PERMEATION SAMPLING OF
PHTHALATE ESTERS

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PERMEATION SAMPLING OF
PHTHALATE ESTERS

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Dissertation

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ABSTRACT

A permeation sampling method for the six phthalate esters that are considered priority pollutants by the United States Environmental Protection Agency (US EPA) was developed. The permeation sampling device utilizes a silicone polycarbonate membrane through which the analytes are able to permeate through and are collected onto an adsorbent. After a timed sampling period, the samplers were removed from the water and the analytes were extracted from the adsorbent using a desorbing solvent, with the resulting solution analyzed using gas chromatography with flame ionization detection. Time-weighted average (TWA) concentrations of the phthalates in the water were determined by creating plots of amount of analyte collected versus the product of concentration and time (ppm·hr) for each phthalate. Experimentation showed that a linear correlation was obtained between the amount of analyte collected and the product of concentration and time for each phthalate. The effects of different sample solution temperatures and sample stirring rates on the amount of phthalates collected were evaluated. Also, the effect on the permeation rates of the phthalates due to the presence of several potential interferents that are commonly present in water, including: humic acid, sodium lauryl sulfate, sodium sulfate, sodium phosphate, sodium nitrate, sodium chloride and pH were studied. An advantage of this method included that minimal
amounts of solvent were used as compared to other liquid-liquid extraction methods use up to 0.5 L of harmful solvents. In a second part of the study, the six phthalate esters were removed from the adsorbent using thermal desorption rather than solvent extraction. After the sampling period, the analyte collected onto the adsorbent was thermally desorbed using a Thermal Desorption Unit. A stream of helium carried the desorbed analytes into a gas chromatograph-mass spectrometer (GC-MS) after the sampling period. As in the case of the solvent extraction method, for all six phthalates the resulting TWA plots had linear correlations, allowing for the determination of permeation constants for the phthalates. Using the thermal desorption method it was possible to determine the lag times for each phthalate.
DEDICATION

To my husband, Chris, who has given his love and support throughout my graduate studies. Also, to my parents because without their love and support this achievement would not have been possible.
I would like to thank my advisor, Dr. James K. Hardy for all of his guidance and support throughout my graduate career. Also, I would like to thank Eric Bodle and Cody Anderson for their friendship and support.
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CHAPTER I
INTRODUCTION

One of the current major world concerns is safe drinking water. A cause for concern is that each year 22-30 million tons of polyvinylchloride (PVC) are produced. In total there are about 400 million tons of PVC in the world, both used and unused (1). PVC is given its specific plastic properties by compounds known as phthalates, which are common plasticizers. Since the phthalates are physically and not chemically bonded in the polymer (2), it is possible for them to leach out into the environment, such as water bodies. As a result of the over 400 million tons of PVC present on Earth and their presence in various consumer products, phthalates have been found in water samples. Theses compounds have qualities that pose a risk to humans if they enter the body. As a result of their widespread presence and harm to humans the US EPA has placed six phthalate esters on the priority pollutant list. The priority pollutants are a list of pollutants that are monitored by the US EPA as a result of the Clean Water Act.

Several techniques have already been utilized for the detection of phthalates in water samples. For example, the United States EPA has three methods which are Methods 506, 606 and 8061A, which involve grab sampling and liquid-liquid or liquid-solid extraction (3-5). There are several problems with these methods. One is that for liquid-liquid extraction up to 0.5 L of dichloromethane and other hazardous chemicals are
used and eventually evaporated into the air. Another problem is the use of grab sampling. Grab sampling only allows for information to be obtained about the sample at that instance the sample is collected. For example, episodic spills could be missed. Also, with grab sampling, pumps are commonly used to collect the sample, which means some sort of external power source is needed to run the pumps.

A new method for sampling phthalates involving permeation sampling has been developed. The method involves the use of a sampler with a polymeric membrane and an adsorbent. This passive sampling method allows for the determination of time-weighted average (TWA) concentrations of analytes. An adsorbent is placed on the membrane to collect analytes that permeate through the membrane.

Membrane samplers were constructed that were allowed to sample for known periods of time and phthalate concentrations. After the sampling period, the analytes must be extracted from the adsorbent using a desorbing solvent. The resulting solution is injected into a gas chromatograph and the amount of phthalate present is determined. This allows for the determination of the permeation constant so that the time weighted average concentrations can be measured. In order to be able to determine time-weighted average concentrations, the rate of permeation must remain constant over the sampling period, so that permeation constants can be determined.

The permeation sampling method has some advantages over the previous techniques used. For example, all the current US EPA methods for the detection of phthalates in water samples involve using grab sampling and some type of extraction. Grab sampling accounts for the concentration only at the time of sampling, while the
permeation sampler can account for varying concentrations over time, since the TWA concentration method is used. These liquid-liquid extraction techniques can use up to 0.5 L of solvent, while the solvent extraction technique of this method uses only 1 mL of solvent. In an effort to be environmentally friendly a thermal desorption technique was used, in which no harmful solvents are used. Since the samples are aqueous solutions they must be refrigerated until analysis so as not to lose any analytes. On the other hand, in this method, the analytes are collected on to an adsorbent that is much more stable and can be stored at room temperature for up to a month until analysis.
CHAPTER II
HISTORICAL

The origin of water pollution is thought to be when man first started building dams and canals for agricultural irrigation. Since no proper drainage techniques were applied to these structures, dirt and other materials would build up in the water effectively polluting the water. A historical example of this occurred in 1167 when soldiers arrived in Rome and found that the city’s waters were expelling poisonous vapors into the air (6). Next, the occurrences of both the industrial revolution and then urbanization compounded the problem of water pollution. These changes resulted in larger people occupying smaller spaces which made it easier to spread pollution (7). Also, with the world population increasing over the centuries, production to give ever increasing amounts of people shelter and food needed to survive greatly amplified the problem (8). Polluted water is an important issue because safe drinking water is essential to life.

Environmental Law

The Refuse Act, passed in 1899, made the disposal of any refuse matter other than those flowing from the streets into any navigable water illegal without a permit.
Breaking this law and being found guilty could result in a fine or imprisonment. Beyond this, though, the issue of water pollution control was usually left to local and state authorities to handle (9).

The next major water pollution law enacted was in 1948 with the Federal Water Pollution Control Act (FWPCA). This act encouraged states to enact measures to prevent water pollution and to help do so, Federal government provided loans for sewers. It also investigated the waste discharged into interstate waters. The law put the Surgeon General in control of making sure that policies were created and if not, handing out formal warnings (10). The Act was amended in 1956 which stated that the Federal funding could be halted if the proposed plan was insufficient (11). Again, it was amended in 1961 which allowed it to cover all navigable waters and not just interstate (12).

The Water Quality Act of 1965 took the state enforcement a step further. It required that states set and enforce water quality standards that the Health, Education and Welfare (HEW) department felt would prevent further degradation of the nation’s waters. They also set a deadline for each state to file letters of intent to administer state quality laws by October 1966 (13). In order to help the states meet the new water quality criteria set under this law, the Federal government passed the Clean Water Restoration Act of 1966. The statue authorized more Federal monetary assistance for the states to be able to comply with the 1965 Act (14). On January 1, 1970 President Nixon signed the National Environmental Policy to help the states meet the new water quality criteria set under this law, the Federal government passed the Clean Water Restoration Act of 1966. The statue
authorized more Federal monetary assistance for the states to be able to comply with the 1965 Act (14).

On January 1, 1970 President Nixon signed the National Environmental Policy Act (NEPA) into law. This statute covered many types of pollution, including water. Its purpose was to:

“Create and maintain conditions under which man and nature can exist in productive harmony and fulfill the social, economic and other requirements of present and future generations of Americans.” (15)

Also, around this time the President’s Advisory Council on Executive Organization (commonly called the Ash Council) was created to make wide-scale changes in the Federal structure. One department the council was interested in modifying was the Department of Natural Resources, since the NEPA bill had recently been passed. The Ash Council was interested in this department because they were looking to create a separate department for pollution control, to be called the Environmental Protection Agency (EPA). The two agencies that were currently in charge of this issue were the HEW department and the Council of Environmental Quality, and both thought that the creation of the EPA was a good idea. After deliberations between the council, Congress and the President, were completed, all were in agreement for the creation of the EPA, and it began its operations in December 1970 (16).

The most important environmental legislation involving water was in 1972 with the passing of the Federal Water Pollution Control Act Amendments of 1972 (Clean Water Act, CWA). The objective of this law was: “To restore and maintain the chemical,
physical and biological integrity of the Nation’s waters.” In order to achieve this objective these provisions were set:

“ (1) it is the national goal that the discharge of pollutants into the navigable waters be eliminated by 1985;
(2) It is the national goal that wherever attainable, an interim goal of water quality which provides for the protection and propagation of fish, shellfish, and wildlife and provides for recreation in and on the water be achieved by July 1, 1983;
(3) It is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited;
(4) It is the national policy that Federal financial assistance is provided to construct publicly owned waste treatment works;
(5) it is the national policy that area wide waste treatment management planning processes be developed and implemented to assure adequate control of sources of pollutants in each State;
(6) it is the national policy that a major research and demonstration effort be made to develop technology necessary to eliminate the discharge of pollutants into the navigable waters, waters of the contiguous zone, and the oceans; and
(7) it is the national policy that programs for the control of nonpoint sources of pollution be developed and implemented in an expeditious manner so as to enable the goals of this chapter to be met through the control of both point and nonpoint sources of pollution (17).”

These provisions and this law set the stage for many advances in water pollution control. The provisions talk about two types of pollution sources, point and non-point. A point source is a single localized source of pollution, while a non-point source causes pollution to spread over a wider, non-localized area. It also laid some goals for the EPA to reach and described what power the EPA held (18). The CWA was amended two times, in 1977 and 1987. The 1977 amendment allowed the government to control the release of toxic substances into sewers and surface waters (19). Then, in 1987 Congress decided to adopt programs to control pollution runoff coming from farms, factories and city streets (18).
In 1974 the Safe Drinking Water Act (SDWA) was passed to regulate the safety of the United State’s public drinking water supply to protect the public’s health. The types of water regulated under this law include rivers, lakes, reservoirs, springs and ground water wells that serve more than 25 people (20). From this act, the National Primary Drinking Water Regulations were created by the EPA to ensure that the public has access to safe drinking water. The regulations allowed the EPA to set maximum contaminant levels (MCL) for certain pollutants in drinking water and required that water plants take the means to treat water to remove undesired contaminants. In order to make sure that the public water systems contaminant levels were in accordance with the regulations, they had to submit water samples for testing to the state. If the amounts of contaminants present exceed the MCL, they are required to let the public know. Also, to prevent contamination, suppliers needed to determine where they may be vulnerable to pollution (21). In 1986, the statue was amended. Two changes were that this amendment required certain numbers of MCL standards to be set each year and it also changed the way drinking water had to be filtered and disinfected (22). In 1996, it was amended a second time. One of the changes included publishing annual consumer confidence reports with information on the detected contaminants. Also, the Federal government gave state governments’ access to more money to use for making sure that their drinking water is safe for human consumption, and those with smaller water systems were given more aid to make sure that they have the ability to meet the EPA standards (23). On the state level, each state government is responsible for keeping the water bodies within its boundaries that are not protected by the Federal government safe. For example, in Ohio
parts of the Ohio River and Lake Erie fall under the state’s jurisdiction. Each state creates and enforces its own rules and regulations for water pollution control. In Ohio the state EPA has the authority to administer all Federal water discharge programs to control water pollution; this authority was rewarded to the state after the U.S. EPA decided Ohio had an effective water control program. The Federal government gives the state money to follow through with programs (24).

Priority Pollutant Phthalate Esters

Since the EPA’s creation in 1970 one of its objectives, which was described in the CWA, was for the EPA to monitor toxicant compounds in water. Their job was to determine which compounds commonly found in water pose a threat to humans and above what concentration level of contaminant this risk is present (17). The National Resource Defense Council (NRDC) noticed in June 1973 that the US EPA had failed to meet 14 of the deadlines described in the CWA. As a result, they filed a suit against the administrator of the EPA, Russell E. Train, in 1974, to force the EPA to meet the law’s requirements (25). Over the next several years the NRDC felt that the EPA was still failing to meet the requirements. The NRDC ended up filing several suits over this issue (26-28). The judge that presided over these hearings was Judge Thomas A. Flannery (25). As an end result of all these suits, a ruling that is commonly known as the Flannery Decree (Flannery Decision) was issued. It required that the EPA create regulations that establish effluent limitations and guidelines for 21 point source categories by December
31, 1979, which was eventually changed to June 30, 1984 (29). The allowed limit of priority pollutant effluents was to be based on the “best technology economically achievable” (BAT) for controlling the effluent. A result of the decree was the list of the 126 priority pollutants that the US EPA would monitor, which are the only pollutants covered by the CWA (25).

On this list of priority pollutants are six phthalates, dimethylphthalate, diethylphthalate, di-n-butylphthalate, butylbenzylphthalate, di-(2-Ethylhexyl)phthalate, and di-n-octylphthalate (30). Phthalates are esters of 1,2-benzenedicarboxylic acid. The six phthalates that were studied can be seen in Figure 1. Some physicochemical properties of phthalates are listed in Table 1. Phthalates are a current worldwide concern because each year 5.5 billion pounds of various phthalate esters are produced worldwide. One of the common uses of phthalates is as additives in plastics to adjust certain properties, with the most common property being flexibility. For example, phthalates are largely used in the production of polyvinyl chloride (PVC) (1). Besides PVC products, phthalates can also be found in a wide variety of consumer products such as facial cosmetics (30), nail cosmetic products (31), and plastic food products (32). Phthalates have also been found in human milk, due to the mother’s exposure to phthalates, which means mothers can unknowingly expose their infants to these dangerous compounds (33). Phthalate esters are physically, not chemically bonded in the polymer, so it is therefore possible for them to leach out into their surrounding environment, and thereby possibly contaminating any nearby bodies of water (2). Studies have found that the presence of phthalates in humans can have adverse effects such as being possible endocrine
disruptors and carcinogenic (34-36). A more detailed list of common uses and exposure concerns for each of the six phthalates studied can be seen in Table 2. As a result of their widespread presence and harmful effects on humans, the US EPA has decided to monitor for phthalates in water bodies as priority pollutants (37). Specifically, the US EPA has set the maximum admissible concentration for di-(2-Ethylhexyl)phthalate at 6 ppb (38).

EPA Methods

In order to determine if water sources are at safe contaminant levels for consumption by humans, the EPA has developed and approved methods for determining the amounts of different pollutants present in water (40). The United States EPA has several methods for determining the amount of phthalate esters in water. There are different method series depending on the type of water source. One example is the 500 series methods, which are cited in the SWDA for measuring contaminants in municipal drinking water (20). The 600 series methods are cited under the Clean Water Act to determine the amounts of pollutants in industrial and municipal waste discharge water (17). The EPA 8000 methods are designed for monitoring organic pollutants in ground water, as discussed in the Resource Recovery and Conservation Act (RCRA) (41).

There are three EPA methods for the determination of phthalate esters in There are three EPA methods for the determination of phthalate esters in water, 506, determination of phthalate and adipate esters in drinking water by liquid-liquid extraction or liquid-solid extraction with gas chromatography with photoionization, 606, methods for
organic chemical analysis of municipal and industrial wastewater-phthalate esters, and 8061A, phthalate esters by gas chromatography with electron capture detection (GC/ED). In all three of these methods, a grab sampling technique is used and the sample must be refrigerated and free from light until it is extracted. Also, the methods involve a liquid-liquid extraction technique to remove the analytes from the water matrix. The extraction involves extractions with hexane and dichloromethane, using about 150 mL of solvent for each extraction. The resulting extracts are combined and then condensed down to 1 mL using a Kuderna-Danish apparatus. A Kuderna-Danish apparatus is used to concentrate a sample of interest from a solvent of a lower boiling point. The resulting mixture from a liquid-liquid extraction is placed into an erlenmeyer flask connected to a concentrating tube and a two or three ball snyder column. The condenser tube and Erlenmeyer flask are heated in a water bath to remove excess solvent to concentrate the sample to a desired volume. In some cases the extract may need to be cleaned using florisil or alumina columns and solvents such as ethyl ether and hexane if the sample does not pass quality control criteria. In methods 506 and 8061A there is also a liquid-solid extraction option in which the sample is slowly added to a disk or cartridge to collect the analytes and then the analytes are removed from the disk or cartridge using solvents. The resulting extracts are then analyzed using gas-chromatography. Method 506 uses photoionization detection, method 606 uses electron capture detection and method 8061A uses both electron capture and mass spectrometric detection. The detection limits for these three methods can be seen in Table 3 (3-5).
Table 1. Physiochemical properties of selected phthalates. These densities were determined at 20°C, and $K_{ow}$ is the octanol-water partition coefficient.

<table>
<thead>
<tr>
<th></th>
<th>Molecular Weight</th>
<th>Boiling Point (°C)</th>
<th>Log $K_{ow}$</th>
<th>Density (g/cm³)</th>
<th>Vapor Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylphthalate</td>
<td>194.18</td>
<td>284</td>
<td>1.6</td>
<td>1.19</td>
<td>3.31E-03</td>
</tr>
<tr>
<td>Diethylphthalate</td>
<td>222.24</td>
<td>298</td>
<td>2.42</td>
<td>1.118</td>
<td>1.67E-03</td>
</tr>
<tr>
<td>Di-n-butylphthalate</td>
<td>278.34</td>
<td>340</td>
<td>4.5</td>
<td>1.042</td>
<td>1.08E-04</td>
</tr>
<tr>
<td>Butylbenzylphthalate</td>
<td>312.36</td>
<td>370</td>
<td>4.73</td>
<td>1.011</td>
<td>7.09E-07</td>
</tr>
<tr>
<td>Di-(2-Ethylhexyl)phthalate</td>
<td>390.56</td>
<td>385</td>
<td>7.27</td>
<td>0.978</td>
<td>3.95E-06</td>
</tr>
<tr>
<td>Di-n-octylphthalate</td>
<td>390.56</td>
<td>220</td>
<td>8.1</td>
<td>0.961</td>
<td>3.84E-07</td>
</tr>
</tbody>
</table>

Figure 1. Structure of: (a) dimethylphthalate, (b) diethylphthalate, (c) di-n-octylphthalate, (d) di-n-butylphthalate, (e) butylbenzylphthalate, and (f) di-(2-Ethylhexyl)phthalate
Table 2. List of materials the six priority pollutant phthalates are present in and human exposure concerns for each.

<table>
<thead>
<tr>
<th>Phthalate</th>
<th>Commonly Found In</th>
<th>Human Exposure Concerns</th>
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<tbody>
<tr>
<td>dimethylphthalate</td>
<td>Flea collars, repellents, plastics</td>
<td>Not enough data</td>
</tr>
<tr>
<td>diethylphthalate</td>
<td>Shampoo, nail polish, soaps, cosmetics, toothbrushes, toys, insectides</td>
<td>Exposure of pregnant women may affect development of offspring</td>
</tr>
<tr>
<td>di-n-butylphthalate</td>
<td>Latex adhesives, cellulose plastics, dye solvents, nail polishes, varnishes, cosmetics</td>
<td>Exposure to children and pregnant women</td>
</tr>
<tr>
<td>butylbenzylphthalate</td>
<td>Perfume, artificial leather</td>
<td>Exposure to children and pregnant women</td>
</tr>
<tr>
<td>di-(2-ethylhexyl)phthalate</td>
<td>PVC, medical devices, food packaging, building materials, shower curtains, toys</td>
<td>Exposure of infants to medical care devices</td>
</tr>
<tr>
<td>di-n-octylphthalate</td>
<td>Floor tiling, carpet, notebook covers</td>
<td>Exposure to children and pregnant women</td>
</tr>
</tbody>
</table>
In all of the methods, grab sampling is utilized. Grab sampling only allows for the determination of phthalates in the water at the point in time the sample was taken, since it is specific to time and location (42). The types of liquid-liquid extraction call for a large amount of dangerous solvents to be used, which is harmful to the environment. Also, the liquid-liquid extraction methods are very labor intensive and time consuming. These methods call for many pieces of glassware to be used, increasing the potential for sample contamination (43).

Other Phthalate Extraction Methods

Methods other than those used by the US EPA to extract and determine the amount of phthalates in water have been developed. These methods include techniques such as solid-phase microextraction (SPME), hollow-fibre liquid-phase microextraction, solid phase extraction, a polar organic chemical integrative sampler (POCIS) and liquid-liquid extraction.

Several groups have explored the option of using SPME for the determination of phthalates in water. Peñalver et al. compared different SPME fibers to determine which was best for extraction of water samples out of vials. From the different fibers studied they found that a polydimethylsiloxane and divinyl benzene (PDMS-DVB) fiber worked best, as it gave the largest detector response as compared to the other fibers (44). On the other hand, Polo et al. used a multivariate optimization technique to determine which SPME fiber was optimal, and whether sampling the head space or directly in the liquid
was better for analyzing water samples in a vial. They found in agreement with the previous group that a PDMS-DVB fiber with direct immersion of the fiber into the sample was the best choice if all six phthalates needed to be sampled (45). Li et al. took a different approach. They decided to create their own SPME fibers by coating a stainless steel wire with polyaniline and compared the results to a commercially available fiber polyacrylate. It was found that the polyaniline fiber they made worked better than the polyacrylate fiber they found to work best out of commercially available SPME fibers (46). solvents were then analyzed using either GC/MS or liquid chromatography-mass spectrometry (LC/MS) (48).

On the other hand, Ballesteros et al. utilized solid phase extraction cartridges to analyze phthalates in aqueous solutions. To collect the analytes onto the cartridge 500 ml of sample was passed through the cartridge. The collected analytes were removed using organic solvents and the resulting elutent was injected into a GC/MS (49).

The last technique to be discussed is a liquid-liquid extraction technique using water soluble organic solvents and the addition of inorganic salts to extract phthalates from water. The organic solvent was added to the aqueous sample solution and different organic salts were added to the mixture to see which solvent-salt pair resulted in the best separation the two phases in order to collect the most phthalates in the organic phase. It was found that (NH₄)₂SO₄ was the best at separating out the two phases, while propanol was found to be the best solvent. Therefore this technique allowed the use of water soluble organic solvents for the trace analysis of phthalates in water (50).

<table>
<thead>
<tr>
<th></th>
<th>EPA Method</th>
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<tbody>
<tr>
<td></td>
<td>8061A</td>
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<tr>
<td>Dimethylphthalate</td>
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<td>Butylbenzylphthalate</td>
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<td>di-(2-Ethylhexyl)phthalate</td>
<td>0.27</td>
</tr>
<tr>
<td>Di-n-octylphthalate</td>
<td>0.049</td>
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</tbody>
</table>

Pervaporation

The concept of pervaporation was discovered in 1917 by Kober. It was discovered when a collodion bag filled with liquid suspended in the air had evaporated, even though the bag had been tightly closed. After more experimentation Kober and his assistant concluded that the aqueous vapor was given off as if there were no membrane present, like the water was suspended as a solid. Kober decided to call this phenomenon pervaporation (51).

Pervaporation is the process by which a liquid mixture is separated by partially vaporizing some of the mixture through a membrane. The mixture is exposed to the membrane, where the permeate is removed by its permeation through the membrane in the vapor state to the outside of the membrane, which is kept under a low pressure and/or
low concentration (52). In the case of this study, an adsorbent was applied to the collecting side of the membrane to keep the pressure low. There are three major types of separations in which pervaporation can be utilized:

1. Dehydration of aqueous-organic mixtures,
2. Removal of trace volatile organic compounds from aqueous solution,

In the case of this study a pervaporation separation of type 2 was performed (53).

Another important aspect of pervaporation is selectivity. Selectivity can be interpreted as how much of a plasticizing effect the different permeates have on the membrane and which analytes tend to permeate through to the permeate side of the membrane more so than other components. Some parameters that have an effect on the selectivity include: the composition of the feed solution and the diffusivities of the permeates. The diffusivities have a larger effect on the selectivity of the individual components than their solubilities. The pervaporation selectivity ($\alpha$) at the steady state is defined by equation (1):

$$\alpha = \frac{J(i) \times(j1)}{J(j) \times(i1)} = \frac{y(i2) \times(j1)}{y(j2) \times(i1)}$$  

where $J(i)$ and $J(j)$ are the molar fluxes of components x and j, $x(j1)$ and $x(i1)$ are the feed solution mole fractions of the two components i and j, and $y(i2)$ and $y(j2)$ are the mole fractions of i and j on the permeate side (54).
The technique of pervaporation though a membrane has been applied to industrial applications because of the method’s simplicity of purification. The most common use is the dehydration of ethanol, isopropanol and other solvents. For example, the supposed largest pervaporation plant in the world, in Bethénville, France is able to purify a 94% wt ethanol feed to 99.8% wt ethanol (55). Pervaporation is also used industrially for separating azeotropic mixtures of alcohols, ketones, esters (ethyl and butylacetate) and pyridines. The advantage of the method of pervaporation in this use that it allows the azeotrope to be broken with recourse to additional components or by lowering the pressure (56).

Permeation Sampling

Permeation sampling utilizes pervaporation through a semi-permeable membrane to extract desired organic compounds from aqueous solutions. The permeation of the organic compounds through the semi-permeable membrane is driven by the difference in chemical potentials between the permeate and collection side of the membrane of each individual component (57). This difference in chemical potential is due to the analyte concentration in the exposure (feed) solution being greater than zero and the concentration on the permeate side being almost zero, due to the permeate side being a “zero” sink. The permeability constant (P) for each individual compound in the sample is defined by:
In equation (2), D is the diffusion coefficient in the membrane and S is the solubility in the membrane. This shows that the permeability of a component in a membrane is dependent on solubility, a thermodynamic term, and diffusion, a kinetic term (58). There are several models that can be applied to permeation sampling, in this case, the resistance-in-series and the solution-diffusion models are used.

One model that can be used to explain the permeation sampling technique is the resistance-in-series model. The model is composed of five steps to describe the movement of an analyte molecule from the exposure solution, permeation through the membrane, to the collecting medium:

1. Diffusion through the boundary layer
2. Sorption into the membrane
3. Diffusion through the membrane
4. Desorption out of the membrane
5. Diffusion through the boundary layer.

Figure 2 shows a depiction of this model to permeate through the membrane (59). In this model, it is assumed that the semipermeable membrane is covered on both sides by a thin layer of immobile fluid, which is considered the boundary layer, which can cause resistance to analyte’s mobility. This is because part of the boundary layer in the exposure solution is laminar which can cause polarization of different compounds at the layer that may cause this area to be different from the bulk exposure (feed) solution. This
resistance tends to be very small and not have a significant effect on the molar flux. The molar flux of the analytes from the exposure solution to the permeate side, is constant and has the same flux value at any point on the membrane under steady state conditions (60). Although, at the moment the sampler is placed into the sample solution, the amount of analyte that passes through the membrane is zero. The rate of permeation will increase until it reaches a point where the rate of transport is linear with respect to time, known as the steady-state. The period of time is takes for the rate of permeation to reach steady state is known as the lag time (61).
Figure 2. Depiction of analyte permeation through a polymeric membrane. The dotted line represents the concentration profile of the analyte in the membrane.
Another model for describing analyte transport through a semi-permeable membrane is the solution-diffusion model. In this model, the first step is that the permeating molecules are dissolved into the membrane from the exposure solution (62). As a result, the target analytes must be soluble in the chosen membrane in order for permeation to occur (57). The second step includes the random molecular diffusion of the molecule through the membrane. This is because analytes are able to diffuse through free volume holes, which are created by the change in position of individual polymer molecules due to normal thermal motion. These holes are created by fluctuation in the polymer chains. The final step is desorption into the vapor phase on the permeate side of the membrane (62). A depiction of this method can be seen in Figure 3 (63). Liu et al. found that the following assumptions about the pervaporation of trace organic compounds in an aqueous solution to be reasonable to help explain the solution-diffusion model:

(1) Small temperature difference across the membrane $T_1 \approx T_2$ (where $T_1$ is the temperature on the feed side of the membrane and $T_2$ is the temperature at the permeate side of the membrane)

(2) Henry’s law is valid for the solute (low concentration): $p_{A1} = H_A C_{A,1}$ (where $p_{A1}$ is the partial pressure of component A on the feed side, $H$ is the Henry’s law constant and $C_{A,1}$ is the concentration of component A in the feed solution)

(3) Vapor pressure of the solvent in the feed solution approximates that of the pure solvent: $p_{B1} \approx p_0^B(T_1) = p_0^B(T_2)$ (where $p_{B1}$ is the vapor pressure of the solvent in the solution, $p_0^B(T_1)$ and $p_0^B(T_2)$ are the vapor pressures of the pure component
B at the feed side of the membrane and the permeate side of the membrane, respectively)

(4) Partition coefficients of the components are constant across the top layer of the membrane: \( \psi_{i1} \approx \psi_{i2} = \psi_i \) (in which \( \psi_{i1} \) and \( \psi_{i2} \) are the partition coefficients of the component i at the feed side surface (i1) and the permeate side surface of the top layer (i2))

Another model used to describe permeation is the pore-flow model. This model differs from the solution-diffusion because it assumes that there is a phase boundary inside the membrane (64).

In order to follow these permeation guidelines, no fouling of the membrane should occur. There are several ways in which membranes may be fouled. Some examples include the presence of large suspended particles, small colloidal particles, and macromolecules and proteins in the sample. Also pH changes can affect the membrane. Lastly, there can biological fouling due to bacterial growth on the membrane (65).

Passive Sampling

Permeation sampling is a type of passive sampling technique. Passive sampling can be defined as “any sampling technique based on free flow of analyte molecules from the sampling medium to a collecting medium as a result of a difference in chemical potentials of the analyte between the two media”. Passive sampling techniques tend to combine sampling, analyte isolation and preconcentration in one step. This helps these
types of methods to be quicker, cheaper and easier to perform. One common use of passive sampling is to determine time-weighted concentrations (TWA) of analytes (66).

There are two types of passive samplers, equilibrium-passive samplers and kinetic passive samplers. In equilibrium-passive samplers, the exposure time needs to be long enough in order for a thermodynamic equilibrium to be reached between the water and reference media (67). The desired properties of an equilibrium sampler are that it has fast

Figure 3. Depiction of the solution-diffusion model (63)
uptake rate and a small uptake capacity for the analyte in order to allow for equilibrium to be reached quickly. As a result, these methods have some disadvantages. One disadvantage is that different chemicals in the sample will take different amounts of time to reach equilibrium. These types of samplers are also vulnerable to temperature and concentration fluctuations (68). On the other hand, with kinetic passive samplers, the rate of mass transfer to the collecting medium is proportional to difference in the chemical activity of the analyte in water and reference phases. A comparison of the two types of passive sampling can be seen in Figure 4. The type of passive sampling utilized in this project was kinetic. Advantages of the kinetic method include: ability to sample episodic events that may not be detected with grab sampling and the possibility to detect ultra-trace concentrations of contaminants over an extended exposure period (67). The rate of the accumulation of chemicals usually follows first order kinetics. For kinetic passive samplers, the sampling rates depend on intrinsic and extrinsic factors. Physiochemical properties of the analytes and the design of the passive sampler are some intrinsic factors. Some extrinsic factors are water turbulence, temperature, water flow and biofouling. In order to account for these factors, the sampling devices must be calibrated in the lab prior to use (69).
Passive sampling also has several advantages over active sampling. In active sampling a pump is used to draw in the sample at a constant flow rate through a collecting medium that extracts the target analytes of interest from the water. As a result, the disadvantages of active sampling include: the high cost of pumping units, the sampling period is limited by battery lifetime and the instability of the pumping units (70).
Diffusion

Diffusion is the migration of a compound through a concentration gradient. The solution-diffusion theory accepts that the mass transfer through the membrane follows Fick’s first law of diffusion. Fick’s first law of diffusion states:

\[ J = -D \frac{dc}{dx} \]  \hspace{1cm} (3)

where \( J \) is the diffusional flux in units of moles/(cm\(^2\cdot s)\), \( D \) is the diffusional coefficient in units of cm\(^2\)/s, \( dc \) is the change in concentration across the membrane, and \( dx \) is the thickness of the membrane. In order for equation (3) to be valid, it is assumed that there is a steady state rate of permeation and that a linear concentration gradient exists throughout the membrane (71). Integration of equation (3) over the thickness of the membrane gives:

\[ J = DA \frac{(C_2 - C_1)}{L} \]  \hspace{1cm} (4)

where \( A \) is the area of the membrane, \( L \) is the length of the membrane, \( C_2 \) and \( C_1 \) are the concentrations on the feed and permeate side, respectively. Since the concentration, \( C_1 \) is effectively zero on the permeate side of the membrane, equation (4) can be simplified to:

\[ J = DA \frac{C_2}{L} \]  \hspace{1cm} (5)
Henry’s law can then be applied:

$$C_2 = SC$$

(6)

In this equation, $C_2$ is the concentration of analyte just inside the membrane surface is related to, $S$ is a solubility proportionality constant, and $C$, the concentration of the feed solution (72). Substituting equation (6) into equation (5) gives:

$$J = \frac{DASC}{L}$$

(7)

In order to get a working form of this equation, the units of $J$ were converted to units of mass rather than mass/time. In order to accomplish this, both sides of equation (7) are multiplied by time:

$$M = \frac{DASTC}{L}$$

(8)

In equation (8) the values $D$, $A$, $S$ and $L$ are constants, so they can be combined to define a permeation constant, $K$:

$$K = \frac{DAS}{L}$$

(9)

Where $K$ often has units of $\mu g/(ppm\cdot hr)$. Substituting equation (9) into equation (8) gives the working form of Fick’s First Law of Diffusion;
where this equation relates the mass of analyte collected, \( M \), to the permeation constant, \( K \), the exposure solution concentration, \( C \), and the exposure time, \( t \). This equation allows for time weighted average plots to be created which are the product of exposure time and concentration versus the mass of analyte collected. Therefore, it can be seen that the slope of the time-weighted average plot is the permeation constant, \( K \). Once the membrane samplers have been calibrated to find \( K \), if the mass of analyte collected is known, and the exposure time is known, the average concentration of the exposure solution can be determined.

There are several factors that can have an influence on the diffusion coefficient (\( D \)) and permeability of a compound through a membrane. For example, the glass transition temperature (\( T_g \)) for a polymeric membrane, which is the temperature at which the membranes changes from a rigid solid (glass) to a flexible rubber state (73). The effect of molar mass on \( T_g \) can be seen in equation (11):

\[
T_g = T_g^* - \frac{K}{M}
\]

In the equation \( T_g^* \) is the asymptotic glass transition temperature for an infinite molar mass, \( K \) is a constant for the specific polymer and \( M \) is molar mass. Studies have been done that show that there is a linear correlation between the \( T_g \) and \( D \) and permeability. As the \( T_g \) rises, the permeability and diffusion coefficients decrease, since below the \( T_g \) the polymer chains can be viewed as frozen and not creating new free volumes (74).
Other influences on D and permeability include polarity, hydrogen bonding, cohesive energy density, chain flexibility, steric hindrance, side group substitution and crystallinity. The effects of these can also interplay with each other (75).

Another important factor that can have an effect on the diffusion and permeation of an analyte through a membrane is temperature. In general, the diffusion and permeation of an analyte through a membrane increase with temperature. Also, the less permeable the membrane, the more affected it is by temperature changes. If Henry’s Law is obeyed and D is constant, then over a range of temperatures the permeation through the membrane follows the Arrhenius equation:

\[ P = P_0 \exp\left(-\frac{E_p}{RT}\right) \quad (12) \]

in which P is the permeability coefficient at the sampling temperature, \( P_0 \) is the permeation constant at the calibrated temperature, \( E_p \) is the energy of permeation, R is the ideal gas constant, and T is the sampling temperature (76). This allows for:

\[ E_p = \Delta H + E_D \quad (13) \]

which states that the energy of permeation is equal to the sum of the enthalpy change and the energy of diffusion, which is true over a wide range of temperatures (77). From previous studies, it can be seen that equation 11 an be related to the permeation constant K to give:
in which $K$ is the permeation at the sampled temperature, $K_0$ is the permeation constant at the calibration temperature, $s$ is the slope of the graph of change in permeation constant vs. change in temperature, and $T$ is the temperature of the sampled solution. Past studies have shown equation (14) allows for the permeation constant to be adjusted to take into account a change in temperature (78-82).

Solubility

In order for an analyte to be able to permeate through a membrane, it must be soluble in the membrane. The solubility of a permeate in an organic polymer is based on the magnitude of the van der Waals force field around each molecule along with the field intensity of the individual chain segments of the polymer membrane. This is true only if the permeate is a hydrocarbon (83). In order for two components to be soluble they should have a negative free energy of mixing, $\Delta G_m$. $\Delta G_m$ is defined by equation (15):

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

where $\Delta H_m$ is the enthalpy of mixing, $T$ is the temperature and $\Delta S_m$ is the entropy of mixing.
In 1916, Hildebrand published a paper in which he described the conditions that must be met in order for two compounds to be soluble. Hildebrand’s Solubility Parameters include:

(a) The components in the pure liquid state have the same internal pressures.
(b) The different molecules are relatively symmetrical or nonpolar.
(c) The tendency to form chemical compounds is absent.

To account for internal pressures that may be different, Hildebrand created a solubility parameter, $\delta$. This parameter can be calculated by:

$$\delta = \left(\frac{\rho(\Delta H - RT)}{M}\right)^{\frac{1}{2}}$$  \hspace{1cm} (16)

in this equation, $\rho$ is the density and $M$ is the molecular weight of the polymer (84). This solubility parameter can be used in an equation to describe the $\Delta H_m$:

$$\Delta H_m = n_1 n_2 V_1 (\delta_1 - \delta_2)$$  \hspace{1cm} (17)

where $\delta_1$ and $\delta_2$ are the solubility parameters of the solvent and polymer, respectively, $n_1$ and $n_2$ are the mole fractions for the solvent and polymer, respectively and $V_1$ is the volume of the solvent. It can be seen from equations (15) and (17) that in order to make $\Delta G_m$ negative, the difference between $\delta_1$ and $\delta_2$, should be as small as possible. In other words both the solvent and the polymer should be of similar polarities (85).
Free Volume

The free volume of a polymer is the mass fraction of the polymer that is not actually occupied by the molecules. Applying this to permeation, it can be seen that permeate molecules “jump” to a vacancy or hole in its vicinity that it fits in. As it diffuses, moves to the next hole, it leaves behind a hole of the same size. The free volume, $\nu_f$ can be defined as:

$$\nu_f = \nu - \nu_s$$  \hspace{1cm} (18)

where $\nu$ is the specific volume of the polymer mass and $\nu_s$ is the volume of solidly packed molecules in the polymer mass. A correlation can be seen between $\nu_f$ and $T_g$, as it has been estimated that $\nu_f/\nu$ for all polymers is 0.025 at the polymer’s $T_g$. The higher the $\nu_f$ value is, the more room that will be available for molecules to move about, and as a result, the lower the $T_g$ (84). Another way to express free volume is by using the parameter, specific free volume (SPV) which is a measure of free volume per unit weight$(M)$ (86):

$$SFV= \frac{\nu_f}{M}.$$  \hspace{1cm} (19)

Combining equations (18) and (19), the fractional free volume $(f')$ can be calculated:
\[ f' = \frac{v_f}{\text{SPV}}. \quad (20) \]

Temperature also has an effect on the fractional free volume. The effect on \( f' \) can be seen in equation (21):

\[ f' - f'_g = \alpha \Delta T \quad (21) \]

where \( \alpha \) is the difference between the expansion coefficients for melt and glass phases, \( \Delta T \) is the current temperature minus \( T_g \) and \( f'_g \) is the fractional free volume at \( T_g \) (87).

One way to calculate the effects of free volume on the diffusion coefficient of individual components, is by using the Cohen Turnbull equation:

\[ D_A = D_0 \exp\left(-\frac{Bv^*}{V_f}\right) \quad (22) \]

in equation (22) \( D_0 \) and \( B \) are empirical constants, \( v^* \) is proportional to the size of the gas molecule and \( V_f \) is the average size of a free volume element in the membrane material. Equation (22) shows that as the average size of a free volume element increases so does the diffusion coefficient. On the other hand, as the size of the gas molecules increases, the diffusion coefficient decreases (88).
Phthalate Ester Permeation Sampling

In this study, the samplers contained a semi-permeable membrane through which the phthalate molecules could permeate. Since the phthalate molecules were much more soluble in the membrane than the water molecules. As a result, more phthalate molecules were collected than water molecules, increasing the phthalate concentration. On the permeate side of the membrane, an adsorbent was placed to create a “zero sink”. This created a concentration gradient across the membrane which caused the permeation to occur. Once the phthalates were extracted, they could be desorbed from the adsorbent via a solvent or thermal desorption. Gas Chromatography and GC-MS were used to analyze the results.
CHAPTER III

EXPERIMENTAL

Permeation Samplers

Permeation samplers were constructed by affixing 0.001 mm silicone polycarbonate sheets (MEM-213 copolymer) (Silicone Specialty Products, Ballston Spa, NY) to glass tubing with a silicone sealant (DAP Aquarium Sealant, Baltimore, MD). The structure of MEM-213 copolymer can be seen in Figure 5. The sealant was then allowed to dry for 24 hours and the excess membrane was then removed.

![Figure 5. Structure of MEM-213 copolymer membrane.](image-url)
Adsorbent/Desorbing Solvent Selection

Initial testing was performed to determine the optimum adsorbent-desorbing solvent pair for the collection of phthalate esters that permeated through the membrane. Each combination was exposed for the same amount of time to a solution of constant concentration and temperature. The adsorbents that were studied included Porapak (Waters Corp., Milford, MA), Chromosorb (Supelco, Bellefonte, PA), Amberlite® XAD16 (Supelco, Bellefonte, PA) and Amberlite® XAD4 (Supelco, Bellefonte, PA). The desorbing solvents tested were: acetone (ACS Certified, VWR, West Chester, PA), hexane (ACS Certified, EMD chemicals, Gibbstown, NJ), methanol (ACS Certified, Fisher, Fairlawn, NJ), dichloromethane (GC Resolv, Fisher, Pittsburgh, PA), acetonitrile (ACS Certified, Aldrich Chemical Co, Milwaukee, WI), and dichloromethane: hexane (50:50 v/v). A total of four adsorbents and five desorbing solvents were paired together as a result. An illustration of the sampler and exposure set up can be seen in Figure 6. All samplers were exposed for 24 hours to a 275 ppb solution of the phthalates studied: dimethylphthalate, diethylphthalate, di-n-butylphthalate, butylbenzylphthalate, di-(2-ethylhexyl)phthalate, and di-n-octylphthalate (Chem Service, West Chester, PA). The samplers were loaded with 0.2 of the adsorbent which was placed in the sampler using weighing paper. After the exposure, the adsorbent added to the membrane is removed and placed into a vial using a funnel with 1 ml of the desorbing solvent, sealed, and sonicated (Solid State Ultrasonic FS-14, Fisher Scientific, Pittsburgh, PA) for 1 hour. A 1
μL aliquot of the resulting solutions was injected into a Hewlett-Packard (Palo Alto, CA) 5890 Gas Chromatograph equipped with a Hewlett-Packard 5870 Mass Selective Detector and a 7673A Hewlett-Packard Autosampler. The analytical column was a J&W Scientific (Agilent, Santa Clara, CA) DB-17 MS 20 m capillary column with an internal diameter of 0.18 mm and a film thickness of 0.18 μm. The injector temperature was set at 25°C and the detector temperature was set at 275°C. The temperature program was used an initial temperature of 35 °C for 5 minutes and ramped up at 35 °C/min to 232°C and held there for 3 minutes. The temperature was then ramped up to 234°C at 0.2 °C/min and held for 1 minute. Finally, the temperature was ramped up to 260°C at 40 °C/min and held constant for 2 minutes. Before use, the Amberlite® XAD16 was filtered and washed with deionized water and heated at 80 °C for 12 hours and was cleaned using a Soxhlet apparatus and dichloromethane for 4 hours.
Figure 6. Illustrations of (a) Permeation sampler and (b) Sampler exposure set-up including holding tank, with stir bars.
Linearity of Membrane

In order to create the necessary calibration curves, 0.2 g of Amberlite® XAD 16 was placed on top of the membrane, and the sampler was exposed to an aqueous solution containing known amounts of phthalates for a known period of time. A standard 1000 ppm solution of the six phthalates was prepared in methanol and was used to achieve the desired solution concentration. A VWR Refrigerated Circulator Model 1160S (VWR, Chester PA) was used to keep the exposure solution at a constant temperature. After the sampling period the adsorbent was removed and placed into a vial along with 1 mL of a dichloromethane: hexane (50:50 v/v) mixture and the vial sealed. The vial was then sonicated for 1 hour. A Hewlett-Packard 5890 Gas Chromatograph with a flame-ionization detector equipped with a 7673A Hewlett-Packard Autosampler was used. The column used was a J&W Scientific (Agilent, Santa Clara, PA) DB-5 MS 20 m column with an internal diameter of 0.18 mm and a film thickness of 0.18 µm. The injector and detector temperatures were set at 270 °C and 310 °C, respectively. For the temperature program, the initial temp. was held for 5 min. at 35 °C, then raised at a rate of 30 °C/min to 160 °C. Then the temperature was raised 15 °C/min to 300 °C and held for 10 min.

The next step was to determine if, when the samplers were exposed to solutions of the same concentrations of all six phthalates over increasing amounts of time, the response also increased linearly. For exposures over 24 hours, the exposure solution was changed daily. In order to test this, samplers were exposed to a 275 ppb solution while the exposure time was varied. Next, samplers were exposed to different concentrations a
constant exposure time. Finally, the samplers were exposed to varying concentrations and varying times to create a time-weighted average plot. Runs were also completed where the solution concentration was changed over the course of the exposure period, to simulate a “real world” situation. The samplers were exposed to fifteen sample solutions ranging in time from 4 hours to 7 days and concentrations from 1-500 µg/L.

Temperature Studies

The effects of differences in temperature of the sample solution on the permeation constant were examined. Trials were run in which the solution concentration and exposure time were kept constant at 250 ppb and 4 hours, respectively, but the temperature of the solution was varied. The temperature was varied from 1 °C to 30 °C in 5 °C intervals, using a refrigerated circulator to keep the temperature constant. The permeation constant, K, was determined for each phthalate at each temperature studied. A plot of K versus temperature was created for each phthalate.

Interferent Effects

The effects of several possible interferents on the rate of permeation were studied given that, in authentic samples, other contaminants may be present. The interferents chosen for this study were common environmental pollutants: humic acid (Aldrich Chemical Co., Milwaukee, WI), sodium lauryl sulfate (Sigma Chemical Co. St. Louis,

The samplers were exposed to 250 ppb solutions for four hours at 20°C while the amount and type of interferent was altered. The effects of sodium sulfate, sodium phosphate, sodium nitrate, and sodium chloride were studied from a solution concentration range of 0 M to 0.01 M. Since sodium sulfate and sodium phosphate are weak bases, the pH change associated with their addition to deionized water was measured. The pH of the deionized water alone was 6.8, while a solution of 0.01 M sodium sulfate had a pH of 7.6 and a 0.01M sodium phosphate solution changed the pH level to 7.3. Sodium lauryl sulfate and humic acid were studied in solution concentrations ranging from 0 to 0.004 ppm. The pH of the exposure solution was adjusted to between 4 and 10. The exposure time, temperature and phthalate concentration was kept constant, the amount of and type of contaminant was the only component adjusted.

Stirring Effect Studies

In order see what effect different stirring rates would have on the amount of phthalates collected, permeation samplers were exposed to 250 ppb sample solutions for four hours at 20°C. The only condition altered was the stirring rate of sample solution.
For previous experiments the exposure stirring rate was kept constant at 550 rotations per minute (rpm). A magnetic stirrer was set to stir the exposure solutions at 0, 250, 400, 550, 700, and 1000 rpm. to see if compared to the 550 rpm results the stirring rate had an effect on the results.

Stability Studies

In order to determine the stability of the phthalates on the Amberlite® XAD16, samplers were exposed to solution concentrations of 67 ppb of each phthalate for 24 hours. Initial runs were preformed as soon as the adsorbent was removed. For other trials, vials containing the exposed adsorbent were either placed in a refrigerator, at 4°C, or in a fume hood, at ~22°C, or stored for up to one month. Extractions were performed weekly on samples exposed to each temperature.

Authentic Sample Studies

Studies were performed on spiked authentic samples to better emulate a “real world” exposure. A wastewater influent sample was obtained from the Department of Environmental Services, Fishcreek Wastewater Treatment Plant in Stow, Ohio. The characteristics of the authentic sample can be seen in Table 4.

This authentic sample was spiked with the methanol/phthalate standard to obtain concentrations ranging from 0-500 µg/L. The samplers were exposed for 4 hours. Also
studies were performed to determine the percent recovery of spiked authentic samples as compared to spiked ultrapure water samples.

Table 4. Characteristics of Wastewater Sample.

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended Solids</td>
<td>213 mg/L</td>
</tr>
<tr>
<td>Carbonaceous biochemical oxygen demand (CBOD)</td>
<td>124 mg/L</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.84 mg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>0.0033 mg/L</td>
</tr>
<tr>
<td>Copper</td>
<td>0.079 mg/L</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.313 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Thermal Desorption Method

An Envirochem Thermal Desorption Unit Model 850 (Supelco, Bellefonte, PA) connected to a Hewlett-Packard 5890 Gas Chromatograph equipped with a Hewlett-Packard 5870 Mass Selective Detector was used. The DB-5 MS column was used with the temperature program being the same as on the GC-FID with the exception of the initial holding time being 7 min. instead of 5 min. Tenax TA was used as the adsorbent. This is because Amberlite® XAD16 is only stable up to temperatures of 150 °C, while Tenax TA (Supelco, Bellefonte, PA) adsorbent is stable at temperatures up to 350 °C. Tenax TA was cleaned by rinsing with methanol and then heated to 325°C for eight hours.

Initial studies were performed to determine what the optimal desorbing temperature was, with the temperatures studied included: 250°C, 275°C, 300°C, and
325°C. Once this was determined, exposures were performed using this method to produce a time-weighted average plot. Samplers were exposed to solutions for times ranging from 2 hours to 24 hours. The solution concentrations ranged from 15-150 ppb.

Next, to determine the sensitivity of the method, the detector was put into selected-ion monitoring mode. The ions that were monitored can be seen in Table 5.

The goal was to see what the lowest concentration that could be quantified after 24 hours. The SIM method resulted in an increase in the signal to noise ratio as compared to the scan method. The signal to noise ratio (S/N) was an average of 16 for the scan method, while the S/N average for the SIM method was 128. The lower level of noise allowed for smaller peaks, or lower concentrations, to be detected. As a result, at higher concentrations scan mode was used because it had a higher linear range. On the other hand, for lower concentrations, SIM mode was utilized because it had a lower linear range.

Table 5. Ions monitored in Selected-Ion-Monitoring Mode.

<table>
<thead>
<tr>
<th>Eluting Phthalates</th>
<th>Time (min)</th>
<th>Ions Monitored (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylphthalate</td>
<td>7</td>
<td>77, 149, 163, 177</td>
</tr>
<tr>
<td>diethylphthalate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>di-n-butylphthalate</td>
<td>15.5</td>
<td>149, 205, 223</td>
</tr>
<tr>
<td>butylbenzylphthalate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>di-(2-dihexyl)phthalate</td>
<td>18.5</td>
<td>57, 149, 91, 206, 167, 57, 279</td>
</tr>
<tr>
<td>di-n-octylphthalate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Lag Time Determination

Since the thermal desorption method proved to be very sensitive, studies were performed to determine the lag time for each of the six phthalates. The lag time is the amount of time it takes an analyte to reach steady-state permeation through the membrane. The determination of the lag time is important so that it can be determined how long a sampling period must be in order for the most of the permeation that occurs to be steady-state. The phthalate concentration was kept constant at 27 ppb for each of the six phthalate esters and sample temperature constant at 20 °C, while the length of the exposure time varied. The exposure times ranged from 15 minutes to 3 hours. Graphs of exposure time vs. amount of analyte collected were then plotted to determine what the actual lag times were.
CHAPTER IV
RESULTS

Selection of Adsorbent/Desorbing Solvent

Initial tests were performed to determine the optimum adsorbent-desorbing solvent pair for permeation sampling of phthalate esters in water. A silicone polycarbonate membrane was chosen for use in this experiment. This is because in past studies it was shown to be an effective membrane for allowing the permeation of several different groups of organic compounds from water samples (78-82). Four different adsorbents, Chromosorb, Porapak, Amberlite® XAD 4 and Amberlite ®XAD 16 were tested to see which collected the most analyte. Five different desorbing solvents, acetone, acetonitrile, dichloromethane, hexane, and methanol were used to see which desorbed the most analyte from the adsorbent into the solution. Each desorbing solvent was paired with each adsorbent and the amount of sample collected over a fixed time period of a constant concentration were compared. A table comparing the percent recoveries of the different pairs was created and can be seen in Table 6. From the table it can be conferred Amberlite®XAD16 was the best adsorbent. For four of the phthalates, the combination of Amberlite® XAD-16 and dichloromethane was the best, while for the other two, the combination of Amberlite® XAD-16 and hexane was best. It could be seen that overall
Amberlite®XAD16 was the best adsorbent. The structure of Amberlite® XAD-16 can be seen in Figure 7. For four of the phthalates, the combination of Amberlite® XAD-16 and dichloromethane was the best, while for the other two, the combination of Amberlite® XAD-16 and hexane was best. As a result, tests were done to compare to see if a (1:1, v/v) mixture of dichloromethane: hexane worked better than the two solvents alone. The results can be seen in Table 7, which shows that the mixture of dichloromethane and hexane worked best, and from then on was used as the desorbing solvent.

Figure 7. Structure of Amberlite® XAD 16 adsorbent.
Table 6. Comparison of percent recoveries as compared to XAD-16 dichloromethane. As compared to various other adsorbent-desorbing combinations for (a) dimethylphthalate, (b) diethylphthalate, (c) di-n-butylphthalate, (d) butylbenzylphthalate, (e) di-(2-ethylhexyl)phthalate, and (f) di-n-octylphthalate.

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Desorbing Solvent</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XAD16</td>
<td>acetone</td>
<td>75.7%</td>
<td>62.4%</td>
<td>73.8%</td>
<td>68.8%</td>
<td>153.8%</td>
<td>52.2%</td>
</tr>
<tr>
<td></td>
<td>hexane</td>
<td>45.2%</td>
<td>46.8%</td>
<td>89.7%</td>
<td>44.3%</td>
<td>150.0%</td>
<td>110.4%</td>
</tr>
<tr>
<td></td>
<td>methanol</td>
<td>51.3%</td>
<td>25.3%</td>
<td>20.2%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>dichloromethane</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>63.3%</td>
<td>50.1%</td>
<td>56.3%</td>
<td>31.4%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>Chromosorb</td>
<td>acetone</td>
<td>0.0%</td>
<td>0.0%</td>
<td>5.1%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>hexane</td>
<td>0.0%</td>
<td>0.0%</td>
<td>4.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>methanol</td>
<td>0.0%</td>
<td>0.0%</td>
<td>2.4%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>dichloromethane</td>
<td>0.0%</td>
<td>0.5%</td>
<td>2.7%</td>
<td>0.0%</td>
<td>3.7%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>0.0%</td>
<td>0.0%</td>
<td>4.1%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>Porapak</td>
<td>acetone</td>
<td>9.6%</td>
<td>14.6%</td>
<td>5.2%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>hexane</td>
<td>8.7%</td>
<td>6.8%</td>
<td>2.2%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>methanol</td>
<td>40.8%</td>
<td>42.0%</td>
<td>23.4%</td>
<td>0.0%</td>
<td>0.0%</td>
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<tr>
<td></td>
<td>dichloromethane</td>
<td>5.3%</td>
<td>10.1%</td>
<td>3.4%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>8.1%</td>
<td>11.4%</td>
<td>3.1%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>XAD 4</td>
<td>acetone</td>
<td>45.3%</td>
<td>32.3%</td>
<td>35.2%</td>
<td>8.2%</td>
<td>0.0%</td>
<td>11.0%</td>
</tr>
<tr>
<td></td>
<td>hexane</td>
<td>16.7%</td>
<td>16.3%</td>
<td>21.8%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>methanol</td>
<td>62.5%</td>
<td>7.2%</td>
<td>2.2%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>dichloromethane</td>
<td>48.3%</td>
<td>34.5%</td>
<td>34.5%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>38.9%</td>
<td>26.8%</td>
<td>22.6%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

Table 7. Percent recovery comparisons of XAD16 with different desorbing solvents. (a) dimethylphthalate, (b) diethylphthalate, (c) di-n-butylphthalate, (d) butylbenzylphthalate, (e) di-(2-ethylhexyl)phthalate, and (f) di-n-octylphthalate.

<table>
<thead>
<tr>
<th>Desorbing Solvent</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane:Hexane(1:1)</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>92.7%</td>
<td>95.8%</td>
<td>81.3%</td>
<td>57.8%</td>
<td>70.5%</td>
<td>50.5%</td>
</tr>
<tr>
<td>Hexane</td>
<td>52.7%</td>
<td>74.8%</td>
<td>74.5%</td>
<td>42.8%</td>
<td>114.7%</td>
<td>97.1%</td>
</tr>
</tbody>
</table>
Exposures were initially performed where the exposure solution was kept constant but the exposure time was varied. A plot of time vs. amount of analyte collected for di-n-butyl phthlate as shown in Figure 8. During this experiment, it was questioned whether the amount of analyte that was removed daily from the solution had a significant effect on the results. Studies were performed and the results are in Table 8. For di-n-butylphthalate, which had the largest change, 3.81% of the phthalates present in the solution were removed daily. As a result, the samplers were transferred to new exposure solutions daily for any sample exposures greater than one day to account for any effects the amount of analyte lost during the sample period may have on the amount of analyte collected.

Table 8. Percent of analyte removed each day.

<table>
<thead>
<tr>
<th></th>
<th>Percent of Analyte Removed Daily</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylphthalate</td>
<td>3.82</td>
</tr>
<tr>
<td>Diethylphthalate</td>
<td>1.88</td>
</tr>
<tr>
<td>Di-n-butylphthalate</td>
<td>3.81</td>
</tr>
<tr>
<td>Butylbenzylphthalate</td>
<td>0.92</td>
</tr>
<tr>
<td>di-(2-Ethylhexyl)phthalate</td>
<td>0.7</td>
</tr>
<tr>
<td>Di-n-octylphthalate</td>
<td>0.33</td>
</tr>
</tbody>
</table>
Figure 8. Example time-dependence plot of di-n-butylphthalate. The conditions were 7.5 L sample, temperature kept constant at 20 °C, sample concentration kept constant at 275 ppb.
It can be seen that the permeation sampler has a linear response with respect to time. Next, studies were done in which the exposure time was kept constant, but the exposure concentration was varied. A plot of concentration vs. amount collected for butylbenzylphthalate can be seen in Figure 9. Again, a linear response is observed. Since the sampler had linear responses for both time and concentration, the six permeation samplers were exposed to varying solution concentrations and times to create time-weighted average (TWA) plots. Samplers were exposed to solution concentrations ranging from 1 μg/L to 500 μg/L. The exposure times ranged from 4 hours to 7 days. The permeation constants, K, can be calculated by using the slope of the calibration curve. It is determined from the plots that the permeation constant, K, ranges from 2.62 μg/L·ppm for dimethylphthalate to 8.41 μg/L·ppm for di-(2-ethylhexyl)phthalate, with all six of the r² values being over 0.98. The permeation constants for the 6 phthalates studied are reported in Table 9. The limit of quantification for a 24 hour exposure period ranged from 0.62 μg/L for butylbenzylphthalate to 2.16 μg/L for di-n-butylphthalate. All of the quantification limits were under the US EPA’s limit of 8 μg/L for di-(2-ethylhexyl)phthalate, as can be seen from Table 9. The calibration curves that were created for each of the six phthalates for the determination of the permeation constant, K, can be seen in Figure 10.
Table 9. List of permeation constants, $K$, (in $\mu g/L\cdot ppm$) of the phthalates. Also included are correlation coefficients, relative standard deviations, quantification limits (in $\mu g/L$), range of concentrations studied (in $\mu g/L$) where the number of samples (n) is 90.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K$</th>
<th>$r^2$</th>
<th>Concentration range</th>
<th>%RSD</th>
<th>LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylphthalate</td>
<td>2.62</td>
<td>0.993</td>
<td>5-500</td>
<td>5.94</td>
<td>1.73</td>
</tr>
<tr>
<td>Diethylphthalate</td>
<td>6.03</td>
<td>0.987</td>
<td>5-500</td>
<td>5.93</td>
<td>1.02</td>
</tr>
<tr>
<td>Di-n-butylphthalate</td>
<td>7.05</td>
<td>0.981</td>
<td>1-500</td>
<td>6.06</td>
<td>2.16</td>
</tr>
<tr>
<td>Butylbenzylphthalate</td>
<td>4.12</td>
<td>0.993</td>
<td>1-500</td>
<td>5.8</td>
<td>0.62</td>
</tr>
<tr>
<td>Di-(2ethylhexyl)phthalate</td>
<td>8.41</td>
<td>0.984</td>
<td>1-500</td>
<td>11.16</td>
<td>0.98</td>
</tr>
<tr>
<td>Di-n-octylphthalate</td>
<td>3.53</td>
<td>0.984</td>
<td>5-500</td>
<td>7.79</td>
<td>1.76</td>
</tr>
</tbody>
</table>
Figure 9. Example plot of butylbenzylphthalate dependence on solution concentration. 7.5 L sample solution, temperature kept constant at 20°C, exposure time kept constant at 24 hours.
Figure 10. Time-Weighted Average Plots for (a) dimethylphthalate, (b) diethylphthalate, (c) di-n-butylphthalate, (d) butylbenzylphthalate, (e) di-(2-ethylhexyl)phthalate, (f) di-n-octylphthalate.
Temperature Effects

The effects of changes in temperature of the sample solution on the permeation constant were evaluated. Exposures were run in which the temperature of the solution was varied from 1 °C to 30 °C in 5 °C intervals. The permeation constant, K, was determined for each phthalate at each temperature studied. A plot of amount of analyte collected versus temperature was created for each phthalate, as shown in Figure 11. It can be seen that as the temperature increases, so does the amount of analyte collected and the permeation constant. This is because as the solution temperature is increased, the rate of diffusion through the membrane also increases. In Table 10 it can be seen that the percent change in permeation constant with respect to a one degree C change in temperature for each phthalate are all lower than five percent. Therefore, samplers can be exposed to solution temperatures other than the calibration temperature. Since in authentic samples, the temperature may vary, the permeation constant can be adjusted to take into account average exposure temperature. In streams, water temperature can vary by up to 4°C in winter and 11°C in summer. Although, unusual variations can occur in the water quality and the variations in temperature can almost disappear (89). One way to account for temperature changes during the sampling period, is to use a minimum-maximum thermometer which gives the minimum and maximum temperatures over a period of time. These temperatures can then be averaged to give the average sampling temperature.
Figure 11. Plots of temperature vs. μg of phthalate collected for (a) dimethylphthalate, (b) diethylphthalate, (c) di-n-butylphthalate, (d) butylbenzylphthalate, (e) di-(2-ethylhexyl)phthalate, (f) di-n-octylphthalate.
Table 10. Percent change in permeation constant (K) versus temperature change.

<table>
<thead>
<tr>
<th>Compound</th>
<th>%ΔK/Δ°C</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylphthalate</td>
<td>4.27</td>
<td>0.993</td>
</tr>
<tr>
<td>Diethylphthalate</td>
<td>3.95</td>
<td>0.982</td>
</tr>
<tr>
<td>Di-n-butylphthalate</td>
<td>2.87</td>
<td>0.96</td>
</tr>
<tr>
<td>Butylbenzylphthalate</td>
<td>4.11</td>
<td>0.992</td>
</tr>
<tr>
<td>di-(2-Ethylhexyl)phthalate</td>
<td>2.15</td>
<td>0.977</td>
</tr>
<tr>
<td>Di-n-octylphthalate</td>
<td>3.68</td>
<td>0.987</td>
</tr>
</tbody>
</table>

Potential Interfering Substances

Other substances that may be in water samples and could possibly affect the permeation of phthalates in the polymeric membrane were investigated, to see if their presence had any effect on the results. The substances that were studied included those that commonly show up in water samples. These interfering substances included sodium lauryl sulfate, sodium nitrate, sodium sulfate, pH, humic acid, sodium phosphate and sodium chloride.

Nitrate and sulfate have similar sources to account for their presence in water. Once source of both interferents is acid rain, which is the product of pollution in the undergoing reactions with water and radicals present in the atmosphere (90). Other sources for these compounds include urban and agricultural runoff. Phosphates can also be found in these two runoff sources as well as in manure and plant residues which can leech into water sources (91).
The pH of water sources is affected by many influences. One cause of water pH changes is acidification by acid rain. Sources of soil acidification include the formation of organic acids in soil, the nitrification of ammonium ions in soil and the anaerobic fermentations of organic compounds, in which the acidic compounds can enter the water source and increase the pH. The presence of leachate from landfills can also alter the pH, either raising or lowering the pH depending on what substances are contained in the leachate (92).

Carbon containing substances that are natural organic matter are present in almost all water bodies. One of these substances, humic acid, can be commonly found. This is because it is formed by the decomposition of leaves and other plant matter (93).

Sodium lauryl sulfate is an anionic surfactant. The compound can be found in many common items, such as: detergents, toothpastes, shaving cream and shampoos. These anionic surfactants can enter into groundwater by way of leachates and wastewaters (92).

Another interference that was investigated was the presence of a compound with high ionic strength. This was to see if the ionic strength of a solution had any effect on the rate of permeation of the phthalates through the membrane. In this case, the high ionic strength compound utilized was sodium chloride. Sodium lauryl sulfate and humic acid were studied in the range of 0 to 0.004 ppm. The resulting graphs of percent deviation of phthalate collected due to differing amounts of interferent added can be seen in Figures 12 and 13. Sodium chloride, sodium nitrate, sodium sulfate and sodium phosphate were investigated from the range of 0 to 0.01 M.
The plots of the percent variation of analyte collected can be seen in Figures 14-17. The pH range studied was from 4 to 10. The percent variation plot due to pH changes can be seen in Figure 18. The sampling devices were exposed to the following concentrations of phthalates for 4 hours, 267 ppm of dimethylphthalate, 284 ppm of diethylphthalate, 267 ppm of di-n-butylphthalate, 274 ppm of butylbenzylphthalate, 265 ppm of di-(2-ethylhexyl)phthalate, 297 ppm of di-n-octylphthalate. The amount of analyte collected was compared for those samples with and without interferences present to see what if any differences there were in the results. It can be seen from Figures 12-18 that the percent variation due to the presence of the six interferents was below 20% for all six phthalates.
Figure 12. Percent Variation due to presence of sodium lauryl sulfate.
Figure 13. Percent Variation due to presence of humic acid.
Figure 14. Percent Variation due to presence of sodium sulfate.
Figure 15. Percent Variation due to presence of sodium phosphate.
Figure 16. Percent Variation due to presence of sodium nitrate.
Figure 17. Percent Variation due to presence of sodium chloride.
Stirring Effect Studies

The effects of changes in the stirring rate of the exposure solution were evaluated to see if a change in the rate had an effect on the results. Samplers were exposed to stirring rates of 0 rpm, 250 rpm, 850 rpm, 1000 rpm, as well as the stirring rate used for all the previous studies, 550 rpm. As a result, the samplers were exposed to the same conditions as the interferent studies, but at stirring rates of 0, half, 3/2, and twice the stirring rate used in other studies. The amount of analyte collected during the exposures was compared for each stirring rate, with the results shown in Figure 19. It was found that a static solution, 0 rpm, resulted in a negative percent variation greater than 20 for the three lighter phthalates dimethylphthalate (-26%), diethylphthalate(-25%), and di-n-butylphthalate(-22%). On the other hand for the three heavier phthalates the variation from average due to no stirring of the solution were all within five percent of the average. For each of the other stirring rates, the percent variations were all within 20% of the average. This shows that a change in the stirring rate does not have a significant effect on the results. The plots show that as the molecular weight increases, the percentage variation from average is smaller for the static solution. This shows that that a static solution has the greatest effect on the results of the lowest molecular weight compound.
Figure 18. Percent Variation due to pH changes
Figure 19. Percent variation due to different stirring speeds (a) dimethylphthalate, (b) diethylphthalate, (c) di-n-butylphthalate, (d) butylbenzylphthalate, (e) di-(2-ethylhexyl)phthalate, (f) di-n-octylphthalate.
Sample Stability

One important factor when developing a sampling method is how long the sample can be stored until it is analyzed. Some methods require that the sample be immediately sampled. Other methods, such as grab sampling, require that the sample be refrigerated until analysis, so that no analyte is lost during storage.

Experiments were performed to determine how long the adsorbent could be stored until analysis with no significant loss in amount of phthalate detected. Samplers were exposed to a solution with the same concentration and for the same exposure time. The first samples were sampled immediately after the exposure. The other samples were either stored in a fume hood at 23°C or in a refrigerator at 4°C. Samples were then analyzed weekly for a month.

The results of the study can be seen in Table 11. It was found that the samples could be stored for up to a month with no significant change in the results. It was also noted that the samples did not need to be stored in the refrigerated for this period, since there was not a significant difference in the amount recovered. This advantageous because samples do not have to be run right after an exposure period, and that they can be stored until it is convenient to do the analysis. Also, not having to use a refrigerator for storage is good since you don’t have to worry about keeping the sample cool as soon as it is taken and that no refrigerator is needed.
Table 11. Percent recoveries after storage times.

<table>
<thead>
<tr>
<th>Weeks</th>
<th>Percent Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4° C</td>
</tr>
<tr>
<td>0</td>
<td>100.0</td>
</tr>
<tr>
<td>1</td>
<td>104.3</td>
</tr>
<tr>
<td>2</td>
<td>90.1</td>
</tr>
<tr>
<td>3</td>
<td>100.8</td>
</tr>
<tr>
<td>4</td>
<td>109.1</td>
</tr>
</tbody>
</table>

Wastewater samples (spiked authentic samples)

From the previous studies, it could be seen that the six potential interferents studied did not have a significant effect on the results, and that any differences in temperature could be accounted for. As a result, a wastewater influent sample was obtained from the Department of Environmental Services of Summit County, Fishcreek Wastewater Treatment Plant in Stow, Ohio to prove that this method can be applied to authentic samples. This authentic sample was spiked with a methanol phthalate standard to obtain exposure solution concentrations ranging from 0- 500 µg/L. Chromatograms of a spiked ultrapure water exposure and a spiked wastewater exposure can be seen in Figure 20. A linear relationship was obtained for the time-weighted average plots of each phthalate. Table 12 shows the correlation coefficients for each time-weighted plot. Also, studies were performed to determine the percent recovery of spiked authentic samples as compared to spiked ultrapure water samples which can also be seen in Table 12. This study proved that the method can be used on authentic samples with no considerable effects on the amount of each phthalate collected. Determination of Optimal
Determination of Optimal Desorbing Temperature

The next phase of the project was to investigate using the technique of solventless desorption to remove the phthalates from the adsorbent. This was accomplished by using heat from a thermal desorption unit, instead of a desorbing solvent. For this part of the experiment, Tenax TA was utilized as the adsorbent rather than Amberlite® XAD16. This is because the maximum temperature limit of Tenax TA is 350 °C, while the temperature limit of Amberlite® XAD 16 is 150 °C. The structure of Tenax TA can be seen in Figure 21. In order to determine what temperature was needed to desorb the most phthalates from the Tenax TA, four temperatures were studied: 250°C, 275°C, 300°C, and 325°C. Table 13 shows a comparison of the efficiency of each temperature. It can be seen from the table that 300°C was the best for desorbing all the phthalates except di-n-butylphthalate. For di-n-butylphthalate, 275 °C, proved to be slightly better than 300°C for desorption. As a result, 300°C was chosen as the desorbing temperature because it gave the best overall response.

Table 12. Correlation coefficients and percent recovery of each phthalate in authentic sample.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r^2$</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylphthalate</td>
<td>0.986</td>
<td>102</td>
</tr>
<tr>
<td>Diethylphthalate</td>
<td>0.968</td>
<td>116</td>
</tr>
<tr>
<td>Di-n-butylphthalate</td>
<td>0.968</td>
<td>90</td>
</tr>
<tr>
<td>Butylbenzylphthalate</td>
<td>0.990</td>
<td>105</td>
</tr>
<tr>
<td>Di-(2-ethylhexyl)phthalate</td>
<td>0.991</td>
<td>107</td>
</tr>
<tr>
<td>Di-n-octylphthalate</td>
<td>0.959</td>
<td>95</td>
</tr>
</tbody>
</table>
Figure 20. Chromatograms of (a) a spiked ultrapure water exposure and (b) a spiked wastewater exposure. The peaks are, 1, dimethylphthalate, 2, diethylphthalate, 3, di-n-butylphthalate, 4, butylbenzylphthalate, 5, di-(2-ethylhexyl)phthalate, and 6, di-n-octylphthalate.

Table 13. Comparison of desorption temperature efficiencies.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Desorption Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250 C</td>
</tr>
<tr>
<td>dimethylphthalate</td>
<td>41.4%</td>
</tr>
<tr>
<td>diethylphthalate</td>
<td>25.0%</td>
</tr>
<tr>
<td>di-n-butylphthalate</td>
<td>1.4%</td>
</tr>
<tr>
<td>butylbenzylphthalate</td>
<td>41.7%</td>
</tr>
<tr>
<td>di-(2-Ethylhexyl)phthalate</td>
<td>93.0%</td>
</tr>
<tr>
<td>di-n-octylphthalate</td>
<td>5.4%</td>
</tr>
</tbody>
</table>
Solventless Desorption Time-Weighted Average Curves

Samplers were exposed to varying solution concentrations and exposure times. Exposure times ranged from 2 to 24 hours. The concentrations ranged from 15 to 150 ppb. The resulting time-weighted average plots can be seen in Figure 22. Figure 22 shows that there was a linear correlation between the amount of analyte collected and the product of exposure time and concentration. Sample chromatograms for the solventless desorption method can be seen in Figure 23. The corresponding permeation constants can be seen in Table 14. The permeation constants for the solventless method were all smaller than those for the solvent method, except for di-n-butylphthalate. This may be because shorter sampling periods and lower concentrations were examined as compared to the solvent method.
Figure 21. Structure of Tenax TA adsorbent
Table 14. Permeation constants, $K$ (in $\mu$g/L·ppm), and correlation coefficients of the solventless desorption time-weighted average curves.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$K$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylphthalate</td>
<td>0.6755</td>
<td>0.974</td>
</tr>
<tr>
<td>diethylphthalate</td>
<td>1.1781</td>
<td>0.976</td>
</tr>
<tr>
<td>di-n-butylphthalate</td>
<td>10.675</td>
<td>0.976</td>
</tr>
<tr>
<td>butylbenzylphthalate</td>
<td>1.5528</td>
<td>0.988</td>
</tr>
<tr>
<td>di-(2-Ethylhexyl)phthalate</td>
<td>1.0877</td>
<td>0.974</td>
</tr>
<tr>
<td>di-n-octylphthalate</td>
<td>0.2957</td>
<td>0.976</td>
</tr>
</tbody>
</table>

Detection limits for solventless desorption method

The thermal desorption method was expected to have lower detection limits than those for the liquid-extraction method. This is because the analytes collected in the liquid method are diluted to 1 ml with solvent, while in the solventless method there is no dilution of the collected analytes. In order to detect even smaller amounts of analyte, a SIM detection method was utilized rather than the scanning method that used to create the TWA curves. The mass spectra that were used to obtain the characteristic masses used in SIM mode can be seen in Figures 24 and 25. The resulting limits of detection for this method can be seen in Table 15. As expected the limits of detection for all six phthalates were lower for the solventless method as compared to the solvent method.
Figure 22. Time weighted average curves for thermal desorption method (a) dimethylphthalate, (b) diethylphthalate, (c) di-n-butylphthalate, (d) butylbenzylphthalate, (e) di-(2-ethylhexyl)phthalate, (f) di-n-octylphthalate.
Figure 23. Sample solventless desorption chromatograms, (a) using scan method and (b) using SIM method. The peaks are, 1, dimethylphthalate, 2, diethylphthalate, 3, di-n-butylphthalate, 4, butylbenzylphthalate, 5, di-(2-ethylhexyl)phthalate, 6, di-n-octylphthalate.
Table 15. Limits of detection (LOD) for the SIM-solventless desorption method, in µg/L.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylphthalate</td>
<td>0.394</td>
</tr>
<tr>
<td>diethylphthalate</td>
<td>0.127</td>
</tr>
<tr>
<td>di-n-butylphthalate</td>
<td>0.091</td>
</tr>
<tr>
<td>butylbenzylphthalate</td>
<td>0.042</td>
</tr>
<tr>
<td>di-(2-ethylhexyl)phthalate</td>
<td>0.04</td>
</tr>
<tr>
<td>di-n-octylphthalate</td>
<td>0.202</td>
</tr>
</tbody>
</table>

Lag Time Determination

The lag time is the amount of time it takes for a compound to reach a steady-state permeation rate through a membrane. This is an important factor to take into consideration because the exposure times should be significantly longer than the lag times in order to get usable data. The sensitivity of the thermal desorption method made it possible to detect the small changes in rate. An example plot used to determine the lag time of dimethylphthalate can be seen in Figure 26. The complete list of lag times determined for each of the six phthalates can be seen in Table 16.
Figure 24. Mass Spectra of (a) dimethylphthalate, (b) diethylphthalate, and (c) di-n-butylphthalate.
Figure 25. Mass Spectra of (a) butylbenzylphthalate, (b) di-(2-ethylhexyl)phthalate, and (c) di-n-octylphthalate.
Table 16. Lag times for the phthalates studied.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lag Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethylphthalate</td>
<td>11.19</td>
</tr>
<tr>
<td>diethylphthalate</td>
<td>8.75</td>
</tr>
<tr>
<td>di-n-butylphthalate</td>
<td>13.35</td>
</tr>
<tr>
<td>butylbenzylphthalate</td>
<td>18.63</td>
</tr>
<tr>
<td>di-(2-Ethylhexyl)phthalate</td>
<td>15.1</td>
</tr>
<tr>
<td>di-n-octylphthalate</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Figure 26. Example lag time plot for dimethylphthalate.
A new method for detecting the six priority pollutant phthalate esters in aqueous solutions has been developed. The method involves the use of a permeation sampler, with a polymeric semi-permeable membrane that allows for the extraction of the phthalates from the water sample. An adsorbent was used to collect the phthalates that permeated through the membrane. The collected analytes were desorbed from the adsorbent using 1 ml of a mixture of dichloromethane: hexane (50:50 v/v).

From the collected data, TWA plots were created that allowed for the determination of the permeation constant, K, for each individual phthalate. These constants were able to be determined because all six TWA plots showed a linear correlation between the product of the exposure time and concentration and the amount of analyte collected. The resulting permeation constants ranged from 2.62 µg/L·ppm for dimethylphthalate to 8.41 µg/L·ppm for di-(2-ethylhexyl)phthalate. The resulting limits of detection for the method ranged from 0.62 µg/L for butylbenzylphthalate to 2.16 µg/L for di-n-butylphthalate. All of the limits of detection were below the 6 µg/L maximum contaminant level for di-(2-ethylhexyl)phthalate set by the US EPA.

Experiments were performed to see what effect the temperature of the water sample had on the permeation rate. Samplers were exposed to temperatures ranging from
1 °C to 30 °C in 5 °C intervals. At each temperature the permeation constant for each phthalate was determined. The slope of a plot of \( \Delta K/\Delta ^\circ C \), allowed for the determination of the permeation constants for each phthalate at temperatures other than that of the calibration temperature. Therefore, temperature changes could be accounted for. It was also seen that the percent change in permeation constant vs. change in temperature was less than 5% for all six phthalates.

Studies were then performed to see if any interferents that could possibly be present in water had any effect on the permeation of the phthalates through the membrane. The possible interferents studied included: sodium lauryl sulfate, sodium nitrate, sodium sulfate, pH, humic acid, sodium phosphate and sodium chloride. The results obtained as the consequence of the presence of different amounts of each interferent were compared to the results from a solution containing no interferents. The percent variations for all six phthalates for all seven interferents were below 20%. This proved that the presence of other compounds did not have a significant effect on the results.

It was also shown that this method was applicable to real world samples, and the exposed adsorbents were stable for a relatively long storage time. The results of the ultrapure spiked samples and the wastewater spiked samples showed no significant differences. Also, studies showed that after the exposure period, the exposed adsorbent could be stored up to 4 weeks in a fume hood at 23°C or in a refrigerator at 4°C, with no significant loss of phthalates.
The use of thermal desorption was evaluated for the extraction of the phthalates from the adsorbent instead of solvent desorption. The resulting linear TWA plots for the six phthalates had permeation constants that ranged from 0.2957 µg/L·ppm for di-n-octylphthalate to 10.675 µg/L·ppm for di-n-butylphthalate. The resulting limits of detection were also lower than those obtained for the solvent extraction method. The limits of detection ranged from 0.04 µg/L for di-(2-ethylhexyl)phthalate to 0.394 µg/L for dimethylphthalate. The thermal desorption method also allowed for the determination of the lag times for each phthalate. From the lag times, it was possible to determine how long an exposure period must be in order to make the lag time have insignificant effects on the data.

The permeation sampling method created has several advantages. One is that time-weighted average concentrations were determined because the concentration over a period of time is determined. This is compared to grab sampling in which only the concentration at the instant the sample is taken is determined. Another advantage of TWA sampling is that variable concentrations over time can be sampled, and can be used to determine an average concentration. The solventless method also had its advantages, with one being lower limits of detection. This is because the analyte collected onto the adsorbent was not being diluted, but instead all of the analyte collected was desorbed and sent into the gas chromatograph column. Also, since no solvent was used, this created a more environmentally friendly method, since no harmful solvents needed to be used for extraction. Finally, the sensitivity of the method for all six phthalates was under the MCL of 6 µg/L for di-(2-ethylhexyl)phthalate set by the US EPA. Overall, the
permeation sampling method (94-95) has LOQ’s comparable to other phthalate sampling methods in water, but in comparison uses a minimal amount of solvent, determines time-weighted average concentrations and is cost-effective.
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