19.15	2.03	76.15	12.07	46.90	22.26
19	20.25	1.73	69.26	12.07	46.92	22.26
20	21.35	1.50	62.95	12.34	48.26	23.00
21	22.45	1.31	55.97	11.85	46.18	21.83
22	23.55	1.16	50.50	12.09	47.40	22.29
23	24.65	1.10	46.17	12.18	47.76	22.40
24	25.75	0.94	41.07	12.21	48.49	22.66
25	26.85	0.90	37.20	12.23	48.77	22.64
26	27.95	0.84	35.31	12.48	49.52	22.86
27	29.05	0.75	31.82	12.62	50.23	23.07
28	30.15	0.61	25.02	11.16	44.59	20.69
29	31.25	0.53	21.30	10.85	43.43	20.14
30	32.35	0.50	19.46	10.98	44.02	20.24
31	33.45	0.46	17.09	10.83	43.65	19.97
32	34.55	0.42	15.21	10.89	43.93	19.87
33	35.65	0.39	13.62	10.63	43.04	19.34
34	36.75	0.36	12.04	10.38	42.15	18.82
35	37.85	0.30	10.35	10.09	41.01	18.28
36	38.95	0.26	8.52	9.51	38.74	17.17
37	40.05	0.24	7.82	9.48	38.74	17.16
38	41.15	0.25	7.51	10.07	41.31	18.13
39	42.25	0.20	5.77	10.73	44.77	19.38
41	44.45	0.16	4.44	8.91	36.87	15.72
42	45.55	0.15	4.07	9.11	37.94	15.95
43	46.65	0.10	3.24	8.27	34.47	14.58
44	47.75	0.06	2.64	7.52	31.40	13.29
45	48.85		2.15	6.96	29.11	12.16
46	49.95		2.10	7.05	29.52	12.36
47	51.05		1.82	6.86	28.80	12.02
48	52.15		1.62	6.78	28.46	11.83
49	53.25		1.35	6.44	27.11	11.20
50	54.35		1.19	6.26	26.45	10.85
51	55.45		1.20	6.45	27.32	11.18
52	56.55		0.98	6.09	25.93	10.56
53	57.65		1.26	6.60	27.84	11.68
54	58.75		0.66	5.45	23.31	9.39
55	59.85		0.60	5.45	23.36	9.36
56	60.95		0.18	5.86	25.14	9.94
57	62.05		0.32	4.63	19.95	7.92

Day	Accum. Volume (L)	Column 1 Smoothed Data (ug/ml)				
		Benzene	Toluene	Ethyl	p-Xylene	o-Xylene
1	0.45	82.77	85.62	8.77	21.90	12.23
2	1.55	76.53	88.83	8.98	22.97	12.72
3	2.65	68.30	94.34	9.19	24.88	13.20
4	3.75	61.25	98.25	9.64	26.93	13.99
5	4.85	50.80	100.76	9.92	28.21	14.35
6	5.95	40.18	103.09	10.25	29.86	14.85
7	7.05	30.93	106.54	10.58	31.36	15.47
8	8.15	19.49	106.41	10.90	34.52	17.04
9	9.25	15.72	105.87	11.27	37.31	18.20
14	14.75	4.23	102.03	11.57	40.49	19.63
15	15.85	3.95	98.90	11.71	43.04	20.79
16	16.95	3.22	90.60	11.91	45.98	21.94
17	18.05	2.57	82.67	11.90	46.05	21.94
18	19.15	2.14	75.89	11.97	46.48	22.15
19	20.25	1.78	68.74	11.95	46.50	22.10
20	21.35	1.54	62.97	12.09	47.13	22.33
21	22.45	1.36	56.97	12.11	47.30	22.36
22	23.55	1.20	51.33	12.13	47.62	22.44
23	24.65	1.08	46.18	12.11	47.72	22.37
24	25.75	0.99	42.05	12.24	48.39	22.57
25	26.85	0.91	38.31	12.34	48.95	22.73
26	27.95	0.81	34.08	12.14	48.32	22.39
27	29.05	0.73	30.13	11.87	47.31	21.88
28	30.15	0.65	26.58	11.62	46.36	21.40
29	31.25	0.57	22.94	11.29	45.18	20.82
30	32.35	0.50	19.62	10.94	43.92	20.18
31	33.45	0.46	17.34	10.84	43.61	19.91
32	34.55	0.43	15.48	10.74	43.36	19.65
33	35.65	0.39	13.66	10.56	42.75	19.26
34	36.75	0.35	11.95	10.30	41.77	18.70
35	37.85	0.31	10.47	10.02	40.74	18.16
36	38.95	0.28	9.25	9.91	40.39	17.91
37	40.05	0.25	7.99	9.98	40.92	18.02
38	41.15	0.22	6.81	9.74	40.09	17.51
39	42.25	0.20	5.92	9.66	39.93	17.27
41	44.45	0.17	5.00	9.42	39.07	16.75
42	45.55	0.13	4.03	8.91	37.09	15.78
43	46.65		3.31	8.16	33.96	14.34
44	47.75		2.84	7.78	32.49	13.67
45	48.85		2.39	7.33	30.66	12.88
46	49.95		2.07	7.03	29.45	12.33
47	51.05		1.81	6.82	28.60	11.91
48	52.15		1.62	6.68	28.07	11.65
49	53.25		1.44	6.56	27.63	11.42
50	54.35		1.27	6.40	27.05	11.12
51	55.45		1.20	6.37	26.93	11.10
52	56.55		1.06	6.17	26.17	10.73
53	57.65		0.94	6.01	25.55	10.43
54	58.75		0.74	5.89	25.11	10.19
55	59.85		0.60	5.60	23.92	9.66
56	60.95					
57	62.05					

Day	Accum. Volume (L)	Column 2 Raw Data (ug/ml)				
		Benzene	Toluene	Ethyl	m&p-Xyleno-	Xylene
1	0.45	83.43	88.58	9.07	23.00	12.72
2	1.55	76.86	96.00	9.96	27.30	14.85
4	3.75	54.63	109.57	10.49	28.98	15.52
6	5.95	39.39	110.71	10.76	30.11	15.94
7	7.05	21.24	98.31	10.84	30.82	16.34
9	9.25	11.06	95.64	11.13	31.98	16.93
12	12.55	2.49	82.07	11.54	34.22	17.98
14	14.75	0.31	77.30	12.01	36.26	18.90
17	18.05		58.72	11.67	35.23	18.33
24	25.75		31.51	11.89	36.98	18.88
25	26.85		27.71	11.37	34.63	17.93
30	32.35		19.95	10.79	43.03	20.03
35	37.85		10.96	9.71	39.18	17.79
40	43.35		6.56	9.09	37.21	16.60
45	48.85		3.04	7.80	32.31	13.95
50	54.35		1.71	7.16	30.00	12.70
54	58.75		1.02	6.30	26.69	11.13
57	62.05		0.53	5.43	23.21	9.58

Day	Accum. Volume (L)	Column 2 Smoothed Data (ug/ml)				
		Benzene	Toluene	Ethyl	m&p-Xylen	o-Xylen
1	0.45	83.43	88.58	9.07	23.00	12.72
2	1.55	71.64	95.75	9.84	26.43	14.36
4	3.75	56.96	100.63	10.22	28.04	15.07
6	5.95	38.42	102.05	10.64	29.84	15.91
7	7.05	23.89	99.26	10.95	31.22	16.54
9	9.25	11.60	92.81	11.26	32.68	17.22
12	12.55	4.62	82.41	11.44	33.70	17.70
14	14.75	0.31	69.05	11.65	34.94	18.20
17	18.05		55.46	11.69	35.47	18.40
24	25.75		34.47	11.54	37.23	18.82
25	26.85		29.77	11.09	37.81	18.59
30	32.35		19.34	10.57	38.21	18.25
35	37.85		13.64	9.75	37.27	17.26
40	43.35		8.44	8.91	36.35	16.21
45	48.85		4.66	8.01	33.08	14.43
50	54.35		2.57	7.16	29.88	12.79
54	58.75		1.09	6.30	26.63	11.14
57	62.05		0.53	5.43	23.21	9.58

Column 1
Methyl t-Bütyl Ether Results

Day	Sample Number	Accum. Volume (L)	Raw Amount (ug/ml)	Smoothed Amount (ug/ml)
1	1	0.04	94.10	94.10
1	4	0.14	64.60	64.60
1	10	0.38	47.96	51.10
1	13	0.50	50.14	48.36
1	16	0.62	47.88	43.56
1	19	0.74	41.41	37.14
1	22	0.86	43.30	33.57
2	2	1.40	16.00	16.00
2	3	1.85	4.12	4.12
3	2	2.50	4.09	4.09
3	3	2.95	2.81	2.81
4	3	4.05	2.07	2.07
5	3	5.15	1.63	1.63
6	1	6.05	1.75	1.75
7	1	7.15	0.95	0.95
8	1	8.25	0.97	0.97
9	1	9.35	0.91	0.91
14	1	14.85	0.89	0.89
15	1	15.95	0.78	0.78
16	1	17.05	0.75	0.75

Column 2
Methyl t-Butyl Ether Results

Day	Accum. Volume (L)	Raw (ug/ml)	Smoothed (ug/ml)
1	0.04	64.11	64.11
1	0.12	57.64	59.64
1	0.20	57.16	54.88
1	0.32	44.60	51.50
1	0.40	50.91	46.82
1	0.56	47.20	42.36
1	0.72	34.24	37.99
1	0.88	34.85	30.57
2	0.92	22.78	23.10
2	1.22	13.81	17.50
2	1.37	9.82	10.88
4	1.80	6.25	6.58
6	5.80	1.73	4.00
7	6.34	1.28	2.20
9	7.08	0.95	1.09
12	12.55	0.77	0.81
14	14.75	0.71	0.63
17	18.05	0.36	0.49
24	25.75	0.36	0.38
25	26.85	0.26	0.28
30	32.35	0.22	0.22