Groundwater Protection by Accelerated Testing of Organic Chemical Breakthroughs of Soil Barriers

James D. Stuart and Harvey D. Luce

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# TABLE OF CONTENTS

Cover Page ................................................................. i
Table of Contents .......................................................... ii
Federal Research Project Technical Completion Report Form .................. iii
Selected Water Resources Abstracts ........................................... vi
List of Tables .............................................................. vii
List of Figures .............................................................. viii
Introduction ................................................................. 1
Methods ....................................................................... 2
Results and Discussion ...................................................... 5
Conclusions ................................................................. 7
Summary ................................................................... 9
References ................................................................. 9
Tables ....................................................................... 11
Figures and Figure Captions ................................................ 16
RESEARCH PROJECT TECHNICAL COMPLETION REPORT

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PROJECT OBJECTIVES:

It has been estimated that over one-half of all organic chemicals used as household solvents, detergents and cleaners, as well as a wide variety of chemicals used in industrial processes are indiscriminately disposed of in landfills. These chemicals have the potential of leaching through the soils beneath and down gradient of the landfill and reaching the groundwater.

Houle and Long have reported using a series of graded, sequential batch extractions to rapidly determine the ability of a soil to remove inorganic chemicals from a leachate. The purpose of this research was to use Houle and Long's general method and to develop an accelerated, laboratory-based method to evaluate the sorption of selected, nonvolatile, partially water soluble, organic chemicals by different types of soils.

ACHIEVEMENT OF OBJECTIVES

It was proven that it is feasible to use the graded, sequential batch extraction method to determine within one day if a soil is effective in sorbing one or a limited number of organic compounds. The accelerated laboratory method allows for control of such experimental parameters, such as moisture and ambient temperature. The sorption properties of two soils, one an
Ap horizon of a Scarboro mucky, loamy sand (mixed mesic, Histic Humaquepts) and an Ap horizon of a Baldwin silty clay, fine montmorillonitic, thermic Vertic Ochraqualf) were compared. For both dimethylphthalate and diethylphthalate, the graded, sequential batch extraction method indicated that the mucky soil removed lower amounts of these chemicals than did the clayey soil.

**RESEARCH PROCEDURES USED:**

Houle and Long's method of using a series, sequential batch extractions was used to obtain, after four extractions, the same exponential decrease in concentration as would have been obtained by taking as many as 19 fractions of equal volume from a continuously-leached column. Experimentally this is accomplished by doubling the liquid-to-soil ratio for each succeeding extraction. Efficient ultrasonic stirring (Ultrasonic Bath, Model B-22-4, Branson Cleaning Equipment Co., Shelton, CT) and an end-over-end, rotary mixer (Rugged Rotator, Model RD-250, Kraft Apparatus, Inc., Mineola, NY) were used to assure the rapid attainment of a reproducible state of equilibrium of the targeted organic compound between the water/soil phases. After sub-micron filtration to remove the solid soil particles, analysis was performed by injecting the water phase into a reversed-phase, high performance liquid chromatograph equipped with a variable wavelength, ultraviolet detector.

**RESULTS OR CONCLUSIONS:**

Using a series of graded, sequential batch extractions, this research has shown that a silty, clay soil was more effective in retaining various concentration of diethylphthalate and dimethylphthalate than was a mucky, high in organic content soil. It was also proven that it is feasible to use the graded, sequential batch extraction method to determine within a long day's work (10-12 hours), a quantitative measurement of the effectiveness of a particular organic chemical to be retained by a soil. Such a short-term, laboratory-based method does provide for tighter control of such experimental conditions as temperature, degree of exposure of the sample to light and the control of aerobic or anaerobic conditions.

Experiments have shown that by the use of a combination of ultrasonic mixing and end-over-end, rotary mixing that a practical state of complete equilibration, within one percent, was obtained within 2.0 hours for 46 and 168 ppm solutions of chlorobenzene and for 52 and 172 ppm solutions of diethylphthalate. Experiments also indicated that for three different types of sub-micron filtering media commonly used for pre-high performance liquid chromatographic analysis that only the nylon and not a fluorocarbon-polymer nor mixed-cellulose filtering media gave one-hundred percent recovery (plus or minus two percent) for dimethylphthalate or diethylphthalate from a water solution.

The following disadvantages to using the graded, sequential batch extraction became evident as a result of this research. First, the organic chemical selected must not be volatile because there are a number of transfers and changes in the headspace volume as the water/soil ratios are varied. Second, a rapid, reversible equilibration both in the sorption and desorption step must be assumed. Third, a correction for the pore water volume change should be made between the different soil types. Lastly, it must be experimentally verified that the selected organic chemical(s) are not lost to filtration, transfer, volatilization or microbial alteration.
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Authors: James D. Stuart, Harvey D. Luce

Department of Chemistry, U-60 and Department of Agronomy, U-67
University of Connecticut
Storrs, CT 06268

It has been estimated that over one-half of all organic chemicals used as household solvents, detergents and cleaners, as well as a wide variety of chemicals used in industrial processes are indiscriminantly disposed of in landfills. These chemicals have the potential of leaching through the soils beneath and down gradient of the landfill and reaching the groundwater. Houle and Long have reported using a series of graded, sequential batch extractions to rapidly determine the ability of a soil to remove inorganic chemicals from a leachate. The purpose of this research was to use Houle and Long's general method and to develop an accelerated, laboratory-based method to evaluate the sorption of selected, nonvolatile, partially water soluble, organic chemicals by different types of soils.

This research has shown that it is feasible to use the graded, sequential batch extraction method to determine within one day if a soil is effective in sorbing one or a limited number of organic compounds. The sorption properties of two soils, one an Ap horizon of a Scarboro mucky, loamy sand (mixed mesic, Histic Humaquents) and an Ap horizon of a Baldwin silty clay, (fine montmorillinitic, thermic Vertic Ochraqualf) were compared. For both dimethylphthalate and diethylphthalate, the graded, sequential batch extraction method indicated that the mucky, loamy sand removed lower amounts of these chemicals than did the clayey soil.

**Abstract**

Groundwater, Leachate, Waste, Organic, Hazardous

**Keywords**

COYRRA Field & Group

05A

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University of Conn.
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**Supplementary Notes**
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Organic Compounds Considered Applicable to this Research</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>Characteristics of Soils Studied</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>Comparison of Disposable, Liquid Chromatographic, Filters Used in this Study</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>Per cent Recovery from Three Types of Disposable, Liquid Chromatographic, Filters Used in this Study</td>
<td>15</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Fig. 1</td>
<td>Effect of the Millex-GV Filter on Aqueous Solutions of Diethylphthalate</td>
<td>17</td>
</tr>
<tr>
<td>Fig. 2</td>
<td>Effect of the Millex-GV Filter on Aqueous Solutions of Chlorobenzene</td>
<td>18</td>
</tr>
<tr>
<td>Fig. 3</td>
<td>Graded, Sequential Batch Extractions on Diethylphthalate</td>
<td>19</td>
</tr>
<tr>
<td>Fig. 4</td>
<td>Graded, Sequential Batch Extractions on Dimethylphthalate</td>
<td>20</td>
</tr>
</tbody>
</table>
INTRODUCTION

It has been estimated that over one-half of all organic chemicals used as household solvents, detergents, cleaners, as well as a wide variety of chemicals used in industrial processes are indiscriminately disposed of in landfills. These chemicals have the potential of being leached through the soils beneath and down gradient of the landfill to reach the groundwater. Soils also receive organic agricultural compounds, such as fertilizers, herbicides and pesticides. These chemicals can be leached from the soils and thereby also enter the groundwater. Once chemical contaminants enter the groundwater, they move slowly and often are not altered or degraded. There are usually no economically feasible methods for decontamination of groundwater aquifers once they are polluted with non-volatile organic chemicals.

There are two principal laboratory approaches for measuring the migration of hazardous substances through soils. These are the batchwise extraction method and the continuously-leached column method. Continuously-leached column experiments provide information as to the ability of a soil to remove chemical substances from a waste leachate. However, an important limitation of this method is the time, often weeks or months, and effort required to obtain and analyze a sufficient number of samples from a slow eluting column to make predictions of the compound’s migration rates.

In two reports, Houle and Long (1,2) reported using a series of graded, sequential batch extractions to rapidly determine the ability of a soil to remove inorganic chemicals from a leachate. By, in effect, doubling the liquid-to-soil ratio for each sequential batch extraction, they were able to obtain after six extractions the same exponential decrease in concentration of targeted inorganic chemicals as would have been obtained by taking 19 fractions of equal volume from a continuously-leached column. They reported that their graded, sequential batch extraction method required much less time to complete, was much easier to perform and provided similar data to that obtained by the slow, continuously-leached column method. In this way, months and even years of slow field (column) leaching may be simulated by a few days of laboratory batch extractions (1). Jackson, et al. (3), have reported that batch extraction methods offer advantages in better reproducibility and in simplicity of experimental design in comparison to the continuously-leached columns. All of the above references involved studies of inorganic chemical pollution.

What follows is a brief summary of selected reports that have detailed the migrational behaviors of organic pollutants in soils. Means, et al. (4), studied the sorption of polynuclear aromatic hydrocarbons (PAHs) by sediments and soils. They reported that the amounts of the four PAHs sorbed were highly correlated to organic carbon content of the soil. An EPA sponsored, research report by Griffin and Shimp (5) on the removal of pollutants in municipal landfill leachate by clay materials is available. Chio, et al. (6), used a Woodburn silt loam soil (having 1.9% organic matter, 68% silt, 21% clay and 9% sand) to study the sorption of 12 aromatic compounds. The extent of the sorption was found to be affected primarily by the solubility of the organic
compound while the effect of the solute's incompatibility with the
soil's organic matter was found to be a significant but secondary
factor. Rogers, et al. (7), reported studying the sorption,
desorption and possible soil degradation of 10, 100 and 1,000 ppb
solutions of benzene in water. Their findings indicated that once
benzene was sorbed onto the soil, it tended to resist desorption.
They postulated that the most probable loss of benzene from the
soil was by volatilization. In a recent paper, A. Sabijic (8)
reported testing the ability of the connectivity model to predict
the soil sorption coefficient for 31 hydrocarbons such as as
alkylbenzenes, chlorobenzenes, chlorinated alkanes and chlorinated
alkenes. He reported that his mathematical model was found to
out-perform the traditional 'empirical models based on the
compound's water solubility or on the compound's 1-octanol/water
partition coefficient. He noted that his model could effectively
be used to prioritize a list of potentially hazardous chemicals
(8).

Arashidani, et al. (9), reported using an ultrasonic stirrer
(bath) to efficiently extract polynuclear aromatics from soil and
sediments with acetonitrile. The reported recovery rates for
benzo(a)pyrene were 98.8% and 99.4%, for perylene 98.8% and 99.4%
and for benzo(k)fluoranthene 102.5% and 98.2% (9). Jenkins and
Grant (10) have reported that by the use of an efficient
ultrasonic stirrer, greater amounts of trinitrotoluene (TNT),
trinitrobenzene, hexahydrotrinitrotriazine and
octahydrotetranitrotetrazocine were extracted from two soils. It
was reported that the rate at which equilibrium was approached
was more rapid with the use of the ultrasonic mixing than with the
use of a wrist-action shaker or soil-plant homogenizer (9).

The purpose of this research was to use the sequential batch
extraction method in order to develop an accelerated, laboratory
method to simulate the long term, field leaching of selected,
nonvolatile, partially water soluble, organic chemicals. The
sorption properties for two organic chemicals by two soils,
(representing major differences in soil classes, one high in clay
content, the Baldwin Horizon Ap, and one high in organic content,
the Scarborough Horizon Ap) were used in this project.

METHODS

1. Important Physical Properties of the Organic Compounds Studied

In a general sorption model, it is assumed that the organic
chemical is first dissolved in the water phase and then is
distributed between the soil surface and the water phase. The
solubility of the organic chemical and the distribution constant,
Keq, of the organic chemical between the soil and water phases at
a specific temperature would be the most important parameters.
The overall polarity or dielectric constant of the organic
molecule is significant in explaining the molecule’s sorptive
behavior and solubility in water. For the sequential batch
extraction method to be effective, the organic chemical must not
be volatile as the aqueous solution/soil mixture will often be
transferred into different size extraction/centrifuge tubes having


very different headspace volumes. It is required that the organic compound(s) being studied have a significant water solubility so that a hundred-to-thousand fold change in its concentration may be easily detected by the variable, ultraviolet absorption (190-380 nm range) detector employed for the analysis. This criteria restricts the number of non-volatile, organic compounds to be considered to those having a water solubility of greater than about 1 part-per-million (ppm) or 1 mg/L. Table 1 summarizes those organic compounds evaluated as potential organic compounds to be studied by the graded, sequential batch extraction method.

2. Soil Properties Considered Important

Such soil properties as surface area, porosity, per cent clay, per cent organic matter and cation exchange capacity (CEC) have been reported to be important in the removal of an organic compound by soil. Unfortunately, a soil’s surface area is not easily obtained as it is dependent on the soil’s moisture content, past history of storage and treatment. Table 2 summarizes the soils and their soil characteristics determined in this research project.

3. Analysis Method Employed

As there was a need to accurately measure the concentration of organic compounds in a water phase before and after exposure to a soil, the analysis method chosen involved using reversed-phase, high performance liquid chromatography (HPLC). In this modern separation method, water already constitutes part of the chromatographic mobile phase, while separation of organic compounds occurs on the basis of a difference in partition between a hydrophobic mobile phase and a hydrophobic stationary phase. In principle, direct injection of the organic compound dissolved or remaining in the water is possible. However, filtration of all solutions prior to injection is required in order to avoid the clogging of the small openings in the HPLC injector, or plugging of the fine, 0.010 in., inner diameter connecting tubing or plugging of the on-line, metal frits placed at the head of the tightly packed chromatographic columns. Customarily, a disposable HPLC filter of 0.22 or 0.45 micron mesh size is used. Of particular concern in this research was the complete removal of all colloidal (suspended) dirt and dust particles from the water layer of each solution prior to direct injection of the solution into the high performance liquid chromatograph.

The liquid chromatographic instrument consisted of a LC/9533, ternary gradient, liquid chromatograph (IBM Instruments, Danbury, CT) which included a Model 7125 liquid sample injector (Rheodyne, Inc., Cotati, CA) having a nominal 20 microliter loop. The ultraviolet detector (IBM Instruments LC/9523) was set to pass either 210 nm (for chlorobenzene and diethylphthalate) or 254 nm (for dimethylphthalate and diethylyphthalate) wavelength radiation on the 0.2 Absorbance range. Chromatograms were recorded using a reporting integrator (LC/9540, IBM Instruments), connected in parallel to a x-time recorder (Model 5111, Omniscribe, Houston Instruments, Austin, TX). The analytical column used was a 250 mm
long by 4.6 mm in internal diameter, stainless steel column packed with 5-micron spherical silica particle that had been octadecylsilane-bonded (Part No. 8635308, IBM Instruments). This analytical column was found to have a column efficiency of 80,000 theoretical plates. To protect the analytical column, a high pressure, pre-column filter with a 0.5 micron stainless steel filter (Part #8635449, IBM Instruments) followed by an on-line guard column packed with 7 micron, octadecyl bonded packing (Part # G18-013, 15 mm x 3.2 mm, Brownlee Labs, Santa Clara, CA) were used. The mobile phase consisted of a 64 per cent volume/volume mixture of acetonitrile (UV grade, Burdick & Jackson, Muskegon, MI) and 34 per cent laboratory prepared distilled/deionized water to which 1.0 milliliter (mL) of concentrated phosphoric acid had been added per liter. The water qualified as Type-1, A.C.S. standard water having a specific conductivity greater than 10 Megohms/cm. The HPLC flow rate was 1.0 milliliter/min throughout. A LC/9550 heating/cooling fluid circulator (IBM Instruments) was used to maintain the temperature of all organic chemical/water saturated solution to 25.0 ± 0.5 °C. All chromatographic separations were performed with the column temperature controlled at 25.0 ± 0.5 °C., and all reported data are the average of at least two experimental replicates.

Initially, it had been proposed to analyze in one chromatogram, using the gradient elution HPLC method, a series of different organic compounds. However, preliminary experiments indicated that it would not be feasible to obtain sufficiently accurate analytical data on more than two different compounds in one HPLC separation run. This is because it was not possible to find more than two different compounds of low volatility, of high water solubility and of a similar detector linear response range for them to be simultaneously analyzed in one HPLC separation. After consideration of the important properties of selected organic compounds as summarized in Table 1, this research focussed upon developing a simultaneous analysis for first chlorobenzene/diethylphthalate and then dimethylphthalate/diethylphthalate. Excellent linear calibrations were obtained in the range of 50 to 150 ppm for chlorobenzene (linear correlation coefficient of 0.9998 and for diethylphthalate (linear correlation coefficient of 0.9994) with the described HPLC analysis system. A coefficient of variance of 2.9 per cent was obtained for 5 manual injections of a 50 ppm chlorobenzene solution and a coefficient of variance of 2.2 per cent was similarly obtained for 5 injections of a 50 ppm solution of diethylphthalate.

4. Preparation of an organic saturated water solution

An excess quantity of an individual organic compound was placed in contact with distilled/deionized water in a brown bottle and thoroughly hand shaken. The resulting solution was kept in the thermostated, 25.0 ± 0.3 °C, re-circulating water bath for at least 24 hours to reach a reproducible state of water solubility.
5. Preparation of diluted organic saturated water solutions

First 3.00, 6.00, 4.00 or 2.00 mL of the distilled/deionized water were placed in individual, 15 mL, Teflon stoppered test tubes. Then 2.00, 4.00, 6.00 or 8.00 mL of the organic saturated water solution was added and mixed by slow hand shaking. Then each solution was thoroughly mixed for 2 min in an efficient ultrasonic bath (Model B-22-4, consuming 1.0 amperes of current, Branson Cleaning Equipment Co., Shelton, CT). The resulting solutions, called 20.0, 40.0, 60.0 and 80.0 per cent of the organic saturated water solution, were then used for detector calibration purposes and for soil sorption experiments. In addition, two solutions, 20.0 and 80.0 per cent of complete water saturation, were similarly prepared for the system reproducibility studies.

RESULTS AND DISCUSSION

1. Attainment of equilibrium

A weighed, 0.500 gram, quantity of the air-dried soil was added to 10.0 mL of the 20.0, 40.0, 60.0 and 80.0 per cent saturated solutions of a given organic chemical, hand-shaken and then mixed for 10 min. using the ultrasonic bath. Thereupon each solution was efficiently stirred for 2.0 hours at a speed of 20 revolutions per min. using an end-over-end, rotary mixer (Model RD-250, Rugged Rotator, Kraft Apparatus, Inc., Mineola, N.Y.). Each solution was again mixed in the ultrasonic bath for 10 min. and then for 20 min. centrifuged at the highest speed (7 speed, Clinical Centrifuge, International Equipment Co., Needham Heights, MA, which is reported to be able to reach 4750 rpm or about 2600 RCF). Less than a 5 per cent difference was found in the concentrations of chlorobenzene (at both the 46 and 168 ppm levels) and of diethylphthalate (at both the 52 and 172 ppm levels) when the solutions had been stirred for 2.0, 5.0, 8.0 and 24.0 hours. This series of carefully conducted experiments substantiated the good reproducibility of the analytical method and the fact that a practical equilibration was achieved within two hours by using a combination of the ultrasonic mixing and the end-over-end, rotary mixing.

Solutions at the 50 ppm level of diethylphthalate and chlorobenzene were allowed to stand up to 24 hours in amber colored vials. There was no significant change in the concentrations of these chemicals in comparison to solutions allowed to stand for 4 or 8 hours, thus effectively indicating the absence of physical loss or of significant bacterial decomposition for the two organic, chemical pollutants studied.

2. Experiments showing that different, commonly-used, disposable HPLC filters removed appreciable quantities of the organic chemicals prior to analyses.

Three popular, disposable, high performance liquid chromatographic (HPLC) filters were compared for their abilities
to filter solutions of the organic chemicals prior to HPLC analyses. (Refer to Table 3 for a comparison of the reported properties of the HPLC filters studied.) It must be emphasized that it is of paramount importance in HPLC to filter all solutions prior to analyses in order not to clog the fine passageways of the injector, the small inner diameter of the connecting steel tubing or the stainless steel frits at the front of the tightly packed HPLC columns.

In the following series of experiments, about 10 mL of each water solution containing an organic chemical was first slowly rinsed through the disposable filter in order to deactivate the filter and hopefully to saturate the sorption sites of the filtering media. Thereupon the last 0.2 mL was used for the duplicate HPLC analyses. Figure 1 shows that 80% of a 52 ppm, 80% of a 94 ppm, 81% of a 138 ppm and 76% of a 172 ppm solution of diethylphthalate in water (compare the first and third bar levels at each concentration level) were recovered upon filtration through a Millex GV, duarapore fluorocarbon polymer, HPLC disposable filter. (This is a very popular, disposable filtering media advertised as having "low protein binding" capabilities). The first bar level at each concentration represents the initial organic concentration of the solution, while the third bar level represents the concentration found after filtration. The second bar levels shows that for the various concentrations of diethylphthalate, there was virtually no loss of diethylphthalate when carried through the normal mixing and stirring operations prior to the final filtration step. As is depicted in Fig. 2, lower amounts of chlorobenzene: 60% of a 46 ppm, 55% of a 90 ppm, 63% of a 134 ppm and 59% of a 168 ppm solution, were recovered upon filtration through the Millex GV filtering media (compare the first and third bar levels of each bar graph of Fig. 2). However, as indicated by the second bar graph for each concentration, considerable amounts of chlorobenzene: 12% of a 46 ppm, 7% of a 90 ppm, 7% of a 134 ppm and 11% of a 168 ppm solution, were lost due to volatilization in the normal mixing and stirring operations even before the final filtration step.

Table 4 presents data that compare the per cent recovery of diethylphthalate (DEP) and dimethylphthalate (DMP) upon filtration through three different types of commercially-available, popular HPLC disposable filters. It should be noted that especially for the higher concentrations of DEP, 180 and 240 ppm, only the nylon filter was found to provide recoveries of close to 100 per cent.

In an attempt to find less sorbing filters, two glass-fiber filtering media were tested (Whatman, EPM 2000 and Gelman A/E glass microfiber filters). The recommended application for these glass-fiber filters is the retention of 0.3 micron and larger particles trapped in air scrubbers. However, this research found that these glass-fiber filters could not be used for water solutions as the glass fibers continued to be leached from the glass filter and visually were evident in the solution found in the receiving vial.
3. Graded, Sequential Batch Extractions of Selected Organic Chemicals

A series of graded, sequential batch extractions, as first described by Houle and Long (1,2), was performed using a mixture of diethylphthalate (DEP) and dimethylphthalate (DMP). The Millex-GS, methyl cellulose filtering media, was used exclusively in these experiments, as it was the only filter available at the time. First, 10.0 mL of a water saturated solution of DEP and DMP was mixed with 4.00 grams of the soil, either the Ap horizon of a Scarboro mucky, loamy sand (mixed mesic, Histic Humaquepts), high in organic content, or the Ap horizon of a Baldwin silty clay (fine, montmorillonitic, thermic Vertic Ochraqualf), dominated by 60% smectite with 20% illite and 20% kaolinite). The water/soil mixture was then efficiently mixed for 24 hours in the end-over-end, rotary mixer. The mixture was centrifuged for 10 minutes and filtered through the Millex-GS filter leaving behind 4.0 grams of heavily, DEP and DMP, sorbed soil. Thereupon, 8.0 mL of fresh, distilled/deionized water was added to the soil. The resulting combination was then mixed for 2.0 hours by the end-over-end mixer, centrifuged and filtered. (This mixture's concentration is then described as having a volume/to weight ratio of 2 mL/g, i.e., 8.0 mL/4.00 g).

In sequence, using similar experimental methods, the following ratios of water to soil were prepared: 4 mL/g, 6 mL/g and 9 mL/g. Fig. 3 shows the results of the graded, sequential batch extraction starting with a saturated DEP solution for both the Scarboro soil and the Baldwin soil. As will be noted in Fig. 3, the concentration levels for DEP in the water layer for each step were higher when in contact with the Scarboro soil than when in contact with the Baldwin soil. This indicates that the mucky soil (high in organic matter) is less effective in removing DEP at several concentration levels than is the silty clay soil.

Similarly, Fig. 4 shows the results of the graded, serial batch extractions with various concentrations of DMP. Again, especially for the last two extractions, the concentration of DMP in the water layer is significantly higher in mixtures exposed to the mucky Scarboro soil (high in organic content) in comparison to the Baldwin soil that had a high clay content.

CONCLUSIONS

1. Advantages of the Graded, Sequential Batch Extraction Method

a. It was proven that it is feasible to use the graded, sequential batch extraction method to determine, within one day (10-12 hours of well-planned work), if a soil is effective in sorbing a particular organic chemical. This laboratory method can provide a quantitative measurement of the potential mobility of an organic chemical from a polluted soil. Such an accelerated laboratory method does allow for tighter control of such experimental conditions as temperature and degree of exposure to sunlight.
b. Landfill leachate could be substituted for distilled/deionized water provided that no components in the leachate interfered with the detection of the organic chemicals being analyzed. There was insufficient time in this one-year project to work with a real landfill leachate.

c. Since soils have very different chemical and physical properties, these properties may be systematically compared using such a one-day, laboratory-based, experimental method.

d. The Nylon-66 HPLC, disposable filtering medium removed the least amount of DEP and DMP of the three filters that were compared.


a. This study demonstrated that an important disadvantage to using the graded, sequential batch extraction method was that only a limited number of organic compounds could be studied by this method. This is because, first the chemical must not be volatile (note the loss in volatilization in the many transfer steps for chlorobenzene). Second, at least when liquid chromatography (HPLC) is the analysis method, the organic chemical must have significant solubility in water (refer to Table 1) so that it may be detected over the hundred-fold decrease in concentration experienced when the graded, sequential extraction method is performed.

b. It was observed that a correction to the change in soil density, pore size or pore water volume would need to be made when comparing the recovery levels of different soil types. (This fact was not considered in the papers first developed by Houle and Long). For example, in this study it was estimated that 4.0 grams of the Baldwin horizon Ap soil occupied about 3 mL, that 4.0 grams of the Scarboro horizon Ap soil occupied about 2 mL and that 4.0 grams of the Hinkley sand occupied about 1 mL.

c. It must be assumed that a rapid, reversible equilibration of the organic chemical between the water layer and the solid soil is achieved. While this may have been achieved at the high concentrations and efficient mixing that was employed in this study, others have reported that at the near trace level, this is not the case. For example, Steinberg, et al., of the Connecticut Agricultural Experiment Station, have recently reported that the soil fumigant 1,2-dibromoethane (EDB) is trapped in the soil micropores from which diffusion release is very slow but highly temperature dependent. This would explain how residual levels of EDB are found in agricultural topsoils up to 19 years after the last known application (11,12).

d. Experimental care must be taken to show that the organic chemicals are not lost due to filtration, transfer, volatilization, or microbial alteration during the many steps of the graded, sequential extraction method.
e. Most soils contain very fine, colloidal size particles. It was found in this study that it was not possible with an ordinary laboratory centrifuge to completely centrifuge to the bottom all of the soil's suspended solids. Thus the pre-analysis micro-filtration is mandatory. A more powerful ultracentrifuge, having a 10-fold increase in rotation speed, is needed. (The cost of such an ultra-centrifuge is in the $5,000 to $15,000 range.)

SUMMARY

It is feasible to rapidly evaluate the sorption/mobility properties of a select, limited number of highly water soluble, non-volatile organic compounds exposed to various types of soils. This study concludes that for diethylphthalate (DEP) and for dimethylphthalate (DMP), soil high in clay content retains these two compounds to a greater extent than does soil high in organic content.

REFERENCES


### Table 1

**Organic Compounds Considered Applicable to this Research**

<table>
<thead>
<tr>
<th>Organic Compound</th>
<th>Density in g/cm³</th>
<th>Solubility in Water parts-per-million</th>
<th>Applicability to this Research</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.874 at 25°C</td>
<td>1791 ppm at 25°C (1)</td>
<td>too volatile</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.862 at 25°C</td>
<td>515 ppm at 25°C (1)</td>
<td>too volatile</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.863 at 25°C</td>
<td>152 ppm at 25°C (1)</td>
<td>too volatile</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.901 at 25°C</td>
<td>310 ppm at 25°C (1)</td>
<td>too volatile</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>solid</td>
<td>31.7 ppm at 25°C (2)</td>
<td>low solubility</td>
</tr>
<tr>
<td>1-chloronaphthalene</td>
<td>1.194 at 20°C</td>
<td>-</td>
<td>low solubility</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.101</td>
<td>488 ppm at 30°C (1,2)</td>
<td>too volatile</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
<td>0.908</td>
<td>28,000 ppm at 25°C (3)</td>
<td>too biodegradable</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>solid</td>
<td>4,500 ppm at 25°C (2)</td>
<td>good for analysis</td>
</tr>
<tr>
<td>2,3,5-trichlorophenol</td>
<td>solid</td>
<td>-</td>
<td>good for analysis</td>
</tr>
<tr>
<td>2,4,6-trichlorophenol</td>
<td>solid</td>
<td>900 ppm at 25°C (2)</td>
<td>good for analysis</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>solid</td>
<td>30 ppm at 50°C (2)</td>
<td>low solubility</td>
</tr>
<tr>
<td>2,6-di-t-butyl-4-methylphenol (or butylated hydroxytoluene)</td>
<td>solid</td>
<td>0.4 ppm at 20°C (2)</td>
<td>low solubility</td>
</tr>
<tr>
<td>Dimethylphthalate</td>
<td>1.19 at 25°C</td>
<td>5000 ppm at 20°C (2)</td>
<td>good for analysis</td>
</tr>
<tr>
<td>diethylphthalate</td>
<td>1.118 at 25°C</td>
<td>210 ppm (2)</td>
<td>good for analysis</td>
</tr>
<tr>
<td>dibutylphthalate</td>
<td>1.043</td>
<td>28 ppm at 26°C (1,2)</td>
<td>low solubility</td>
</tr>
<tr>
<td>2-chlorobiphenyl</td>
<td>-</td>
<td>5.9 ppm (4)</td>
<td>low solubility</td>
</tr>
<tr>
<td>3-chlorobiphenyl</td>
<td>-</td>
<td>3.5 ppm (4)</td>
<td>low solubility</td>
</tr>
<tr>
<td>4-chlorobiphenyl</td>
<td>-</td>
<td>1.19 ppm (4)</td>
<td>low solubility</td>
</tr>
<tr>
<td>4,4'-Dichlorobiphenyl</td>
<td>-</td>
<td>0.08 ppm (4)</td>
<td>low solubility</td>
</tr>
<tr>
<td>2,5,2',5'-Tetrachlorobiphenyl</td>
<td>-</td>
<td>0.046 ppm (4)</td>
<td>low solubility</td>
</tr>
</tbody>
</table>
Continue - Table 1


(4) O. Hutzinger, S. Safe, V. Zitko, The Chemistry of PCB's, CRC Press, Inc., Cleveland, Ohio, 1974, p.16.
Table 2

Characteristics of Soils Studied

<table>
<thead>
<tr>
<th>Name</th>
<th>% Sand</th>
<th>% Silt</th>
<th>% Clay</th>
<th>Total % Organic Matter by Combustion</th>
<th>% Active Organic Matter by Walkley-Black</th>
<th>Cation exchange Capacity with NH4OAc</th>
<th>% Free iron oxide</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hinkley C2</td>
<td>98.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0.12</td>
<td>0.01</td>
<td>0.20</td>
<td>&lt;0.01</td>
<td>5.18</td>
</tr>
<tr>
<td>Scarboro</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>18.88</td>
<td>7.93</td>
<td>200</td>
<td>1.79</td>
<td>3.47</td>
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<td>Horizon Ap</td>
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</tr>
<tr>
<td>Baldwin</td>
<td>1.9</td>
<td>57.2</td>
<td>40.9</td>
<td>8.05</td>
<td>2.81</td>
<td>29.1</td>
<td>0.50</td>
<td>7.0</td>
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<tr>
<td>Horizon Ap</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Baldwin</td>
<td>1.4</td>
<td>65.7</td>
<td>32.9</td>
<td>3.32</td>
<td>0.50</td>
<td>22.8</td>
<td>0.34</td>
<td>6.8</td>
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<td>Horizon 8 Bt1</td>
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<tr>
<td>Dossman</td>
<td>7.1</td>
<td>83.1</td>
<td>9.8</td>
<td>3.63</td>
<td>1.17</td>
<td>8.5</td>
<td>0.57</td>
<td>5.6</td>
</tr>
<tr>
<td>Horizon Ap</td>
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<td></td>
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<tr>
<td>Dossman</td>
<td>2.1</td>
<td>62.2</td>
<td>35.7</td>
<td>2.99</td>
<td>0.66</td>
<td>13.7</td>
<td>1.53</td>
<td>5.3</td>
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<tr>
<td>Horizon Bt1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Dossman</td>
<td>2.4</td>
<td>76.9</td>
<td>20.7</td>
<td>1.43</td>
<td>0.17</td>
<td>12.0</td>
<td>0.85</td>
<td>5.4</td>
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<td>Horizon BC1</td>
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</tr>
<tr>
<td>Memphis</td>
<td>4.8</td>
<td>79.1</td>
<td>16.1</td>
<td>2.16</td>
<td>0.40</td>
<td>11.7</td>
<td>1.23</td>
<td>5.9</td>
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<tr>
<td>Horizon Bt1</td>
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<td></td>
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<tr>
<td>Memphis</td>
<td>6.6</td>
<td>81.4</td>
<td>12.0</td>
<td>0.89</td>
<td>0.13</td>
<td>8.2</td>
<td>1.00</td>
<td>5.2</td>
</tr>
<tr>
<td>Horizon C1</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Not able to be determined as this soil is very high in organic matter.
### TABLE 3
Comparison of Disposable, Liquid Chromatographic, Filters Used in this Study

<table>
<thead>
<tr>
<th>Trade Name with Manufacturer</th>
<th>Millex-GV (Millipore Corp.)</th>
<th>Millex-GS (Millipore Corp.)</th>
<th>Nylon-66 (Rainin Corp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Filtering Membrane</td>
<td>Durapore, a fluoro-carbon polymer (polyvinylidene difluoride)</td>
<td>Mixed cellulose esters, acetate and nitrate</td>
<td>Nylon with no additives</td>
</tr>
<tr>
<td>Pore Size in Microns</td>
<td>0.22</td>
<td>0.22</td>
<td>0.3</td>
</tr>
<tr>
<td>Membrane Diameter in millimeters</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Normal Applications as recommended by the manufacturer</td>
<td>low protein binding, especially useful for many biological applications</td>
<td>recommended for aqueous filtrations</td>
<td>recommended for applications when very low concentrations of extracts from the filtering membrane can be tolerated</td>
</tr>
</tbody>
</table>
Table 4

Per cent Recovery from the three types of disposable, Liquid Chromatographic, Filters Used in this Study

<table>
<thead>
<tr>
<th>Concentration</th>
<th>A. Recovery for Dimethylphthalate after Filtration</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Millex-GV (Durapore)</td>
<td>Millex-GS (mixed cellulose)</td>
<td>Nylon-66 (nylon)</td>
</tr>
<tr>
<td>400 ppm</td>
<td>101</td>
<td>98</td>
<td>103</td>
</tr>
<tr>
<td>700 ppm</td>
<td>97</td>
<td>99</td>
<td>102</td>
</tr>
<tr>
<td>1100 ppm</td>
<td>100</td>
<td>99</td>
<td>102</td>
</tr>
<tr>
<td>1400 ppm</td>
<td>97.0</td>
<td>97</td>
<td>99</td>
</tr>
</tbody>
</table>

B. Recovery for Diethylphthalate after Filtration

<table>
<thead>
<tr>
<th>Concentration</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>60 ppm</td>
<td>98</td>
<td>97</td>
</tr>
<tr>
<td>120 ppm</td>
<td>92</td>
<td>96</td>
</tr>
<tr>
<td>180 ppm</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>240 ppm</td>
<td>90</td>
<td>76</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1 Effect of the Millex-GV Filter on Aqueous Solutions of Diethylphthalate

Fig. 2 Effect of the Millex-GV Filter on Aqueous Solutions of Chlorobenzene

Fig. 3 Graded, Sequential Batch Extractions on Diethylphthalate

Fig. 4 Graded, Sequential Batch Extractions on Dimethylphthalate