MONITORING PHTHALATES AND CHLORINATED VOLATILE ORGANIC COMPOUNDS IN GROUNDWATER AND TAP WATER

by
Irmarie Cotto Ramos

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Approved by:

_____	_____
Ingrid Y. Padilla, Ph.D. President, Graduate Committee	Date
_____	_____
Pedro J. Tarafa, Ph.D. Member, Graduate Committee	Date
_____	_____
Félix R. Román, Ph.D. Member, Graduate Committee	Date
_____	_____
Ismael Pagán-Trinidad, MSCE Chairperson of the Department	Date
_____	_____
Pedro Vásquez, Ph.D. Representative of Graduate Studies	Date

ABSTRACT

Pollutants such as phthalates and chlorinated volatile organic compounds (CVOCs), which threaten the public health and the environment, have to be monitored and analyzed to minimize their exposure. Phthalates and CVOCs are of concern because they are frequently detected in water, with CVOCs being among the most frequently detected groundwater contaminants in United States. These contaminants are associated with several adverse health effects. The goal of this research is to develop efficient, practical, and more environmentally friendly methods to monitor the presence and concentrations of phthalates and CVOCs in groundwater and tap water. Strong emphasis is given to the development of reliable methods for chemical analysis in water. The developed methods are applied on samples collected from the karst region of northern Puerto Rico to assess general contamination distribution in source and point of use waters. The samples are extracted using modified EPA liquid-liquid extraction methods and analyzed with Gas Chromatography (GC) techniques. Because a wide variability in recoveries is observed in several phthalates studies, an extraction efficiency study is performed. Statistical analysis, including graphical techniques, regression, distribution, covariance analysis, are applied to assess method performance and partitioning characteristics of phthalates between water and dichloromethane (DCM). Efficiencies studies demonstrate the modified extraction methods for phthalates are quantifiable and reproducible, but not highly efficient. Efficiency is concentration-dependent, but not highly dependent on sample and solvent volume. This research shows that DEHP is distributed between water and DCM after water extractions and described by an overall partitioning coefficient of K_{sw} = 1.58. Like efficiencies, K_{sw} show to be concentration-dependent. Low K_{sw} and efficiencies are attributed to cosolvent effects of DCM on phthalates solubility. The data analysis shows the presence of phthalates and CVOCs in

groundwater and tap water for the studied area. Detected contaminants include chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, di-n-butyl phthalate, di-ethyl phthalate, and di(2-ethyl hexyl) phthalate.

RESUMEN

Contaminantes como ftalatos y compuestos orgánicos volátiles clorinados (CVOCs por sus siglas en inglés) amenazan la salud humana y el ambiente. Por esta razón, éstos contaminantes tienen que ser observados y analizados con el propósito de minimizar la exposición humana y ambiental. Los ftalatos y CVOCs son contaminantes de gran preocupación debido a que son frecuentemente detectados en agua, estando los CVOCs entre los contaminantes más detectados en agua subterránea en los Estados Unidos. Estos contaminantes están asociados a algunos efectos adversos para la salud. El objetivo de este estudio es desarrollar métodos eficientes, prácticos y ambientalmente amigables para monitorear la presencia y concentraciones de los ftalatos y los CVOCs en agua subterránea y agua potable. Los métodos desarrollados son aplicados en las muestras colectadas de la costa norte de Puerto Rico para evaluar la distribución de la contaminación en las fuentes de agua. Las muestras son extraídas usando métodos de extracción líquido-líquido (métodos modificados de la EPA) y son luego analizadas con técnicas de cromatografía de gas. Ya que en los estudios que se han reportado para los ftalatos se observa una gran variabilidad en los resultados, un estudio de eficiencia es realizado en esta investigación. Análisis estadísticos como gráficas, regresión, análisis de distribución y análisis de covarianza son aplicados para evaluar el desempeño del método y las características de partición de los ftalatos entre agua y diclorometano (DCM). Los estudios de eficiencia demuestran que los métodos de extracción modificados para los ftalatos son cuantificables y reproducibles, pero no eficientes. La eficiencia es altamente dependiente de la concentración, pero no del volumen de las muestras y el solvente. Esta investigación concluye que DEHP es distribuido entre agua y DCM después de la extracción, lo cual es descrito por un coeficiente de partición global de K_{sw} = 1.58. Como las deficiencias, K_{sw} muestra ser dependiente

de la concentración. El bajo K_{sw} y las bajas eficiencias son atribuidos a un efecto de cosolvencia de DCM en la solubilidad de los ftalatos. En el análisis de las muestras de campo se detectó la presencia de ftalatos y CVOCs en el agua subterránea y agua potable del área estudiada. Los contaminantes detectados son: cloroformo, tetracloruro de carbono, tricloroetileno, tetracloroetileno, ftalato de di-n-butil, ftalato de di-etil, y ftalato de di(2-etil hexil).

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1. INTRODUCTION

Any pollutant that threatens the public health and the environment has to be monitored and analyzed to minimize their exposure to humans and ecosystems. This is the case for phthalates and chlorinated volatile organic compounds (CVOCs), as they are commonly found in the environment and have been associated with adverse health effects.

Phthalates are used as plasticizers, which are chemicals that impart flexibility and durability to plastics (Stanely et al., 2003). Approximately 1.5 million tons of Di-(2-ethylhexyl) phthalate (DEHP), which is one of the most used phthalates, are produced annually (Tienpont, 2004). As consequence of it widespread use, phthalates have been found in surface water, groundwater, drinking water, soil, wastewater, food, vegetation and wildlife (Clark et al., 2011). Phthalates are contaminats of concern because they are fequenly detected in water (ATSDR, 2002) and have a very low degradation rates (Cousins et al., 2003). Some studies in laboratory animals show that phthalates exposure can cause serious health effects. They have been associated with endocrine disruptions, adverse reproductive health (Barlow et al., 2007; Meeker et al., 2009; Meeker e al., 2012), development abnormalities and skeletal malformations and increased fetal death (USEPA, 2007c).

CVOCs are low weight hydrocarbons that contain chloride, and have relatively low boiling points and high vapor pressures (Patnaik, 2010). Many CVOCs are used as solvents in industrial applications. Tetrachloroethene (PCE) and trichloroethene (TCE) are among the most commonly used chlorinated solvents and are, as a consequence, found in many contaminated sites (ATSDR, 2013). In addition to entering and contaminating the environment from anthropogenic sources, many CVOCs may also form as a by-products of degradation and other practices. For instance, TCE is a known source of contamination, but it also form as a

degradation of PCE. Trichloromethane, or chloroform, is a degradation by-product of carbon tetrachloride (CT), but can also form as a disinfection by-product.

CVOCs are suspected to be human carcinogens and can cause central nervous system depression (Zogorki et al,. 2006). Exposure to TCE, for instance, has been related to several adverse health effects including: cardiac, neurological, hepatic, renal, dermal, immunological, and reproductive effects, increased birth defects, perinatal mortality and cancer, and decreased birth weights (ATSDR, 2014; Forand et al., 2012; Sonnenfeld et al., 2001).

Phthalate and CVOCs contaminants have been identified as potential precursors of preterm birth complications (Forand et al., 2012; Meeker et al., 2009; Meeker et al., 2012; Sonnenfeld et al., 2001), and are being evaluated as one of the causes for the extremely high rates of preterm birth (PTB) rates in Puerto Rico (PRoTECT, 2013). The 2012 rate was at 17.7% (Hamilton et al., 2012), the highest rate compared to any jurisdiction in the U.S. (50% higher than the average U.S. rate of 11.7%), and below Malawi's (18.1%) (Blencowe et al., 2012). Known risk factors for prematurity (e.g., prenatal care, tobacco use, etc.) (Behrman and Butler, 2007) do not explain the high rates of preterm birth in Puerto Rico (Cordero, 2013), and contaminant exposure is being evaluated as a potential contributor to high PTBs (PRoTECT, 2013). Of particular interest is the potential exposure to CVOCs and phthalates that may be present in the water from the karst region in the northern Puerto Rico.

The karst aquifer region of northern Puerto Rico (Figure 1) has been affected by a long history of toxic spills into the subsurface (Hunter and Arbona, 1995; Padilla et al., 2011) and is coincidentally among the areas with the highest groundwater extraction in Puerto Rico (Molina-Rivera and Goméz-Goméz, 2008). Serious contamination has prompted inclusion of 12 National Priority List (NPL) and 15 corrective action sites within the Resource Conservation and

Recovery Act (RCRA) in the north coast region of Puerto Rico between 1983 and 2012. Recent (Padilla et al., 2011) and past (Guzmán-Ríos et al., 1986) studies in this region have reported the presence of organic contaminants in the karst groundwater system with particular concern in the contamination of phthalates and chlorinated organic compounds. Data indeed shows that phthalates and CVOCs have been detected in groundwater wells throughout the north coast of Puerto Rico (Padilla et al., 2011; USEPA, 2009; USGS, 2009; Yu et al., 2015).

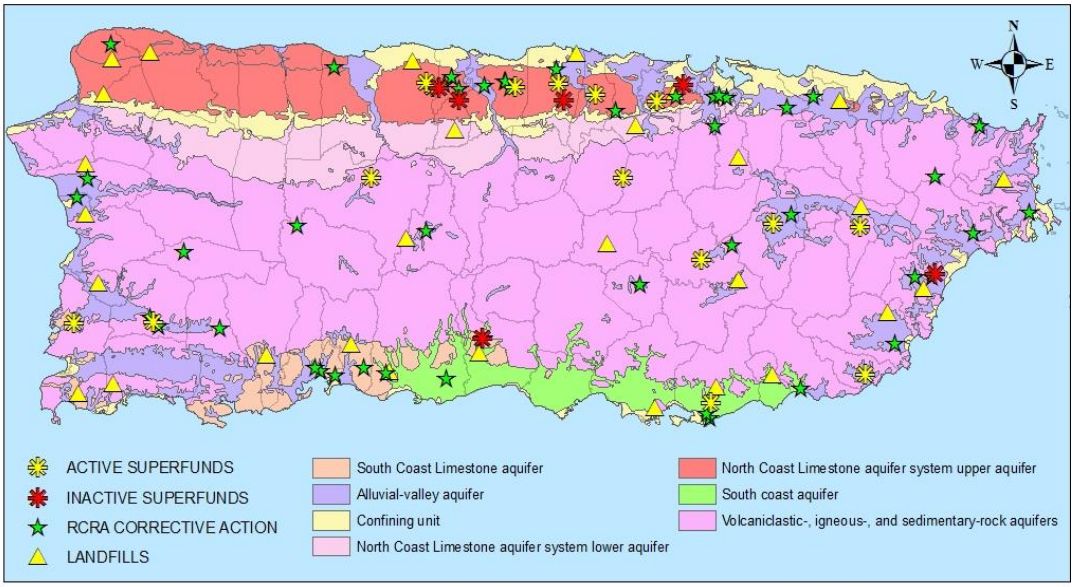


Figure 1 Hydrogeology and Major Potential Contamination Sites in Puerto Rico (Torres et al., 2013).

The ubiquitous presence of many phthalates and CVOCs contaminants in the environment, particularly water, and their potential for exposure and adverse health impacts require refined monitoring of these contaminants in water supply source (e.g.; groundwater, surface water) and point of use (e.g.; tap water). Monitoring both, source and point of use water serve to establish direct links between environmental contamination and potential exposure. This research focuses on the analysis of water samples to monitor the presence and concentrations of

phthalates and CVOCs and assess their distribution in groundwater and tap water within the karst region of northern Puerto Rico.

Several methods have been developed by the Environmental Protection Agency (EPA) for the analysis of phthalates (USEPA, 1994; 1996a; 1996b; 1996c; 1996d; 2007b; 2014a) and CVOCs (Munch and Hautman, 1995; USEPA, 1996e; 1996f; 2003a; 2014b). Many of these methods require specialized equipments which, are intensive, and produce high volumes of hazardous waste. There is thus, a need to develop efficient, practical and more environmentally friendly technologies for analysis and spatial-temporal monitoring of phthalates and CVOCs in water.

1.1 OBJECTIVES

The general goal of this research is to develop efficient, practical, and more environmentally friendly methods to monitor the presence and concentrations of phthalates and CVOCs in groundwater sources and tap water. Strong emphasis is given to the development of reliable methods for chemical analysis in water. The developed methods are applied on samples collected from the karst region of northern Puerto Rico to assess general contamination distribution in source and point of use waters.

Specifically, this work

- Develop and test EPA modified methods to analyze phthalates and CVOCs of interest in water samples. Phthalates of interest include bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP) and diethyl phthalate (DEP). Those for CVOCs include carbon tetrachloride (CT); 1,1-dichloroethane (1,1-DCA); 1,2-dichloroethane (1,2 DCA); 1,1-dichloroethene (1,1-DCE); 1,2-dichloroethene (1,2-DCE); 1,1,1-trichloroethane (1,1,1-TCA); 1,1,2-trichloroethane (1,1,2-TCA); trichloroethene (TCE); tetrachloroethene (PCE); and chloroform (TCM).
- Assess distribution of phthalates and CVOCs in groundwater and tap water of the northern karst region of Puerto Rico.

2. LITERATURE REVIEW

This research focuses on the development of efficient and practical methods to monitor the presence and concentrations of phthalates and CVOCs in groundwater and tap water. The developed methods are applied on samples collected from the karst region of northern Puerto Rico. This chapter addresses the state of known ledge regarding the phthalates and CVOCs contaminants of concern, their chemical properties, environmental distribution, health impacts, standard methods of analysis and presence in karst water systems. The chapter also addresses some fundamental concepts on karst water systems and their potential to serve as route for contaminant exposure.

2.1 CONTAMINANTS OF CONCERN

Environmental pollutants that are carried out or transported by any water system are of concern because, if exposure exists, they can pose threats to public health and the environment. Of particular concern are phthalates and CVOCs because of their common presence in the environment, high risk of exposure, and adverse health impacts. Several physico-chemical properties play important roles controlling the fate, transport, and potential exposure of these contaminants in water. These include: water solubility, vapor pressure, and distribution properties between environmental phases. Water solubility reflects the compound's ability to dissolve and be moved in water. Solubility also reflects the compound's hydrophobicity and lipophilicity, as compounds with lower solubility tend to be more hydrophobic and lipophilic (such as organic phases). The vapor pressure reflects the ability of the compound to volatilize into and be held by the vapor phase.

In the presence of multiple environmental phases, contaminants are distributed among the phases present according to their phase distribution properties, often described by a distribution constant or partitioning coefficient (Berthod and Carda-Broch, 2004). Distribution constant or partitioning coefficients (K_D) are defined as the ratio of the concentration of a substance A, in one phase (I) over another phase (II) at equilibrium (equation 1):

$$K_D = \frac{[A]_I}{[A]_{II}} \quad (1)$$

Commonly used distribution constants in environmental studies include the air-water partitioning coefficient (often given by Henry's constant) and the octanol-water distribution constant (K_{ow}), which gives a measure of the distribution of a compound in an octanol-water liquid-liquid system. Liquid-liquid partitioning and solvent extraction processes are very important in environmental systems, as well as in the quantification of chemicals equilibrium concentrations in environmental compartments. The octanol-water distribution coefficient (K_{ow}), which is defined by the concentration of solute A in octanol over that in water, also reflects the hydrophobicity of that substance, as more hydrophobic compounds tend to get distributed more into the organic octanol phase than the water phase. It is often seen that contaminants with lower water solubility tend to have greater K_{ow}, and vice-versa (Schwarzenbach et al., 2003). Contaminants with high K_{ow} are considered lipophilic, which mean they like to partition into hydrophobic organic matter, tissues, and organisms. The octanol-water partition coefficient (K_{ow}) of phthalates increases by orders of magnitude with increasing size (Cousins et al., 2003). Increased in hydrophobicity is reflected in higher sorption to surface particles, organic matter, soil and vegetation.

From an analytical point of view, knowledge of how co-solvents influence the solubility of a given organic compound in organic solvent-water mixture is essential. It is well-recognized that the nature of the solvent has a significant impact on the solubility of organic contaminants (Schwarzenbach et al., 2003). The majority of the systematic studies have focused on the effects of completely water-miscible organic solvents (CMOSs, e.g. methanol, ethanol, propanol, acetone and many more) and on the solubility of the sparingly soluble organic solvents (Schwarzenbach et al., 2003). Contrary, only very limited data are available on the effect of partially miscible organic solvents (PMOSs, e.g. n-alcohols n>3, ethers, halogenated C_1- and C_2 compounds, among others) on the aqueous solubility in the presence or the absence of a CMOS.

In general, the solubility of an organic solute increases in an exponential way with increasing volume fraction of CMOSs (Pinal et al, 1990), but a significant effect is observed only at cosolvent volume fraction greater than 1%. The magnitude of the cosolvent effect, as well as its dependence on the amount of cosolvent present, is a function of both, the type of cosolvent and the type of organic solute (Schwarzenbach et al., 2003).

Few published data are available for hydrophobic organic chemicals (HOC) solubility in mixed solvents containing PMOSs, or for HOC solubility in biphasic solvents (Pinal et al, 1990). If present at sufficiently high concentrations, PMOS can act as a cosolvent for a HOC, adding to the cosolvency produced by the CMOS (Pinal et al., 1990). It has been observed that the cosolvency of CMOSs increases with decreasing solvent polarity, whereas the opposite is true for PMOSs (Pinal et al., 1990). In ternary mixed solvents, nonpolar PMOSs did not appreciably increase HOC solubility while polar PMOSs enhance significantly HOC solubility. Polar PMOSs have greater cosolvent effect, not because they are stronger solvents, but because they are present

in greater concentrations as a result of their higher aqueous solubilities ($l0^4$ mg/L or 1% volume fraction).

2.1.1 PHTHALATES

Phthalates are a group of industrial chemicals commonly used as plasticizers, and as solvents in consumer products and pharmaceuticals (Stanely et al., 2003). High molecular weight phthalates are generally used as plasticizers, which when added to other polymeric substances imparts flexibility and durability to plastics (Godwin, 2010; Stanley et al., 2003). Di-(2-ethylhexyl)phthalate (DEHP) is among the most used plasticizer in the market (Stanely et al., 2003), and is commonly used in flooring tiles, hoses, paint lacquers, medical devices and materials, shoes, food and beverage packaging, and wiring cables (Godwin, 2010; Zia et al., 2013). The annual production of DEHP, which takes 50% of the total phthalic acid ester production, is estimated around 1.5 million tons (Tienpont, 2004). Low molecular weight phthalates have a diverse set of uses, but are commonly used as solvents in many consumer products and pharmaceuticals (Stanley et al., 2003) to help solubilize necessary ingredients or to aid in spending or applying the product (Godwin, 2010). Diethyl phthalate (DEP) and dibutyl phthalate (DBP) are common chemicals used in cosmetics creams, fragrances, candles and shampoos, among other uses (Godwin, 2010; Zia et al., 2010).

2.1.1.1 PHTHALATES PROPERTIES

Phthalates, or phthalate esters, are diesters of benzenedicarboxylic acid (Figure 2). The symbols R and R' are ester side chains that vary in length and structure. Long ester side chains (C8-C13) are considered high molecular weight, while those with short chains (<C4) are considered low molecular weight.

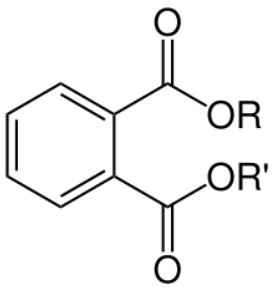


Figure 2 General Chemical Structure of Phthalates (Barlow et al., 2007)

Phthalates in pure form are usually clear liquids at room temperature, some with faint sweet odors and some with faint yellow color (USEPA, 2007c). Low molecular weight phthalates such as DEP have low viscosity, but phthalates become more viscous and oily as the size of the ester chain increases (Stanley et al., 2003). Water solubility of the alkyl phthalate varies inversely with the length of the side chain, ranging from 4000 mg/L for dimethyl phthalate to <0.001mg/L for high molecular weight phthalates, such as DEHP (Stanley et al., 2003). Phthalates are considered semi-volatile compounds that are represented by vapor pressures between 10^{-9} to 10 Pa (Weschlera and Nazaroffc, 2008). As solubility, vapor pressure of phthalates tends to decrease with increasing size of side-chain.

The wide range of phthalate chain-size give rise to a high range of physical-chemical properties values that vary over orders of magnitude (Cousins et al., 2003). Data for most commonly found phthalates such as DEP, DBP, and DEHP, (Refer to Table 1) show that water solubility and vapor pressure are high for phthalates with shorter chains and lower molecular weight. Values for K_{ow} are inversely related to chain size. Some physical-chemical properties published by Cousins et al., 2003 (water solubility, liquid vapor pressure and, octanol-water partition coefficient), may vary by several orders of magnitude. For example, reported aqueous solubility of DEHP at 25^{o}C varies between $1.9x10^{-3}$ and 0.4 mg/L, which is by a factor of 210,

and the $\log K_{ow}$ varies between 5.11 and 8.35 (over three orders of magnitude). Table 1 shows reported values and standard deviations (SD) of some phthalates properties. These variations occur due to variability of measurements methods, error, and challenges (e.g. measurements near detection limits, formation of emulsions, sorption to glassware).

Table 1 Physical-Chemical Properties of Phthalate Esters

Phthalate Ester	Acronym	Formula	MW (g/mol)[a]	SG [b]	C^{S}_{WL} (mg/L)[c]	P_L (Pa)[d]	Log K_{OW}[e]	Log K_{AW}[f]
Diethyl Phthalate	DEP	$C_{12}H_{14}O_4$	222.2	1.118	896.0 (164.8)	1.18×10^{-1} (0.089)	2.42 (0.278)	-5.01
Dibutyl Phthalate	DBP	$C_{16}H_{22}O_4$	278.4	1.042	10.8 (1.653)	4.60×10^{-3} (0.003)	4.44 (0.372)	-4.27
Di-(2-ethylhexyl) Phthalate	DEHP	$C_{24}H_{38}O_4$	390.6	0.986	0.230 (0.167)	3.20×10^{-4} (0.0003)	7.26 (1.064)	-2.80

[a] MW is the molecular weight published by Stanely et al., 2003
[b] SG is the specific gravity at 20ºC published by Stanely et al., 2003
[c] C^{S}_{WL} is the average solubility of phthalate in water at 25ºC calculated using the values published by Cousins et al., 2003
[d] P_L is the average liquid vapor pressure at 25ºC calculated using the values published by Cousins et al., 2003
[e] Log K_{OW} is the average ocanol-water partition coefficient calculated using the values published by Cousins et al., 2003
[f] Log K_{AW} is the air-water partition coefficient published by Cousins et al., 2003.
Values in parenthesis are the standard deviation (SD) of reported values

2.1.1.2 PHTHALATES IN THE ENVIRONMENT

The greatest amount of phthalate esters found in the environment result from their slow release from plastics and other phthalates' containing materials. Release of phthalates compounds from plastics is possible due to the lack of covalent bounding between phthalates and plastics (Dumitraşcu, 2012). Very little release of phthalates is believed to occur during production and processing, although the wastewater and sewage sludge produced may results in some release to soil and water (Stanley et al., 2003).

Phthalates have been measured and detected in various environments including surface water, groundwater, landfill leachates, drinking water, sediment, suspended particulate matter, soil, air (outdoor and indoor), dust, precipitation, wastewater, sewage sludge, food, vegetation and wildlife (Clark et al., 2011). Measured DEHP concentrations in surface waters range in the parts per billion concentrations (up to 336 ppb; Clark et al,. 2003). The range in groundwater concentration tends to be higher (up to 470 ppb), (Clark et al., 2003). Wastewater and landfill leachates show considerable higher concentrations of DEHP, ranging from below-detection concentrations to 4.4 mg/L (Clark et al., 2003). DEHP is considered one of the more recalcitrant phthalate esters (Shailaja et al., 2008) and degradation is not considered significant under typical environmental conditions (Cousins et al., 2003; Herrmann, 2001; Peterson and Stapples, 2003). Given the low aqueous solubility and the multiple potential environmental paths (e.g. sorption and degradation), it has been often believed that phthalates, particularly those of high molecular weight should not be found at significant levels in water. Frequent detection of DEHP in surface-water, groundwater, and drinking water (ATSDR, 2002; Clark et al, 2003; Loraine and Pettigrove, 2006) together with relatively low degradation rates (Cousins et al., 2003; Herrmann, 2001; Peterson and Stapples, 2003) and potential long-term loads should however be of concern,

even at low concentrations. Rapid flow of groundwater in karstic limestone may further limit its potential for degradation before potential exposure. High K_{ow} values for DEHP (Log K_{ow} ~5.1-8.4; Cousins et al., 2003) indicate that its partition into organic tissue has much greater extent than to water and could bioaccumulate. For instance, water concentrations of DEHP detected in a diffusely-recharged karts spring in Arkansa at low ppb consentrations, can not describe the concentration of DEHP found in cavefish (Graening and Brown, 1999). The higher-than-expected concentrations in the fish were attributed to bioaccumulation of recurring DEHP in the cave system. Even at low concentrations, the potential continuous release of phthalates into karstic groundwater may, therefore, pose a potential for cumulative exposure. Data, indeed, show that phthalates, mainly DEHP and DEP, have been detected at low ppb levels (up to 22 µg/L) in groundwater wells throughout the north coast of Puerto Rico (Padilla et al., 2011; USEPA, 2009; USGS, 2009).

2.1.1.3 PHTHALATES HEALTH IMPACTS

Recent studies show increasing and widespread exposure to phthalates in the US population (CDC, 2005). Concerns have been raised about some phthalates because studies in laboratory animals have shown that exposure can cause adverse health effects. They are considered endocrine disruptor and have been associated with adverse reproductive health (Barlow et al., 2007) including effects on development of male reproductive system (CHRP, 2008), decreased gestation length (Latini et al., 2003) and rise in preterm birth (CERHR, 2006; Meeker et al., 2009; Meeker, 2012). One study in Puerto Rico found that girls with premature breast development (younger than 8 years) had higher blood levels of several phthalates, particularly DEHP, than a control group of girls without premature breast development (Colón et al., 2000). Exposure to phthalates has also been associated with increased incidence of

development abnormalities, such as cleft palate and skeletal malformations and increased fetal death in experimental animal studies (USEPA, 2007c). Table 2 summarized common adverse health effects associated with the phthalates used in this study.

Table 2 Summary of Adverse Health Effects of Selected Phthalates (USEPA, 2007c).

Phthalate	Health Effects
DEP	• Prenatal exposure resulted in skeletal variations and delayed ossification (hardening) of bones. • Prenatal and lactational exposure resulted in abnormal sperm and decreased testosterone in male offspring during adulthood.
DBP	• Teratogenic effects in offspring included skeletal malformations, increased incidence of cleft palate, and decreased number of live fetuses at birth. • Defects in male reproductive organ increased incidence of undescended testicles, hypospadias, and other anatomical differences.
DEHP	• Increased incidence of asthma in children. • Exposure from medical devices was associated with cholestasis (reduced bile flow) and unusual lung disorders. • Prenatal exposure resulted in skeletal malformations, increased incidence of cleft palate, and decreased number of live fetuses at birth. • Defects in male reproductive organ included increased incidence of undescended testicles, hypospadias, and other anatomical differences. • Prenatal exposure led to adverse effects on lung tissue development.

2.1.1.4 EPA METHODS FOR EXTRACTION AND ANALYSIS OF PHTHALATES

The methods discussed in this section are those used to determine the concentration of semi-volatile organic compounds, such as phthalates, in extracts prepared from water samples. The information contained in these methods is provided by EPA SW-846 as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application (USEPA, 2014a). The EPA publication SW-846, entitled Test Methods for Evaluating Solid Waste, Physical/Chemical

Methods, is a official compendium of analytical and sampling methods that have been evaluated and approved for use in complying with the RCRA regulations (USEPA, 2015).

The SW-846, generally, a sample of a known volume is extracted or diluted with a solvent. Different extraction methods options are available for aqueous samples, including liquid-liquid extraction (LLE) by separatory funnel (USEPA, 1996a) or by continuous extractor (USEPA, 1996b), and solid-phase extraction (SPE; USEPA, 2007b). In LLE methods, the resultant extract is dried and concentrated in a Kuderna-Danish (K-D) apparatus. Solvent recovery apparatus is recommended during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. USEPA recommends the incorporation of this type of reclamation systems as a method to implement an emissions reduction program (USEPA, 2007a).

Phthalate esters are commonly found in many types of laboratories products, and could results in cross contamination if consistent quality control practices are not implemented (USEPA, 2007a). Plastics, in particular, must be avoided as phthalates are commonly contained in and easily extracted from plastics. Indeed, analysis of phthalates at trace levels in samples pose serious challenges because phthalate esters are present in many laboratory products, including glassware, chemicals and plastic accessories that can be easily transferred to the water samples (Liang et al., 2008; Shen, 2004). To minimize phthalates contamination glassware must be cleaned with different solvents such as acetone, hexane, and methanol, among others.

In EPA Method 3510 (USEPA, 1996a) and 3520 (USEPA, 1996b) a measured volume of sample, usually 1 liter, is extracted using liquid-liquid extraction. In method 3510, samples are serially extracted with dichloromethane (DCM) using a separatory funnel. In method 3520 samples are placed into a continuous liquid-liquid extractor and extracted with organic solvent

for 18 - 24 hours. The extract is dried, concentrated and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used. EPA Method 3520 is not recommended for the extraction of aqueous samples containing phthalates because the longer chain esters (dihexyl phthalate, DEHP, di-n-octyl phthalate and dinonyl phthalate) tend to adsorb to the glassware and, consequently, their extraction recoveries are less than 40 percent (USEPA, 1996a). EPA Method 3535 (USEPA, 2007b) is a solid phase extraction method where a measured volume of sample is extracted by passing it through the solid-phase extraction medium (disks or cartridges), which is held in an extraction device designed for vacuum filtration of the sample. Target analytes are eluted from the solid-phase media using an appropriate solvent, which is collected, in a receiving vessel. The resulting solvent extract is dried using sodium sulfate and concentrated, as needed.

Once extracted into an appropriated solvent, solvent extracts can be analyzed using several methods, including EPA methods 8270D (USEPA, 2014a), 8250A (USEPA, 1994), 8061A, (USEPA, 1996d) and 606 (USEPA, 1996c). Methods 8270D and 8250A analyze extracts using Gas Chromatography/Mass Spectrometry (CG/MS). Method 8250A is a packed column version of EPA Method 8270D. Method 8061A and 606 analyze extracts using a GC with Electro Capture Detector (GC/ECD). Method 606 (USEPA, 1996c) covers the determination of certain phthalate esters in municipal and industrial wastewater. Although ECD detectors are relative sensitive for phthalates, the specificity is restricted since ECDs respond much more towards halogenated compounds (Tienpont, 2004). The most important detector for phthalate analysis is mass spectrometric detection. All types of MS analyzers, including quadrupole analyzers, triple quadrupole analyzers, ion traps and magnetic sector instruments have been used for phthalates analysis (Tienpont, 2004). Detection of phthalates can be done by flame ionization

detection (FID), electron capture detection (ECD) or mass spectrometry (MS). GC-FID is not frequently used since the detector is not specific for phthalates.

Extraction and analytical methods for phthalates in water have been tested for detection limits, recovery, accuracy, and precision. Detection limits for several phthalate esters (Table 3) using GC/MS analysis (Method 8270D) are reported at 10 μg/L in groundwater and 660 μg/kg for soil/sediment samples (USEPA, 2014a). Limits of quantification are higher if samples are diluted to avoid detector saturation (USEPA, 1996c; 2014a).

Table 3 Limits of Quantification for Phthalates (USEPA, 2014a)

Compound	**Limits of Quantification**	
	Groundwater (μg/L)	Low Soil/Sediment (μg/kg)
Bis(2-ethylhexyl) phthalate	10	660
Butyl benzyl phthalate	10	660
Di-n-butyl phthalate	10	ND
Diethyl phthalate	10	660
Di-n-octyl phthalate	10	660

ND - Not Determined

Recovery of phthalates in water using a separatory funnel liquid-liquid extraction (Method 3510) and a modified continue liquid-liquid extraction (Method 3520) have been performed for single-laboratory demonstration of capability data (USEPA, 1996d; 2014a) and for multi-laboratory performance (USEPA, 1994; 1996c). Single-laboratory performance data for phthalates, using Method 8270D and 8061A, show high percent recovery (Table 4 and Table 5).

Table 4 Single Laboratory Performance Data for Phthalates (Method 3520/8270D)

Compound	Average Recovery Concentration (µg/L)	% Recovery
Bis(2-ethylhexyl) phthalate	50.2	100
Butyl benzyl phthalate	49.6	99.3
Di-n-butyl phthalate	50.5	101
Diethyl phthalate	50.0	99.9
Dimethyl phthalate	48.5	97.0
Di-n-octyl phthalate	51.1	102

Test concentration = 50 µg/L
Average recovery for five measurements

Table 5 Single Laboratory Performance Data for Phthalates (Accuracy and Precision Data for Method 3510/8061)

Compound	%Average Recovery (%RSD)*					
	Spike Concentration (20 µg/L)			Spike Concentration (60 µg/L)		
	Water	Estuarine	Groundwater	Water	Estuarine	Groundwater
Bis(2-ethylhexyl) phthalate	81.4 (4.1)	93.0 (15.0)	90.4 (4.9)	86.5 (6.9)	108 (15.1)	91.1 (3.0)
Benzyl butyl phthalate	84.1 (6.4)	105 (20.5)	89.6 (6.1)	92.7 (5.6)	117 (24.7)	93.0 (2.0)
Di-n-butyl phthalate	83.2 (6.5)	97.5 (22.3)	91.0 (10.7)	87.0 (8.0)	106 (17.4)	87.7 (2.7)
Diethyl phthalate	71.2 (3.8)	82.8 (19.3)	88.5 (15.3)	71.0 (7.7)	88.5 (17.9)	75.3 (3.5)
Dimethyl phthalate	84.0 (4.1)	98.9 (19.6)	87.1 (8.1)	87.1 (7.5)	112 (17.5)	90.9 (4.5)
Di-n-octyl phthalate	59.5 (6.1)	77.3 (4.2)	67.2 (8.0)	97.2 (7.0)	108 (17.9)	90.1 (1.1)

Average recovery for three measurements
*%RSD (Percent Relative Standard Deviation)

Multi-laboratory performance was determined by sending spike water samples for analysis to multiples laboratories. Method 8250A was tested by 15 laboratories, while Method 606 was tested by 16 laboratories. In both methods organic-free reagent water, drinking water, surface water, and industrial wastewater were spiked at various concentrations of phthalates ranging from 5 to 1300 μg/L for Method 8250A and from 0.7 to 106 μg/L for Method 606. Different than the single-laboratory, the multi-laboratory performance shows a wide range and high variability of samples recoveries (Table 6 and Table 7).

Table 6 Multilaboratory Performance Data for Phthalates (Method 3520/8250A)

Compound	Range of Recovery (μg/L)	Standard Deviation	Range of %Recovery
Bis(2-ethylhexyl) phthalate	28.9-136.8	41.1	8-158
Butyl benzyl phthalate	D-139.9	23.4	D-152
Di-n-butyl phthalate	8.4-111.0	16.7	1-118
Diethyl phthalate	D-100.0	26.5	D-114
Dimethyl phthalate	D-100.0	23.2	D-112
Di-n-octyl phthalate	42.9-121.3	31.4	26-137

Test concentration = 100 μg/L
Average recovery for four measurements
D = Detected; result must be greater than zero

Table 7 Multilaboratory Performance Data for Phthalates (Method 3510/606)

Compound	Range of Recovery (μg/L)	Standard Deviation	Range of %Recovery
Bis(2-ethylhexyl)phthalate	1.2 - 55.9	38.4	D – 158
Butyl benzyl phthalate	5.7 - 11.0	4.2	30 – 136
Di-n-butyl phthalate	10.3 - 29.6	8.9	23 – 136
Diethyl phthalate	1.9 - 33.4	9.0	D – 149
Dimethyl phthalate	1.3 - 35.5	9.5	D – 156
Di-n-octyl phthalate	D - 50.0	13.4	D -114

Test concentration = 100 μg/L
Average recovery for four measurements
D = Detected; result must be greater than zero

Methods accuracy and precision have been reported for various methods. Method accuracy is generally reported as average phthalates recovery. The precision is focused on the standard deviation of measurements. Accuracy and precision estimations reported for extraction/analysis methods 3520/8250A (USEPA, 1996b/1994), 3510/8061A (USEPA, 1996a/1996d), and 3510/606 (USEPA, 1996a/1996c) are provided in Table 5, 8 and Table 9. Accuracy and precision estimates of methods 3520/8250A and 3510/606 involve multi-laboratory testing. Estimations for methods 3510/8061 involve a single laboratory testing.

Table 8 Accuracy and Precision as Functions of Concentration for Phthalates (Method 3520/8250A)

Compound	Accuracy (µg/L)[1]	Precision (µg/L)[2]	Overall Precision (µg/L)
Bis(2-ethylhexyl) phthalate	0.84C-1.18	0.26Ẋ+0.73	0.36Ẋ+0.67
Benzyl butyl phthalate	0.66C-1.68	0.18Ẋ+0.94	0.53Ẋ+0.92
Di-n-butyl phthalate	0.59C+0.71	0.13Ẋ+1.16	0.39Ẋ+0.60
Diethyl phthalate	0.43C+1.00	0.28Ẋ+1.44	0.52Ẋ+0.22
Dimethyl phthalate	0.20C+1.03	0.54Ẋ+0.19	1.05Ẋ-0.92
Di-n-octyl phthalate	0.76C-0.79	0.21Ẋ+1.19	0.37Ẋ+1.19

[1]Recovery or Accuracy is proportional to the phthalate concentration (C).
[2]Standard Deviation or Precision is proportional to the average recovery (Ẋ)

Table 9 Accuracy and Precision as Functions of Concentration for Phthalates (Method 3510/606)

Compound	Accuracy (µg/L)[1]	Precision (µg/L)[2]	Overall Precision (µg/L)
Bis(2-ethylhexyl) phthalate	0.53C+2.02	0.80Ẋ-2.54	0.73Ẋ-0.17
Benzyl butyl phthalate	0.82C+0.13	0.26Ẋ+0.04	0.25Ẋ+0.07
Di-n-butyl phthalate	0.79C+0.17	0.23Ẋ+0.20	0.29Ẋ+0.06
Diethyl phthalate	0.70C+0.13	0.27Ẋ+0.05	0.45Ẋ+0.11
Dimethyl phthalate	0.73C+0.017	0.26Ẋ+0.14	0.44Ẋ+0.31
Di-n-octyl phthalate	0.35C-0.71	0.38Ẋ+0.71	0.62Ẋ+0.34

[1]Recovery or Accuracy is proportional to the phthalate concentration (C).
[2]Standard Deviation or Precision is proportional to the average recovery (Ẋ)

All studies indicated that accuracy and precision are directly related to the analyte concentration. Some of the studies suggest that accuracy and precision estimates are independent of sample material (USEPA, 1996c; 2014a), whereas others have found these estimates to depend in type of material (USEPA, 1996d). Review of accuracy and precision estimates of the different methods for the phthalates compounds of interest for this study (DEP, DBP and DEHP) show solute recoveries to be lower than 100%. It also reflects high variability among the measurements. For instance, solute recovery for DEHP range from 29 to 137 μg/L for a 100 μg/L test concentration for extraction/analysis method 3520/8250A (USEPA, 1996b/1994), and from 1.2 to 55.9 μg/L for a 50 μg/L test concentration for extraction analysis method 3510/606 (USEPA, 1996a/1996c). Similar high variability is observed for other phthalate esters (Table 6 and 8). It is important to know that the performance data presented by the USEPA (USEPA, 1994; 1996c,d; 2014a) should only serve as guidance, and that each laboratory should generate their own acceptance criteria depending on extraction and analytical methods used.

2.1.1.5 OTHERS PHTHALATE WATER EXTRACTION METHODS

Analysis of trace levels of phthalate esters in water samples often require extraction and pre-concentration steps prior to their analysis by GC (Luks-Betleja et al., 2001; Shen, 2004; Serôdio and Nogueira, 2006; USEPA, 2014a; Xu et al., 2007) or HPLC (Cai et al., 2003; Li et al., 2008; Liang et al., 2008). Extraction and pre-concentration techniques include liquid–liquid extraction (USEPA, 1996a,b), liquid-phase microextraction (LPME) (Xu et al., 2007), liquid-liquid microextracion (LLME) (Liang et al., 2008), solid-phase extraction (SPE) (Cai et al., 2003; Li et al., 2008), solid-phase microextraction (SPME) (Holadová et al., 2007; Luks-Betleja et al., 2001), and stir bar sorptive extraction (SBSE) (Serôdio and Nogueira, 2006). Table 10 show comparison for some of these methods. LLE and SPE are widely applied to determine

phthalate esters in water samples (Liang et al., 2008), but the pretreatment of the samples is expensive, time-consuming, and labor-intensive methods, and often result in high blank values. SPE relies on extracting the solute onto a solid phase, to be later eluted into a solvent prior to analysis. Advantages of the SPE include simplicity, sensitivity and portability (Luks-Betleja et al., 2001). Li et al. (2008) developed a method that uses ionic liquid mixed hemimicelles-based solid-phase extraction for pre-concentration of phthalates in environmental water samples. Br-coated silica was used as the SPE material. The method was tested for five phthalates analytes (DEP, di-n-propyl-phthalate (DnPP), di-n-butyl-phthalate (DnBP), di-cyclohexyl-phthalate (DcHP) and DEHP at spiked concentrations of 1 μg/L, and yielded recoveries ranging from 85 to 108%. No phthalates were found in the tap water measurements. Cai et al. (2003) developed a solid-phase extraction system that uses multi-walled carbon nanotubes packed cartridges for the determination of four phthalates. This method showed recovery estimates measurements range between 80.3 and 104.5%. The method was applied to determine DEP, DnPP, DnBP and DcHP in tap water, river water, and seawater samples. No phthalate esters were found in the river water and seawater samples. Tap water samples showed DEP at concentrations of 2.0 ng/mL.

LPME and SPME were developed to attain efficient economical, and miniaturized sample preparation methods (Xu et al., 2007). LPME was developed as a solvent-minimized sample pretreatment procedure that is inexpensive and uses very little solvent. This method, however, tends to form air bubbles, require time-consuming extractions and may not reach to equilibrium conditions (Xu et al., 2007). Optimum extraction involves extraction of 22.5 mL sample to 2 μL of n-hexane as the extraction solvent. It requires an extraction frequency of 30 times. The recovery of the LPME method, determined by consecutively extracting six aqueous samples spiked at 100 μg/L, varies between 84 and 102% (Liang el al., 2008). Another microextraction

technique is the dispersive liquid–liquid microextraction (DLLME). In this technique the appropriate mixture of extraction solvent and dispersive solvent is injected rapidly into the aqueous sample by syringe, and a cloudy solution is formed (Xu et al,. 2007). The advantages of the DLLME method are simplicity of operation, fast, low cost, high recovery and enrichment factors. A mixture of extraction solvent (41 µL carbon tetrachloride) and dispersive solvent (0.75 mL acetonitrile) are rapidly injected into 5.0 mL aqueous sample for the formation of cloudy solution; the analytes in the sample were extracted into the fine droplets of carbon tetrachloride. The Xu et al report (2007) shows recoveries of the compounds ranging between 84 and 113%.

Solid-phase microextraction (SPME) is a method that has been used for a wide variety of organic contaminants (Luks-Betleja et al., 2001). It relies on the adsorption of analytes onto a solid phase fiber, with subsequence desorption into analytical instrument (GC or HPLC). SPME is simple, fast, solventless and efficient pre-concentration technique that enables determination of phthalate esters at low µg/L (Liang et al., 2008). SPME, however, suffers from some drawbacks: its fiber is expensive, fragile and has limited lifetime, and sample carry-over could be a problem (Liang et al., 2008; Xu et al., 2007). Testing of the SPME method has shown high variability in recoveries of phthalates raging from 0.04% to 59.31% in a spiked 5mL water samples (10 µg/L). DBP had the highest extraction recoveries in this method (2.99% -59.1%), and DEP and DEHP had the lowest extraction recoveries (0.04% - 12.5%). Table 10 shows a comparison between some phthalates extraction methods documented in the literature.

Table 10 Comparisons of Phthalates Extraction Methods

Method	Sample Volume	Extraction Solvent/ Desorbent	Extraction Solvent/ Desorbent Volume/Time	Dispersive Solvent	Dispersive Solvent Volume	Solid Phase	Spike	Recovery
LPME[a]	22.5 mL	n-hexane	2 µL	N/A	N/A	N/A	100 µg/L	84 - 102%.
DLLME[b]	5 mL	carbon tetrachloride	41 µL	acetonitrile	0.75 mL	N/A	50 µg/L	84 - 113%.
SPE[c]	300 mL	methanol	3 mL	N/A	N/A	Br-coated silica	1.0 µg/L	85 - 108%
SPE[d]	1000 mL	acetonitrile	5 mL	N/A	N/A	multi-walled carbon nanotubes	10 and 20 ng/mL	80.3 - 104.5%.
SPME[e]	5 mL	At 270^{o}C in the chromatograph injector	5 mins	N/A	N/A	70-mm Carbowax–divinylbenzene fibre	10 µg/L	0.04 - 59.31%

[a]Liang et al., 2008
[b]Xu et al., 2007
[c] Li et al., 2008
[d] Cai et al., 2003
[e] Luks-Betleja et al., 2001

2.1.2 CHLORINATED VOLATILE ORGANIC COMPOUNDS (CVOCS)

CVOCs are a broad class of organic chemicals that contain chloride, and have relatively low boiling points and high vapor pressures (Patnaik, 2010). These compounds are commonly used in the manufacture of industrial, chemical, electric, and consumer's products (Lawrence, 2006). In addition, CVOCs are heavily used as solvents in cleaning, degreasing, and paint and spot remover products. Tetrachloroethene (PCE), trichloroethene (TCE), chloroform or trichloromethane (TCM) and, trichloroethane (TCA) are among the most common chlorinated solvents used. PCE is used as a solvent by more than 80 percent of commercial dry cleaners and TCE is mostly used as a solvent, but also can be formed from the biodegradation of its parent compound, PCE, especially in non-oxygenated groundwater conditions (Zogorki et al., 2006). Chloroform has many industrial uses, including the production of refrigerants for home air conditioners and large commercial freezers, as reagents in extraction solvents, fumigants, insecticides, and dyes (Zogorki et al., 2006). TCA is used as a solvent for adhesives and in metal degreasing, pesticides, textiles processing, cutting fluids, aerosols, lubricants, cutting oil formulations, drain cleaners, shoe polish, spot cleaners, printing inks and stain repellents (ATSDR, 2006).

2.1.2.1 CVOCS PROPERTIES

CVOCs share the common characteristics of high volatility and strong persistence in environment (Huang et al., 2014). Physico-chemical properties of CVOCs (Table 11 Physical-Chemical Properties of CVOCs show that most CVOCs found in environment are liquids at room temperature with densities higher than water (Lawrence, 2006). Their solubilities range from 10^2 to 10^3 mg/L for the higher and lower molecular weight compounds, respectively.

Table 11 Physical-Chemical Properties of CVOCs

IUPAC name[a]	Abbreviation	Formula	MW[c] (g/mol)	ρ (g/cm^3)[d]	H (kPa m^3/mol)[e]	S (mg/L)[f]	Log K_{OW}[g]
1,1-Dichloroethene	1,1-DCE	$C_2H_2Cl_2$	96.94	1.213	2.63 (0.014)	2,390 (127.7)	2.13 (0.00)
1,2-Dichloroethene	1,2-DCE	$C_2H_2Cl_2$	96.95	1.256	0.95 (0.007)	5,266 (929.2)	2.01 (0.08)
1,1-Dichloroethane	1,1-DCA	$C_2H_4Cl_2$	98.96	1.176	0.60 (0.05)	5,353 (560.8)	1.76 (0.05)
1,2-Dichloroethane	1,2-DCA	$C_2H_4Cl_2$	98.96	1.235	0.11 (0.03)	8,606 (90.1)	1.47 (0.01)
Chloroform[b]	TCM	$CHCl_3$	119.38	1.485	0.39 (0.03)	7,783 (308.6)	1.95 (0.03)
1,1,2-Trichloroethene	TCE	C_2HCl_3	131.39	1.464	1.03 (0.01)	1,220 (103.9)	2.55 (0.15)
1,1,1-Trichloroethane	1,1,1-TCA	$C_2H_3Cl_3$	133.40	1.339	1.74 (0.02)	1,206 (180.1)	2.49 (0.01)
1,1,2-Trichloroethane	1,1,2-TCA	$C_2H_3C_{l3}$	133.40	1.440	0.092 (0.00)	4,503 (85.0)	2.40 (0.07)
Tetrachloromethane	-	CCl_4	153.82	1.594	3.03 (0.06)	789 (5.66)	2.67 (0.05)
Tetrachloroethene	PCE	C_2Cl_4	165.83	1.623	1.80 (0.09)	187 (32.1)	2.82 (0.13)

[a] International Union of Pure and Applied Chemistry (Lawrence, 2006)
[b] Chloroform properties (ATSDR, 1997; Huang et al., 2014; USEPA, 1996d)
[c] MW is the molecular weight published by Lawrence, (2006
[d] ρ is the density at 20ºC published by Lawrence, (2006)
[e] H is the average Henry's law constant at 25ºC calculated using the values published by Lawrence, (2006) and, USEPA, (1996d)
[f] S is the water solubility at 25ºC calculated using the values published by Huang et al. (2014), Lawrence, (2006) and, USEPA, (1996d)
[g] Log K_{OW} is the ocanol-water partition coefficient calculated using the values published by Huang et al. (2014), Lawrence, (2006) and, USEPA, (1996d)
Values in parenthesis are the standard deviation (SD)

Different from phthalates, CVOCs properties (water solubility, Henry's constant and, octanol-water partition coefficient) hardly vary. For example, reported aqueous solubility of Chloroform at 25ºC varies between 7,430 and 8000 mg/L, which is by a factor of 1.08, and the $\log K_{ow}$ varies between 1.92 and 1.97 (less than 3% of difference). Table 11 shows low SD relative to the average values, showing minimal variation in CVOCs properties compared to phthalates.

2.1.2.2 CVOCS IN THE ENVIRONMENT

As CVOCs are widely used in human activities (Lawrence, 2006; Zogorki et al., 2006; ATSDR, 2006) and have strong resistance to biodegradation (Huang et al. 2014), they are frequently detected in the environment. CVOCs are among the most frequently detected groundwater contaminants in the United States (ATSDR, 2013). Their frequent uses promote release into the environment, and their chemicals properties allow them to be transported by groundwater. Unfortunately, municipal water supply treatment is not commonly design to remove CVOCs to acceptable concentrations for humans (Holt et al., 1997). Even more, several CVOCs including chloroform form as disinfection by-product (DBPs) (ATSDR, 1997). The most frequently detected CVOCs in the US include: TCM, PCE, TCE, TCA, DCE and DCA (Lawrence, 2006; Zogorki et al., 2006).

A national assessment of 55 volatile organic compounds (VOCs) in groundwater (Zogorki et al., 2006) detected one or more VOCs in almost 20 percent of the water samples from aquifers, at an assessment level of 0.2 μg/L. This detection frequency increased to more than 50 percent for an order-of-magnitude lower assessment level (0.02 μg/L). Although 42 VOCs were detected in aquifer samples, only 15 occurred in about 1 percent or more of the

samples. The most frequently detected VOCs in the Zogorki et al. (2006) assessment, include 7 solvents, 4 THMs, 2 refrigerants, 1 gasoline oxygenate, and 1 gasoline hydrocarbon of which 11 are chlorinated (CVOCs). In this study, chloroform was the most frequently detected compound and the solvent PCE and the gasoline oxygenate methyl tert-butyl ether (MTBE) were the second and third most frequently detected compounds, respectively (Zogorki et al., 2006). Eight compounds, including TCE and PCE, were detected at concentrations of potential concern. Concentrations reported for the 15 most frequently detected VOCs in aquifers ranged from 0.002 to 350 μg/L. However, most of the VOC concentrations were less than 1 μg/L (Zogorki et al., 2006).

In Puerto Rico, extensive contamination resulted in the closure of 41% of drinking water supply wells in the north coast aquifer by 1987 (Zack et al., 1987). Preliminary data assessment from field sampling and analysis during March–April, 2011 (Padilla el al., 2011) show persistent contamination of CVOCs in 56% of wells/springs sampled.

2.1.2.3 CVOCS HEALTH IMPACTS

Drinking water containing high levels of CVOCs may be harmful to human health (Lawrence, 2006). CVOCs are suspected to be human carcinogens, and their concentrations in drinking water systems are regulated by the U.S. Environmental Protection Agency (Zogorki et al,. 2006). At high levels of exposure, many CVOCs can cause central nervous system depression and may be harmful to the kidney and the liver. CVOCs may also cause irritation when they contact the skin, or may irritate mucous membranes if they are inhaled (MDH, 2015). Exposure to TCE has been related to several adverse health effects including cardiac, neurological, hepatic, renal, dermal, immunological, reproductive effects, increased birth defects, perinatal mortality and cancer, and decreased birth weights (ATSDR, 2014). Some

epidemiologic studies of women exposed occupationally to TCE and other solvents have reported increased risk for spontaneous abortion (Lipscomb and Fenster, 1991) and lower birth weight (Ha and Cho, 2002; Khattak et al., 1999; Lipscomb and Fenster, 1991).

2.1.2.4 METHOD FOR EXTRACTION AND ANALYSIS OF CVOCs

Several EPA methods exist for the analysis of CVOCs from water samples. Although purge-and-trap (Methods 5030/5035) is the most commonly used technique for volatile organic analytes (USEPA, 1996e, 2003a; 2014b), other techniques are also appropriate for some analytes. These include headspace by Method 5021 (USEPA, 2003b; 2014b); closed system vacuum distillation by Method 5032 (USEPA, 1996e; 1996f; 2014b); and liquid-liquid extraction by Method 551.1 (Munch and Hautman, 1995).

Purge and trap can be used for most volatile organic compounds that have boiling points below 200^{o}C and are insoluble or slightly soluble in water (USEPA, 2003a). Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. In this method an inert gas is bubbled through a portion of the aqueous sample at ambient temperature or an elevated temperature depending on the desired target analytes, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

The headspace method is applicable to a wide range of organic compounds that have sufficiently high volatility to be effectively removed from samples using an equilibrium headspace procedure (USEPA, 2003b). For water samples a 40-mL vial is filled with water. When the vial is headspace free, it is capped. At the laboratory, that vial is sub-sampled into a

headspace vial. A matrix modifier is added to the headspace vial, along with internal standards and surrogates, and the headspace vial is then capped. The matrix modifier acts to partition the volatile organic compounds into the headspace.

The vacuum distillation method is used to determine VOCs in a variety of liquid, solid, oily waste matrices, and animal tissues (USEPA, 1996f). This method can be used to quantitate most VOCs that have a boiling point below 180^{o}C and are insoluble or slightly soluble in water. The sample is introduced into a sample flask, which is then attached to the vacuum apparatus. The sample chamber pressure is reduced using a vacuum pump and remains at approximately 10 torr (vapor pressure of water) as water is removed from the sample. The vapor is passed over a condenser coil chilled to a temperature of 10^{o}C or less, which results in the condensation of water vapor. The uncondensed distillate is cryogenically trapped on a section of 1/8 inch stainless steel tubing chilled to the temperature of liquid nitrogen (-196^{o}C). After an appropriate distillation period, which may vary due to matrix or analyte group, the condensate contained in the cryotrap is thermally desorbed and transferred to the gas chromatograph using helium carrier gas.

Once the analyte is transferred from the aqueous phase to the vapor phase, the contaminant can be analyze using Methods 8021B or 8260B. Method 8021B provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. In this method detection is achieved by a photoionization detector (PID) or/and a Hall electrolytic conductivity detector (HECD). In Method 8260B the analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed

to separate the analytes, which are then detected with a mass spectrometer interfaced to the gas chromatograph.

Because of the lack of purge and trap system, the method used in this research is based on Method 551.1 (Munch and Hautman, 1995), which is applicable to the determination of DBPs, chlorinated solvents and pesticides/herbicides in finished drinking water, drinking water during intermediate stages of treatment and raw source water. MTBE is recommended as the primary extraction solvent in this method since it effectively extracts all of the target analytes. In this method, a 50 mL sample aliquot is extracted with 3 mL of MTBE or 5 mL of pentane (Munch and Hautman, 1995). 2 μL of the extract is injected into a GC equipped with a fused silica capillary column and linearized electron capture detector (GC/ECD) for separation and analysis. Procedural standard calibration is used to quantitate method analytes. This method is a micro-extraction procedure that uses a minimal amount of extraction solvent per sample. Hence, reduces the hazards involved with handling large volumes of potentially harmful organic solvents needed for conventional liquid-liquid extractions.

Glassware must be carefully cleaned washing with hot water and detergent and thoroughly rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for one hour. Do not muffle volumetric ware but instead rinse three times with HPLC grade or better acetone. To prevent any accumulation of dust or other contaminants, store glassware inverted on clean aluminum foil or capped with aluminum foil.

Single laboratory accuracy and precision data reported for methods 5030C/8260 (USEPA, 2003a/1996e), 5032/8260B (USEPA, 1996f/1996e), 5030C/8021B (USEPA, 2003a/2014b) and 551.1 (Munch and Hautman, 1995) are provided in Table 12-Table 16. Method accuracy is reported as average CVOCs recovery and precision is reported as the

standard deviation of measurements. Method 8260 has been tested using purge-and-trap (Method 5030) at concentrations between 0.5 and 10 μg/L and vacuum distillation (Method 5032) at concentrations of 50 ppb for 5-mL samples and 25 ppb for 20-mL. Method 8021B has been tested using purge-and-trap (Method 5030) using organic-free reagent water which was spiked at 10 μg/L. In Method 551.1, analyte recoveries from reagent water with MTBE as the extracting solvent were determined at high (Table 15) and low (Table 16) concentrations (Munch and Hautman, 1995). In this Method eight replicate analyses were conducted to assess precision.

As can be seen from Table 15 and Table 16, low concentrations have a slightly higher percent of recovery than high concentrations. Contrary to phthalates, recoveries and standard deviations of the CVOCs studies show high accuracy and precision, and less variability. In general, the range of recoveries for all the studies varies between 84 and 120 percent.

Table 12 Single Laboratory Performance Data for CVOCs in Water (Accuracy and Precision Data for Methods 5030/8260)

Compound	Concentration Range (µg/L)	Number of Samples	%Recovery	%RSD[a]
Carbon tetrachloride	0.5 - 10	24	84	8.8
Chloroform	0.5 - 10	24	90	6.1
1,1-Dichloroethene	0.1 – 10	34	94	6.7
1,2-Dichloroethene	0.5 - 10	18	101	6.7
Tetrachloroethene	0.5 - 10	24	89	6.8
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6
Trichloroethene	0.5 - 10	24	90	6.5

[a]Standard deviation was calculated by pooling data from three concentrations.

Table 13 Single Laboratory Performance Data for CVOCs in Water (Accuracy and Precision Data for Methods 5032/8260)[a]

Compound	5 mL H_2O[b]		20 mL H_2O[c]	
	%Recovery	%RSD	%Recovery	%RSD
1,1-Dichloroethene	105	11	89	4
1,2-Dichloroethene	105	11	107	14
1,1-Dichloroethane	118	10	119	11
1,2-Dichloroethane	104	6	109	8
Chloroform	114	6	104	8
1,1,1-Trichloroethane	118	9	109	9
1,1,2-Trichloroethane	98	7	100	4
Tetrachloroethene	101	3	97	7
Trichloroethene	98	4	99	2
Carbon tetrachloride	102	6	108	12

[a]Results are for 10 min. distillation times, and condenser temperature held at -10°C.
[b]Concentrations of analytes were 50 ppb for 5-mL samples
[c]Concentrations of analytes were 25 ppb for 20-mL samples

Table 14 Single Laboratory Performance Data for CVOCs in Water (Accuracy and Precision Data for Methods 5030/8021)[a]

Compound	PID		HECD	
	%Recovery	%RSD	%Recovery	%RSD
1,1-Dichloroethene	100	2.4	103	2.9
1,2-Dichloroethene	93	3.7	99	3.7
1,1-Dichloroethane	-[b]	-	100	5.7
1,2-Dichloroethane	-	-	100	3.8
Chloroform	-	-	98	2.5
1,1,1-Trichloroethane	-	-	104	3.4
1,1,2-Trichloroethane	-	-	109	6.2
Tetrachloroethene	101	1.8	97	2.4
Trichloroethene	100	0.78	96	3.5
Carbon tetrachloride	-	-	92	3.3

[a]Recoveries and standard deviations were determined from seven samples and spiked at 10 µg/L of each analyte.
[b]Detector does not respond.

Table 15 Single Laboratory Performance Data for CVOCs in Water (Accuracy and Precision Data for Method 551.1 using MTBE as Extraction Solvent at High Concentrations)

Compound	Fortified Concentration (µg/L)	Mean Measured Concentration (µg/L)[a]	%RSD	%Recovery
Carbon Tetrachloride	5.00	5.07	1.72	101
Chloroform	5.00	5.10	1.30	102
Tetrachloroethylene	5.00	5.07	162	101
1,1,1-Trichloroethane	5.00	5.02	1.22	100
1,1,2-Trichloroethane	2.80	2.92	0.91	100
Trichloroethylene	5.00	4.87	1.48	97

Table 16 Single Laboratory Performance Data for CVOCs in Water (Accuracy and Precision Data for Method 551.1 using MTBE as Extraction Solvent at Low Concentrations)

Compound	Fortified Concentration (µg/L)	Mean Measured Concentration (µg/L)[a]	%RSD	%Recovery
Carbon Tetrachloride	0.250	0.299	1.60	120
Chloroform	0.250	0.264	1.94	105
Tetrachloroethylene	0.250	0.263	1.93	105
1,1,1-Trichloroethane	0.250	0.291	3.65	116
1,1,2-Trichloroethane	0.560	0.531	0.85	95
Trichloroethylene	0.250	0.252	1.20	101

[a]Based upon the analysis of eight replicate MTBE sample extracts.
%RSD = Percent Relative Standard Deviation

2.2 KARST GROUNDWATER SYSTEM

Karst terrains are underlain by soluble rocks, primarily limestone and dolomite, which undergoes considerable dissolution of joints, fractures, bedding planes, and other openings in which groundwater flow (Steele-Valentín and Padilla, 2009). Well-developed conduct porosity and highly transmissive zones in karst systems make karst aquifers highly productive and important fresh water resources for human consumption and ecological integrity of streams, wetlands, and costal zones. It has been estimated that karst occupy large areas of the planet's ice-free continental areas (~20%) and provide roughly 20-25% of the global population water needs (Ford and Williams, 2007). In United States, karst aquifers underlie 20% of the continent and provide over 40% of the groundwater used for drinking purposes (Veni et al., 2001).

The high aquifer productivity of karst groundwater attracts the development of industrial facilities and agricultural activities, and induces growth in population and urban development. Industrial, agricultural, and urban development however, induces the potential contamination of the aquifers that are being used for water consumption. The same characteristics that make these systems highly productive make them highly vulnerable to contamination (Göppert and Goldscheider, 2008). As a result, karst aquifer can serve as an important route for contaminant exposure to humans and wildlife.

Extensive contamination of the groundwater system has been documented in the karst aquifer (Calò and Parise, 2009; Einsiedl et al., 2010; Green et al., 2006; Guzmán-Ríos et al., 1986; Guzzella et al., 2005; Marín et al., 2010; Metcalfea et al., 2010; Padilla et al., 2011; Parise and Pascali, 2003; Schwarz et al., 2011; Yu et al., 2015). An overlay of Superfund sites (USEPA, 2013) on karst regions in U.S. (Tobin and Weary, 2004) show that 23% of all superfund sites are located in karst areas.

Karst terrains show distinctive surface and subsurface features associated with sinkholes, springs, caves, and sinking, losing, and gaining streams (Ford and Williams, 2007). Many of these features provide easy access for contaminants to enter the subsurface and contaminate large volumes of water. Well-developed conduit porosity in karst systems reduces the capacity for physical and chemical filtration and other attenuation processes. As a result, contaminants can move and disperse rapidly over long distances. The porous matrix of the karst forming rocks and the significant amount of sediments trapped in karst formations in many systems may provide high storage capacity for contaminants that can be slowly release for long period of time. This result in a potential for continues or intermittent exposure over long periods of time. Potential exposure of contaminants from contaminated groundwater in karst systems requires a link between the sources of contamination and the areas or point of potential exposure.

Some work has shown contamination in drinking water lines from leaching of old pipes (Aschengrau et al., 2012; NRDC, 2013; Nathan, 2006), residues of water treatment, storage and distribution (Pitkänen et al., 2008; EWG, 2009), contaminant intrusion while in transit (Mohan et al., 2004), and disinfection by products (EWG, 2009).

2.3 CASE STUDY AREA: KARST REGION OF NORTHERN PUERTO RICO

In Puerto Rico, karst areas cover over 17% of the island (Veve and Taggart, 1996). The north coast karst aquifer is the most productive aquifer of the island (Veve and Taggart, 1996), serving as a significant source of drinking water and supporting important ecosystems. During 1990, groundwater provided over 60% of the water supplied to the region for public, industrial, and agricultural uses (Molina-Rivera, 1996; 1997).

Because of the aquifer productivity, among other reasons, many pharmaceutical, chemical, and manufacturing industries settled in the North Coast of Puerto Rico, with subsequent growth

in population and urban development (Padilla et al., 2011). Many of these industries rely on the use of hazardous materials, which can enter the karst groundwater from accidental spills and deliberate disposal. Urban growth brought construction of municipal landfills and clandestine waste disposal sites. Many of the clandestine sites were developed in sinkhole depressions, which serve as a direct route of contaminants into the underlying groundwater formations. The unintended consequence of the industrial and urban development has therefore been an extensive contamination of the groundwater resources in the northern karst aquifer (Padilla et al., 2011; Hunter and Arbona, 1995)**.** Indeed, 45% of superfund sites in Puerto Rico are within the northern karst of Puerto Rico. Twelve National Priorities List (NPL) superfund sites and many other corrective actions sets under the Resources Conservation and Recovery Act (RCRA) are included in the northern region of Puerto Rico between 1983 and 2012. Nine of these NPL sites are still active, but the others could have contributed to contamination at the system level. Seven of these sites (Barceloneta Landfill, Scorpio Recycling, Upjohn, Vega Alta Landfill, Vega Baja Landfill, Papelera Puertoriqueña and Corozal Well Site) have been contaminated with chlorinated solvents including: TCE, DCE, TCM, CT, PCE, TCA, DCA and DCM. Four of the sites (Pesticide Warehouse III, Scorpio Recycling, and the Vega Baja Landfill, and the Barceloneta Landfill) have reported phthalate contamination, mostly with DBP and DEHP. Recently, the EPA issued orders to close landfills in Toa Baja, Florida, Vega Baja, Aguadilla and Santa Isabel due mainly to substantial concern of the drinking water quality associated with the landfills (USEPA, 2006). Also, in the northern area of Puerto Rico, these landfills are typically located on karst areas where pollutants can get directly to the groundwater.

Water quality surveys (Guzmán-Ríos et al, 1986) and historical assessments (Padilla et al., 2011; Yu et al., 2015) have shown significant groundwater contamination in the northern karst

aquifer of Puerto Rico. Of particular concern are CVOCs and phthalates. This contamination has extended beyond determined sources of contamination (Padilla et al., 2015)

The long and extensive history of contamination, high vulnerability for contamination, and potential for exposure and significant adverse health impact make the karst region of northern Puerto Rico an ideal site to study potential exposure to hazardous contaminants, related adverse impacts, and effective strategies to reduce exposure and protect public health and the environment. This work builds the fundamental framework for monitoring contamination in groundwater sources and tap water point of use. This is attained through strong collaboration with a multidisciplinary team of researchers for the Puerto Rico Testsite for Exploring Contamination Threats (PRoTECT) Center.

3. METHODOLOGY

The goal of this project is to monitor phthalates and CVOCs contamination in groundwater and tap water in the karst region of northern Puerto Rico and assess the distribution of contamination in groundwater and tap water. Monitoring the presence and concentration of phthalates and CVOCs in water require proper sampling and analytical methodology. Strong emphasis is placed on the development of analytical methods for the analysis of water samples. Sampling, analytical and statistical methods used in this research are described in this section.

3.1 GROUNDWATER AND TAP WATER SAMPLING

Groundwater and tap water sampling is conducted by other members of the PRoTECT Center. Groundwater samples are collected from several predetermined wells and springs throughout the karst region of northern Puerto Rico. Selection criteria and detailed information of selected sites are provided elsewhere (Irizarry, 2014). A total of 21 wells and springs sites have been sampled since 2011 (Refer to Table 17). Many sites are sampled periodically throughout the year, depending on site availability. Between 2011 and 2014, groundwater samples were collected twice a year: once around March and once around October during the historically dry and rainy seasons, respectively. A summer sampling campaign around July has been added since 2013. These sampling schemes amount to a large number of samples that must be analyzed within a short period of time. The analysis of high numbers of samples require the use of an efficient method of analysis that minimizes preparation procedures, time, and generation of solvent waste.

Table 17 Sampled Wells and Springs

Well ID	Groundwater Sampling									
	Mar 31-Apr 2, 2011	**Oct 11-13, 2011**	**Mar 12-14, 2012**	**Oct 16-18, 2012**	**Mar 12-14, 2013**	**Jun 26-28, 2013**	**Nov 12-14, 2013**	**Feb 24-26, 2014**	**Aug 12-14, 2014**	**Oct 21-23, 2014**
MON	x	x	x							
OWE	x	x	x	x	x	x				
SRA	x	x	x	x	x			x		
MAG	x	x	x	x	x			x	x	x
MA4		x								x
ARE	x	x	x	x	x	x	x	x		
MIT	x	x	x	x	x	x	x	x	x	x
HIL	x				x	x	x	x		
POL	x	x	x	x	x	x	x	x	x	x
RSO	x	x	x	x	x	x	x		x	x
FOR	x									
MAR	x									
RAM	x	x	x	x	x	x	x	x		x
MEN	x									
MA6			x	x	x		x			
ODA	x				x	x	x	x	x	x
ODG	x	x	x	x	x		x	x	x	x
ZAN	x	x	x	x	x	x	x	x	x	x
SPE					x	x	x	x	x	x
TRO					x					
MAS										x

Samples are collected following standard methods for sampling groundwater-monitoring wells (ASTM, 2013; Koterba et al., 1995; Wilde, 2010) and surface water for springs (Compton et al., 2007). Tap water samples are collected throughout the year in the houses a human subject cohort through the northern karst region of Puerto Rico. This cohort is part of an epidemiological study conducted by the PRoTECT Center and the sampling sites are selected, under strict IRB protocols, by Public Health researchers within PRoTECT. Collections of tap water samples follow a modified method from Illinois Environmental Protection Agency (IEPA, 2009).

In summary, the water samples for phthalates and CVOCs analysis are collected in 1 L amber bottles (Thermo Scientific 349-1000) and 40 mL amber glass vials (Thermo Scientific 141-40A/EP/CT), respectively. CVOCs samples are collected with zero headspaces. Ascorbic acid (Sigma 66H0926, 0.02g) and sodium thiosulfate (Fisher S445-500, 0.08g) are used as a preservative in the tap water samples for CVOCs and phthalates, respectively. No preservative are used for groundwater samples. Sample replicates and field, shipment and laboratory blanks are used for quality assurance and control (QA/QC). Samples are stored in a freezer (4^{o}C) and analyzed within 21 days of been collected. Because of the risk of phthalates contamination the use of any plastic materials is avoided during sampling.

3.2 ANALYSIS OF WATER SAMPLES

Water samples are extracted using modified LLE methods before analysis. Groundwater and tap water samples are extracted within 7 days of collection and analyzed within 14 days after extractions. Because phthalates recoveries (Table 4 -Table 9) in previous studies have shown high variability, an efficiency study is conducted for the phthalates modified method. The efficiency study is not conducted for CVOCs because the method has shown high analyte

recoveries and low recovery variability (Table 12Table 16). The extractions and analysis methods are described in greater detail below.

3.2.1 EXTRACTION METHODS

This research applies liquid-liquid extraction methods for the analysis of phthalates and CVOCs. The analysis of these contaminants requires different extraction methods for phthalates and CVOCs. These used methods are described below.

3.2.1.1 PHTHALATES EXTRACTIONS

Samples extractions of phthalates follow modifications of the EPA methods for phthalate esters (Method 606; USEPA, 1996c) and semi-volatile compounds (Method 8270D; USEPA, 2007a and Method 3510C; USEPA, 1996a). In both methods, 1L sample is extracted consecutively three times with 60 mL DCM each time, for a total of 180 mL DCM, in a separatory funnel. However, both methods use a large amount of solvent and produce a large amount of DCM waste. This work explores the development of a modified method that produces less solvent waste. Two methods are explored.

The initial method uses 1 mL DCM (Sigma-Aldrich 270997-2L) to extract 10 mL of water sample (1:10) in a 15 mL sample vial (Fisherbrand FS60920D-4). The sample is shaken for 15 minutes in a shaker and left still for 15 minutes to allow for separation of the water and solvent. The 1 mL of solvent resting at the bottom of the vial is extracted using a Pasteur pipette. Because DCM is heavier than the water phase, the pipette is introduced through the water into the solvent phase before it is drown up. This must be done very carefully to avoid withdrawing water. Then the 1-mL is transferred into a 2 mL analysis vial (National Scientific C4013-2), where it is allowed to evaporate in a fume hood using STP conditions. After proximally 8 hours, 1 mL of hexane (Sigma-Aldrich 34493-2.5L) is added to the evaporated sample for analysis in a

GC/MS. All samples including quality control samples are handled and extracted in the same way. The sample concentration is calculated using equation 2:

$$C_{w,10} = C_H * \frac{V_H}{V_W} \quad (2)$$

where: $C_{w,10}$ is the concentration in the water sample
C_H is the measured concentration of DEHP in hexane
V_H is the hexane volume (1mL)
V_w is the water volume (10mL)

In a second method, a total of 18 mL of DCM is used to extract 100 mL of water sample in a 250 mL separatory funnel (Figure 3). This modified method follows the same EPA methods water-solvent ratio, but with less volume to try to reduce DCM waste. Therefore, a water sample is extracted consecutively three times with 6 mL DCM for a total of 18 mL of solvent. The separatory funnel is sealed and shaken vigorously for 1-2 minutes with periodic venting to release excess pressure. The organic layer is allowed to separate from the water phase for a minimum of 5 minutes.

Figure 3 250 mL Separatory Funnels for Phthalates Extraction

The extracted DCM is thereafter concentrated in a Kuderna-Danish Apparatus (Organomation H6161-TUWHPL), which is placed in a water bath at approximately 75 ^{o}C (Figure 4). This apparatus consist of a 10 mL concentrator tube (inside the water bath), a 250 mL

evaporation flask (b), a three-ball 253 mm Snyder column (c), an inverted Hopkins condenser (d) and a 250 mL solvent collector (e). The concentrator is assembled attaching a 10-mL concentrator tube to a 250 mL evaporation flask. The solvent vapor recovery glassware is thereafter attached to the Snyder column of the K-D apparatus. Finally, one or two clean boiling chips are added to the flask and a three-ball Snyder column is attached to the evaporation flask. DCM is evaporated and the concentrated volume is accumulated in the concentrator tube. When the apparent volume of liquid in the concentrator tube reaches 3 mL, the K-D apparatus is removed from the water bath and allowed to drain and cool for at least 10 minutes. The concentrated DCM solvent is thereafter exchanged by adding 3mL of hexane to the apparatus. Since the hexane boiling point is 68.7 ºC and the DCM boiling point is 39 ºC (USEPA, 1996g), the DCM is evaporated entirely, and the hexane is evaporated to 1 mL in the concentrator tube. The concentrated hexane is transferred to a 2 mL vial for analysis in a GC/MS. All samples, including quality control samples, are handled and extracted in the same way. The sample concentration is calculated using equation 3:

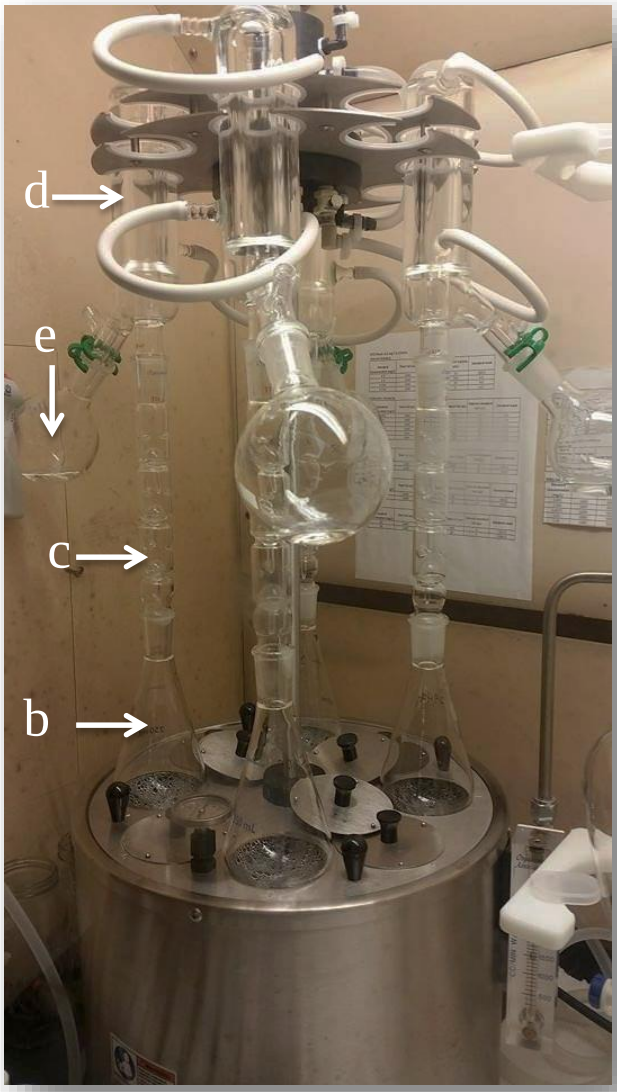


Figure 4 Kuderna-Danish (K-D) Apparatus

$$C_{w,100} = C_H * \frac{V_H}{V_W} \quad (3)$$

where: $C_{w,100}$ is the concentration in the water sample
C_H is the measured concentration of DEHP in hexane
V_H is the hexane volume
V_w is the water volume

3.2.1.2 CVOCS EXTRACTION

CVOCs extraction from water samples follows a modified procedure of the EPA Method 551.1 Method (Munch and Hautman, 1995). In this method, 50 mL sample aliquot is extracted with 3 mL of MTBE or 5 mL of pentane. This research extracts 25 mL of the CVOCs samples with 1.5 mL of MTBE (Sigma-Aldrich 850560-1L), following the same EPA methods water-solvent ratio but using less volume. Sodium chloride (5mg; Fisher BP358-10) is added to the sample to reduce the CVOC's solubility in water. The water/MTBE samples are shacked in a table shaker for 15 minutes and allowed to rest for another 15 minutes to allow for separation of the water and solvent. The solvent in each water/MTBE sample is thereafter extracted with a Pasteur Pipette and placed in a 2 mL vial for analysis un a GC/ECD. All samples, including quality control samples are handled and extracted in the same way. The sample concentration is calculated using the equation 4:

$$C_{w,CVOC} = C_{MTBE} * \frac{V_{MTBE}}{V_W} \quad (4)$$

where: $C_{w,CVOC}$ is the concentration in the water sample
C_{MTBE} is the measured concentration of DEHP in hexane
V_w is the water volume
V_{MTBE} is the MTBE volume

3.2.2 SAMPLE ANALYSIS

After extractions, samples extracts are analyzed analytically using GC techniques. Phthalates analysis is conducted using a GC equipped with a mass spectrometer. CVOCs are analyzed in a GC/ECD. The methods used are described below.

3.2.2.1 PHTHALATE ANALYSIS

Phthalates are analyzed in a GC equipped with a mass spectrometer (GC/MS Agilent Technologies 7820A GS System/Agilent Technology 5975 Series MSD; Figure 5) following a modified procedure of EPA Method 8270D (USEPA, 2014a). The 5975 Series MSD is a rectangular box, approximately 42 cm high, 26 cm wide and 65 cm deep. The basic components of the instrument are: the frame/cover assemblies, the local control panel, the vacuum system, the GC interface, the electronics, and the analyzer (Agilent, 2013). An Agilent 19091S-733HP-1MS 100% Methyl Silox Column (30m x 250µm ID, 1.00µm film thickness) is used for separations. The carrier gas is helium and the flow rate is 1mL/min. The column initial temperature and pressure are set at 100^{o}C and 10 psi, respectively. The oven temperature is programmed from 100^{o}C (1 min) at 15 ^{o}C/min to 280 ^{o}C for 8 min in a 21 min running time. The transfer line, ion source and quadrupole analyzer temperatures are maintained at 280, 230 and 150 ^{o}C, respectively and, a solvent delay of 5 min is selected. The identification of target compounds is based on the relative retention time and the

Figure 5 GC/MS used for Phthalates Analysis

relative abundance. Six ions, for each phthalate, are chosen to be monitored by the mass spectrometer detector with select ion monitoring (MS-SIM) mode according to the mass spectra characteristic. The ions are those with mass spectra of: 76, 105, 149, 150, 176, and 177 for DEP; 41,76,104, 149, 205, and 223 for DBP; 57, 70, 71, 149, 167, and 279 for DEHP.

3.2.2.2 CVOCS ANALYSIS

CVOCs extracts are analyzed in a GC equipped with electron capture detector (GC/ECD, Varian CP-3800; EPA Method 551.1; Figure 6). In a standard configuration, the CP-3800 accommodates up to three injectors and three detectors, all operating simultaneously. The standard detectors available on the 3800 are the Electron Capture Detector (ECD), and Thermionic Specific Detector (TSD). The Electron Capture Device (ECD) is selected in this project as it is proven to be very sensitive to polar halogenated compounds. Helium is used as a carrier gas, and nitrogen as a makeup gas. A J&W Scientific High Resolution Gas Chromatography Column (125-1035 DB-1) 30 m in length with a 0.53 mm ID and a 5 μm film layer is used to achieve optimum separation of CVOCs. Temperature in the GC oven is maintained at 35 ºC at injection, ramped to 200 ºC after 22 minutes and maintained there for 15 minutes. The flow pressure is maintained at 3 psi and the flow is adjusted by the instrument according to the set pressure.

Figure 6 GC/ECD used for CVOCs Analysis

3.2.2.3 ANALYTE QUANTIFICATION

The quantification of phthalates and CVOCs can be done by external or internal standard calibration (David et al., 2003; Munch and Hautman, 1995). An internal standard is a compound that must be show similar behavior to the target analyte that is added to samples, the blank and calibration standards. This substance can be used for calibration by plotting the ratio of the analyte signal to the internal standard signal as a function of the analyte standard concentration to correct analyte losses during sample preparation (Cruz de Oliveira et al., 2010). An external standard is like the internal standard (known behavior), but is not added to the unknown. Rather it is run alone, as a sample at different concentrations to generate a standard curve. The peak areas are related to the known amounts of external standard run (Cruz de Oliveira et al., 2010). The gas chromatographic system is calibrated using the external standard technique. For the phthalates and CVOC's methods, multi-point calibration curves are constructed for each analyte. For phthalates, a custom-made mix standard 1000 μg/mL (DEP, DBP and DEHP) in hexane (AccuStandard® S-21960) is used to perform the calibration curves. For CVOCs, a custom-made mix standard 1000 mg/L (CT, 1,1-DCE, 1,1,1-TCA, PCE, TCE, 1,2-DCE, 1,1-DCE, 1,2-DCA, 1,1,2-TCA and TCM) in methanol (AccuStandard® S-21973) is used to perform the calibration curves. An instrumental limit of detection (LOD) ranging between 0.5 and 1μg/L was found for phthalates, and of 0.06 μg/L for CVOCs. The instrument is calibrated every 24 hours with standard mixtures, and running calibration and system performance check compounds during samples analysis. QC samples, using calibration and system performance check compounds, is performed every 10 samples. The analysis includes method blanks, duplicates, and spike samples. Method blanks, spiked samples and replicate samples are subjected to the same analytical procedures. Blank samples are obtained from the laboratory distilled water system.

3.2.2.3.1 QUALITY CONTROL

QC of analytical methods is of vital importance for analyte quantification. QC measurements involve the injection of a QC sample with each batch of samples processed. A QC is a sample prepared to a given reference concentration value from a certified standard.

For phthalates analysis, a certified standard (AccuStandard PLAS-PL-019S) is used to prepare QC samples at 0.05 mg/L DEHP with a standard of 1000 mg/L in hexane. These QCs are injected every ten samples in the GC/MS to monitor the performance of the system. Measured QC concentrations during an analysis period from 2011 to 2014 (Figure 7) show a high variability in the measured concentrations during the first year of analysis (late 2011-2012), but lower variability for the following years (2013-2014).

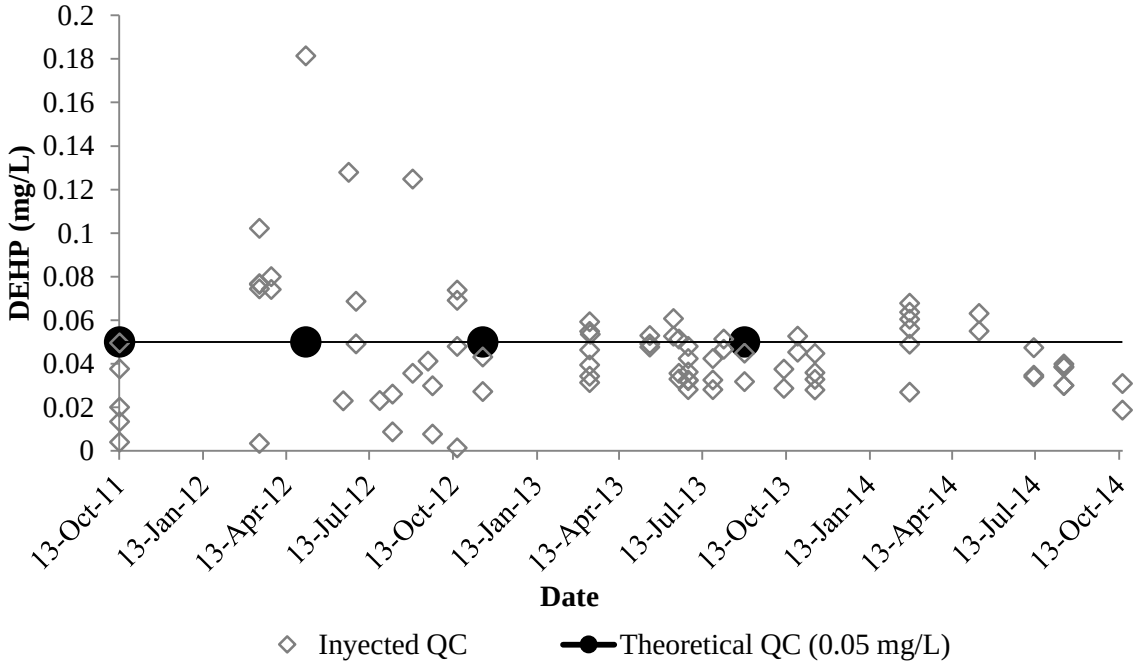


Figure 7 DEHP QC Concentrations (Dark circles indicate a standard open that day)

Errors associated with QC measurements are quantified by calculating the root-mean-square error (RMSE) and the mean absolute error (MAE) of the QC measurements. The RMSE

and MAE are the most widely reported error measurements in the climate and environmental literature (Willmott and Matsuura, 2005). Both of these error measurements are dimensioned in the units of the variable of interest (e.g., mg/L). DEHP QC measured concentrations for all QCs averaged 0.046 mg/L and show an RMSE and MAE of 0.045 and 0.042 mg/L, respectively. Because the high variability during the 1st year of analysis influence the variability of all QCs, averages and errors are also estimated for the two periods. QCs analyzed from late 2011 to 2012 show a DEHP concentration average of 0.053 mg/L, a RMSE of 0.042 mg/L, and a MAE of 0.033 mg/L. The QCs analyzed from 2013 to 2014 show a DEHP concentration average of 0.042 mg/L, a RMSE of 0.016 mg/L, and a MAE of 0.012 mg/L. Both periods have average concentrations errors within 6% and 16% of the prepared concentrations (0.050 mg/L), but the RMSE and the MAE show that the second period of analysis is more accurate and precise than the initial period.

For CVOCs analysis, a certified standard (AccuStandard PLAS-PL-019S) is used to prepare QC samples at 0.0075 mg/L TCE with a standard of 1000 mg/L in MTBE. These QCs are injected every ten samples in the GC/ECD to monitor the performance of the system. Measure QC concentrations during the analysis period from 2011 to 2014 (Figure 8) show that almost all the QCs are over the theoretical concentration estimated for the prepared QC, except for the QCs injected the same day that the standard is opened. This is attributed to differential vapor pressures between TCE and MTBE. Because MTBE has a relative higher vapor pressure than TCE (245 mmHg and 74 mmHg, respectively), it evaporates faster than TCE, causing TCE concentrations to increase. As a result TCE is more concentrated days after the standards are opened. For this reason, the QC error is estimated based on the QCs injected the same day that

the standard is opened. CVOCs QCs show an average concentration of 0.0099 mg/L TCE (representing an error of 32%) a RMSE of 0.0044 mg/L and a MAE of 0.0033 mg/L.

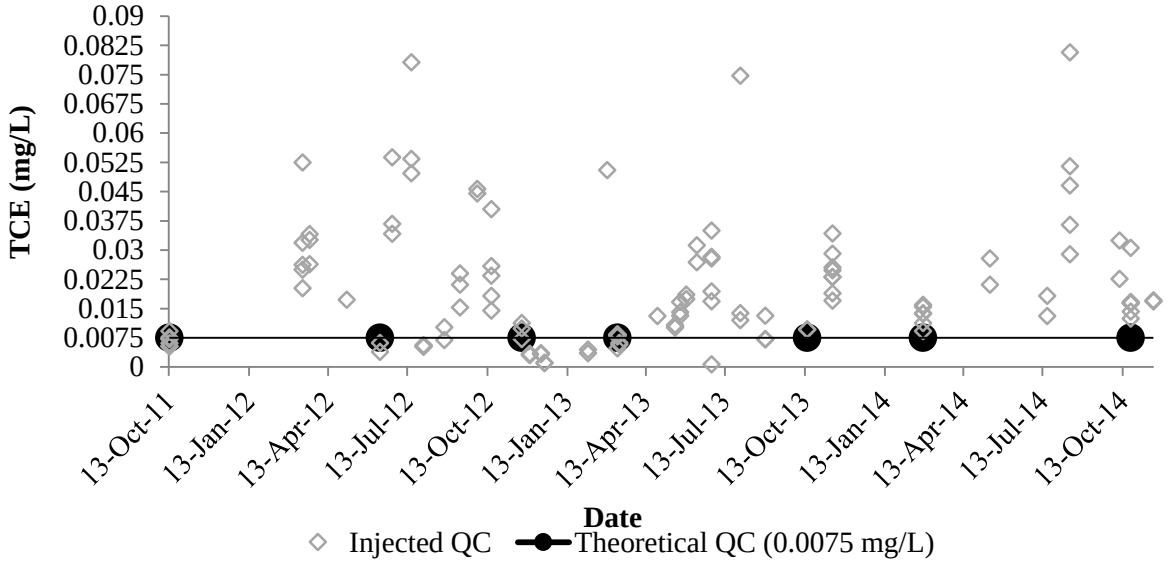


Figure 8 TCE QC Concentrations (Dark circles indicate a standard open that day)

3.2.3 SOLVENT EXTRACTION EFFICIENCIES AND PARTITIONING PROPERTIES

High variability in the percent recoveries of many phthalates, since there high potential of cross-contamination, poses analytical challenge for the proper quantification of these contaminants in water. This variability in measurements is also reflected in the wide range of values reported in the literature for physicochemical properties of phthalates contaminants, including: water solubility, and water and octanol partitioning coefficient, among others. This work performs an extraction efficiency study of the modified methods to quantify the efficiency of the solvent extraction and the precision and accuracy of the methods. Because DEHP show the highest variability in the recoveries and physicochemical properties of the targeted phthalates contaminants on this work, efficiency is quantified for DEHP.

Accuracy and precision studies for CVOCs, as well as their range of physicochemical properties, show little variability among measurements. For this reason, and the limitations, an efficiency study is not conducted for CVOCs. It is, however, recommended for future work.

3.2.3.1 PHTHALATES EXTRACTION EFFICIENCIES

The solvent extraction efficiency study consists of spiking water samples with DEHP known concentrations, and applying extraction methods to quantify measured concentrations. Efficiency tests are conducted for both extraction methods described in section 3.2.1.1. In these tests, measured concentrations are compared with estimated concentrations (theoretically calculated based on mass and volume) to calculate the efficiencies of the methods. For comparison purposes, efficiency studies are also conducted for EPA Method 3510 (USEPA, 1996a). In this method 180 mL of DCM are used to extract 1 L of water.

Water samples of known concentrations are prepared by diluting a stock solution with laboratory-grade distilled water. The stock solution is prepared in methanol using a certified standard of 1000 mg/L in methanol (AccuStandard® APP-9-029-10X). A predetermined volume of standard solution is diluted in different volumes of methanol to attain stock solution concentrations of 1.0 and 10.0 mg/L. Predetermined volumes of stock solutions are then injected into laboratory-grad distilled water to obtain estimated solution concentrations ranging between 0.00 and 0.10 mg/L. This range is assumed to be below a DEHP solubility of 0.230 mg/L, the average solubility of phthalate in water at 25^{o}C calculated using the values published by Cousins et al., (2003).

The initial extraction study (10-mL samples) assessed efficiencies at six concentrations tested in triplicates. All samples were prepared separately from the same stock solution. Four experiments are performed to obtain up to 12 replicates per concentration (Table 18). These

solution concentrations are prepared in 10 mL volumetric flasks, shaken for 30 minutes, and allowed to mix for 24 hours in a refrigerator (4ºC). Finally, the water solutions are extracted with the 10-mL water extraction method described in section 3.2.1.1 and analyzed in the GC/MS instrument. The efficiencies of the extraction are calculated as (equation 5):

$$\%Ef = \frac{C_E}{C_T} * 100 \quad (5)$$

where: %Ef is the percent of efficiency at the prepared concentration (C_T)
C_E is the experimental concentration
C_T is the theoretical concentration

Table 18 Preparation of 10-mL DEHP Water Solutions

Estimated Concentration[1] (mg/L)	Stock Solution Volume (mL)	Water Volume (mL)
0.00	0.00	10.00
0.01	0.10	9.90
0.025	0.25	9.75
0.05	0.50	9.50
0.075	0.75	9.25
0.10	1.00	9.00

[1]Based on the volume of stock solution added to a volume of water for a final total volume of 10mL. DEHP stock concentration is 1mg/L.

The 100-mL sample extraction study (second extraction method), used four concentrations (0.0, 10.0, 50.0, and 100.0 μg/L) in triplicates, which were prepared separately in a series of four experiments for a total of 12 replicates per concentration. In this method, samples are prepared from a 10 mg/L DEHP stock solution (Table 19). These concentrations are prepared in 100 mL volumetric flasks, shaken for 30 minutes, and allowed to mix for 24 hours in a refrigerator (4ºC). Finally, the water solutions are extracted with the 100-mL K-D water extraction method described in section 3.2.1.1 and analyzed in the GC/MS instrument. The efficiencies of the extraction are calculated with the Equation 5.

Table 19 Preparation of 100-mL DEHP Water Solutions

Estimated Concentration[1] (mg/L)	Stock Solution Volume (mL)	Water Volume (mL)
0.0	0.0	100.0
0.01	0.1	99.9
0.05	0.5	99.5
0.1	1.0	99.0

[1]Based on the volume of stock solution added to a volume of water for a final total volume of 100 mL. DEHP stock concentration is 10 mg/L.

The 1000-mL sample extraction study used six concentrations in triplicates, which are prepared separately in a series of three experiments to obtain up to 9 replicates per concentration. In this extraction test, the samples are prepared from a 10 mg/L DEHP stock solution (Table 20). These concentrations are prepared in 1000 mL amber bottle, shaken for 30 minutes and allowed to mix for 24 hours in a refrigerator (4^{o}C). Finally, the water solutions are extracted with the K-D water extraction method described in section 3.2.1.1 and analyzed in the GC/MS instrument. The efficiencies of the extraction are calculated with the Equation 5.

Table 20 Preparation of 1000-mL DEHP Water Solutions

Estimated Concentration[1] (mg/L)	Stock Solution Volume (mL)	Water Volume (mL)
0.00	0.0	1000
0.005	1.0	99.0
0.01	2.5	97.5
0.05	5.0	95.0
0.075	7.5	92.5
0.10	10.0	90.0

[1]Based on the volume of stock solution added to a volume of water for a final total volume of 1000mL. DEHP stock concentration is 10mg/L.

3.2.3.1.1 CONCENTRATION AND SOLVENT EXCHANGE EFFICIENCY

The 100- and 1000-mL sample studies consist of three steps: water extraction, solvent concentration (evaporation), and solvent exchange. To evaluate possible losses in the process, individual experiments are performed for each step for the 100-mL sample study. To assess the efficiency in the concentration and solvent exchange steps, four DEHP concentrations (0, 10, 50, and 100 μg/L) are prepared in DCM from 1 mg/L DEHP stock solution. These concentrations are prepared in 50 mL volumetric flask. Because the 100-mL sample study uses 18 mL of DCM for the extraction process, 18 mL of the prepared samples are evaporated in the K-D apparatus twice per concentration. The concentrated DCM solvent is thereafter exchanged by adding 3mL of hexane to the apparatus, and the hexane is evaporated to 1 mL in the concentrator tube. The concentrated hexane is transferred to a 2 mL vial for analysis in a GC/MS.

3.2.3.2 PHTHALATES PARTITIONING IN DCM

Quantification of DEHP partitioning into DCM solvent is based on a mass balance approach, in which the equilibrium solvent concentration in equation 1 is the measured concentration and the equilibrium water concentration is calculated using a mass balance equation (equation 6):

$$C_{wf} = \frac{(C_{wi} * V_w) - (C_s * V_s)}{V_w} \quad (6)$$

where: C_{wf} is the final concentration of the analyte in water after water extraction (water concentration in equation 1).
C_{wi} is the initial concentration of the analyte in water before the water extraction
V_w is the water volume
C_s is the concentration of the analyte in solvent after the water extraction
V_s is the extraction solvent volume

The DEHP partitioning coefficient (K_D in equation 1) between water and the solvent is estimated as the slope of a graph plotting the concentrations of the analyte in the solvent (C_s) vs. the final concentration of the analyte in water (C_{wf}).

3.3 DATA ANALYSIS

Statistical analysis is a essential aspect of environmental monitoring. To evaluate efficiencies and partitioning properties of the sample studies, basic statistical analysis is performed. Basic statistical analysis is applied to calculate quantile distribution, averages and standard deviations; generate box plots; among others. Variance and covariance analysis using SAS (SAS Enterprise Guide® 5.1) is applied to assess differences between experimental methods.

4. RESULTS AND DISCUSSION

This chapter presents the results obtained in this study and their respective discussion. The results include the extraction methods efficiencies, a suggested partitioning coefficient of DEHP between water and DCM, and a distribution analysis of phthalates and CVOCs in groundwater and tap water.

4.1 DEHP EXTRACTION METHODS EFFICIENCIES

Because of the complexity that represents the phthalates analysis, efficiency studies were performed to establish the capability of each phthalate extraction method used in this research. For this analysis distilled water samples were spiked with a DEHP standard in methanol, (refer to section 3.2.3.1). Samples were extracted following the three phthalates extraction methods mentioned in section 3.2.1.1 and analyzed in a CG/MS as is discuss in section 3.2.2.1. To evaluate possible losses in the K-D apparatus process (water extraction, solvent concentration, and solvent exchange) individual experiments are performed for each step.

A plot of experimental (C_{exp}) and theoretical (C_{theo}) concentrations for the 10-mL sample extracts (Figure 9) shows a positive linear tendency, indicating higher experimental concentrations for higher theoretical concentrations. A slope lower than one indicates a low recovery of the contaminant in the extraction. The data also shows a high variability between the replicates, and background levels about zero. Blanks, which are supposed to be zeros, show detection in almost all replicates. The average DEHP concentration for blanks (Figure 10) in the 10-mL samples study was 1.2 µg/L. This is attributed to possible cross-contamination during samples preparation, despite the great effort made to avoid the contamination. This background level may come from the sample preparation (e.g. water, standards, pipets, glassware, etc.),

sample extraction (e.g. solvents, funnels, glassware, etc.) or the samples analysis. It is assumed for this research the background result from sample preparation and extraction treatments.

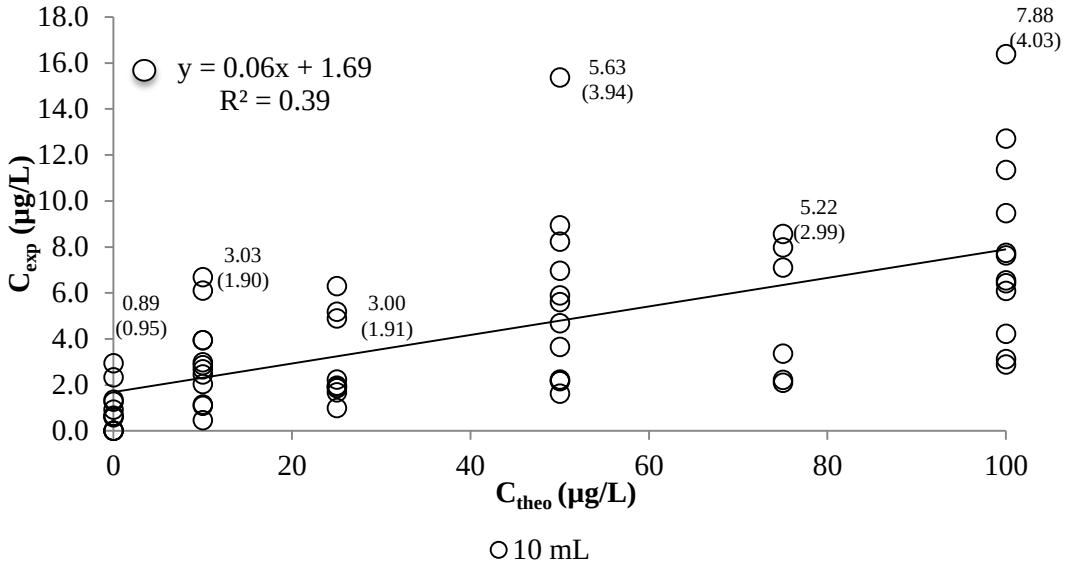


Figure 9 Linear Correlation between Theoretical (C_{theo}) and Experimental (C_{exp}) Concentrations for the 10-mL Samples Study: Number for each theoretical concentration represents average experimental concentrations; numbers in parenthesis show standard deviations

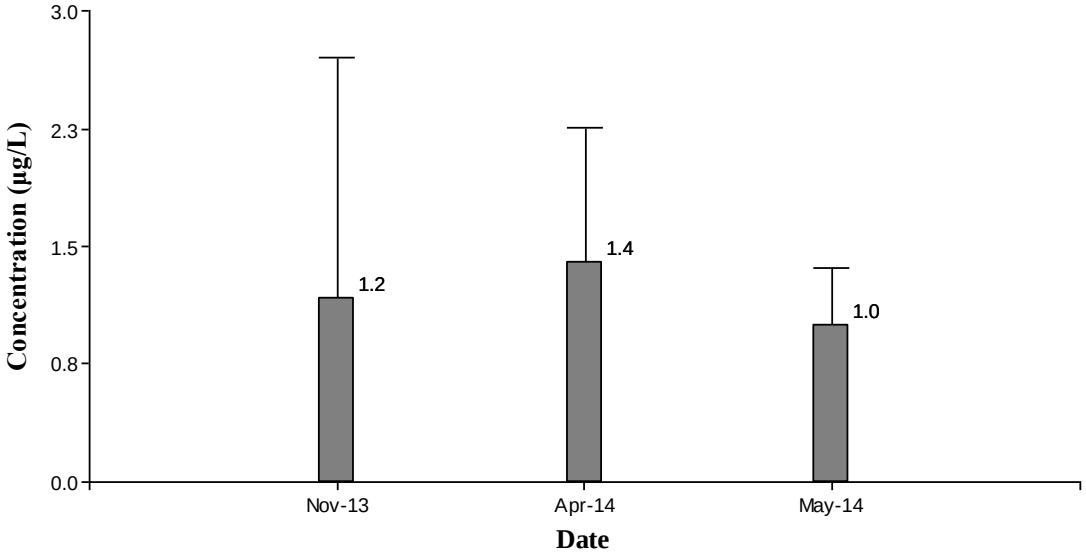


Figure 10 Average Blank Concentrations in the 10-mL Samples Study per Experiment. Bars and Numbers represent the Average Blanks Concentration per Study

To calculate the recoveries or percent efficiencies (Table 21), the theoretical concentrations are considered as the sum of the prepared concentration plus the higher background concentration found in the blanks. For example, the concentrations that are supposed to be zero will be now 2.9 µg/L, which is the highest concentration measured in blank samples. With this presumption, the ranges of recoveries for each concentration are calculated considering the background error in the calculations. Table 21 shows high variability on the recoveries for the 10-mL samples study, ranging from 2.7 to 51.9%. Similar to the EPA methods reports (USEPA, 1994; 1996c; 1996d; 2014) recoveries are found to be directly related to the concentration of DEHP. In the case of the 10-mL sample study, lowest average recoveries 6.7 and 7.6% are observed for the highest concentration (77.9 and 102.9 µg/L, respectively), and a highest average recovery of 30.7% is observed for the lowest concentration (2.9 µg/L).

Table 21 Efficiencies Estimates for the 10-mL Sample Study per Concentrations

Compound	Adjusted Concentration (C_o +HBG) (µg/L)	Range of Recovery (µg/L)	Average Recovery (µg/L)	Standard Deviation (µg/L)	Range of Percent Recovery (%)	Average of Percent Recovery (%)
DEHP	2.9	0.0 – 2.9	0.89	0.96	0.0 - 100	30.7
	12.9	0.47 – 6.7	3.0	1.9	3.6 – 51.9	23.3
	27.9	1.0 – 6.3	3.0	1.9	3.6 – 22.6	10.7
	52.9	1.6 – 15.4	5.6	3.9	3.0 – 29.1	10.6
	77.9	2.1 – 8.6	5.2	3.0	2.7 – 11.0	6.7
	102.9	2.8 – 16.4	7.8	4.0	2.7 – 15.9	7.6

C_o = Prepared concentration in water samples
HBG = Highest background concentration
Based on 12 replicate per concentration.

A plot of experimental versus theoretical concentrations (Figure 11) for the 100-mL sample extraction show, as expected, a positive linear tendency, but is higher than the 10-mL sample study (Figure 9). A higher slope indicates a higher recovery of the contaminant in the extraction, although full recoveries are not achieved. Similar to the 10-mL samples extractions, data shows high variability between the replicates and above-zero detection for blanks.

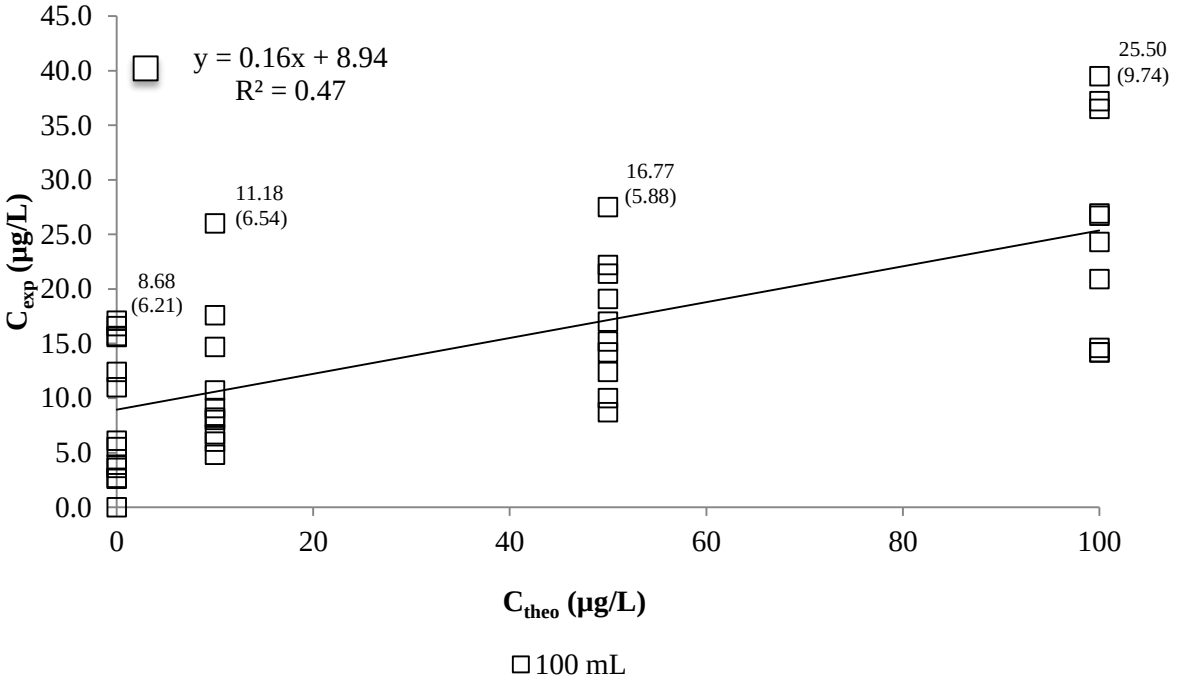


Figure 11 Linear Correlation between the Theoretical (C_{theo}) and Experimental (C_{exp}) Concentrations for the 100-mL Samples Study. Number for each theoretical concentration represents average experimental concentrations; numbers in parenthesis show standard deviations

Blanks DEHP concentrations in the 10- mL samples study, averaged 9.2 µg/L (Figure 12). This background involves an error that may come from sample preparation (e.g. water, standards, glassware, etc.), sample extraction (e.g. solvents, funnels, etc.), sample concentration

(K-D apparatus) or sample analysis (GC/MS). Blanks backgrounds have been decreasing overtime (Figure 12), due to improvement of technique and analysis.

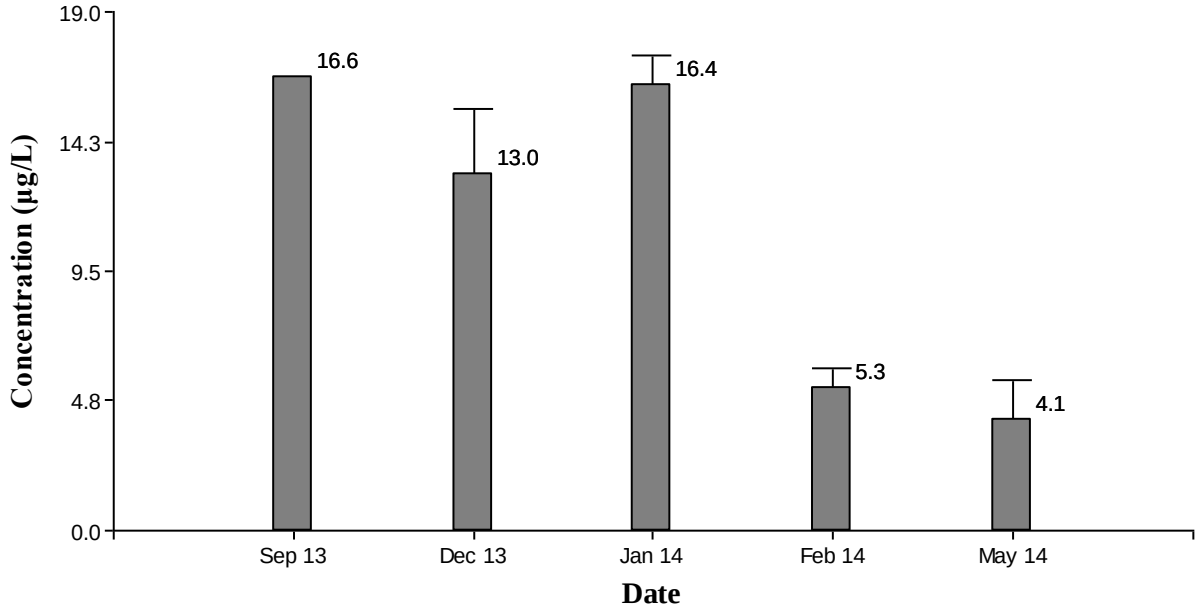


Figure 12 Average Blank Concentrations Overtime in the 10- mL Sample Study per Experiment. Bars and Numbers represent the Average Blanks Concentration per Study

Recovery estimates (Table 22) were calculated as described for the 10-mL sample study. Briefly, the highest concentration measured in the blanks was added to the $C_{theo,}$ and the C_{exp} was divided by the adjusted value to estimate the recovery efficiency. Recoveries for 100-mL sample study range widely from 13.0 to 95.9%. Similar to the previous study (10-mL samples), recoveries are found to be directly related to the concentration of DEHP having the lowest average recovery (21.8%) for the highest concentration (117.1 µg/L) and the highest average recovery (54.9%) for the lowest concentration (17.1 µg/L).

Table 22 Efficiency Estimates for the 100-mL Sample Study per Concentrations

Compound	Adjusted Concentration (C_o +HBG) (µg/L)	Range of Recovery (µg/L)	Average Recovery (µg/L)	Standard Deviation (µg/L)	Range of Percent Recovery (%)	Average of Percent Recovery (%)
DEHP	17.1	2.6 – 17.1	9.4	8.6	15.2 – 100.0	54.9
	27.1	4.8 – 26.0	11.2	6.5	17.7 – 95.9	41.3
	67.1	8.7 – 27.5	16.8	5.9	13.0 – 41.0	25.0
	117.1	14.2 – 39.5	25.5	9.7	12.1 – 33.7	21.8

C_o = Prepared concentration in water samples
HBG = Highest background concentration
Based on 12 replicate per concentration

A plot of C_{exp} versus C_{theo} for the 1000-mL sample extractions (Figure 13) shows a positive linear tendency with a slope that range slightly higher than 100-mL sample studies. Although the data shows high variability between the replicates, specifically in the higher concentrations, blanks show lower concentration detections.

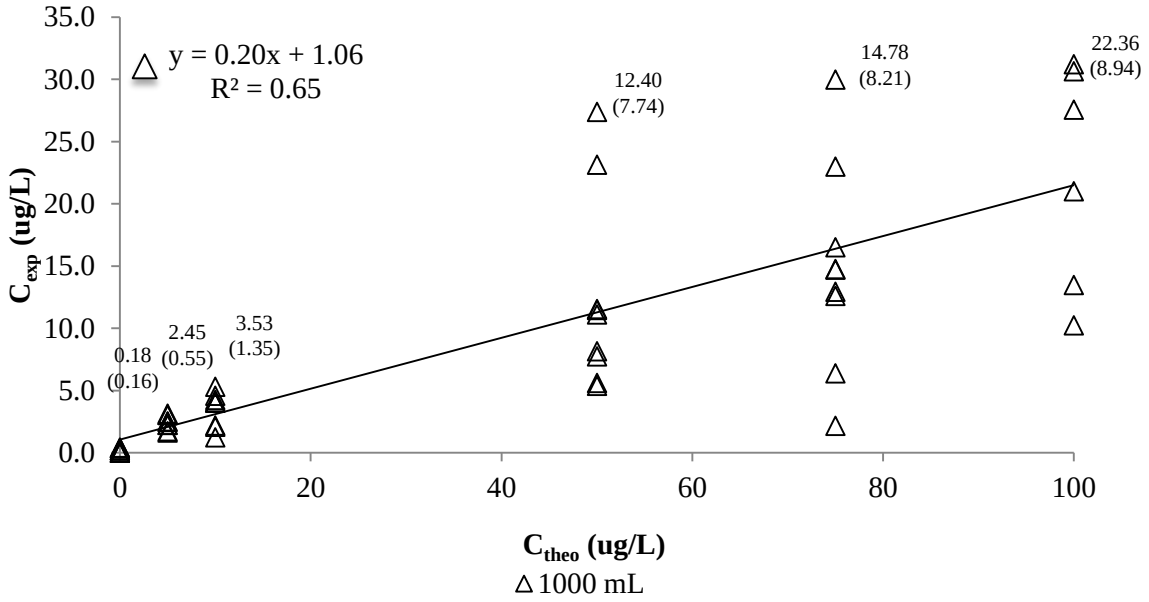


Figure 13 Linear Correlation between the Experimental (C_{exp}) and the Theoretical (C_{theo}) Concentrations for the 1000-mL Samples Study. Number for each theoretical concentration represents average experimental concentrations; numbers in parenthesis show standard deviations

Blanks DEHP concentrations for the 1000-mL sample extractions (Figure 14) detected an average of 0.3 µg/L. This is the lowest background found in all efficiencies studies. Although the reason for this is unknown, these results suggest that greater samples volumes yield lower background concentrations and suggest that the background contamination is related to a less extent to the water and solvent sources. It is possible that a greater volume to contact area of sample vials and separatory funnels results in lower background contamination.

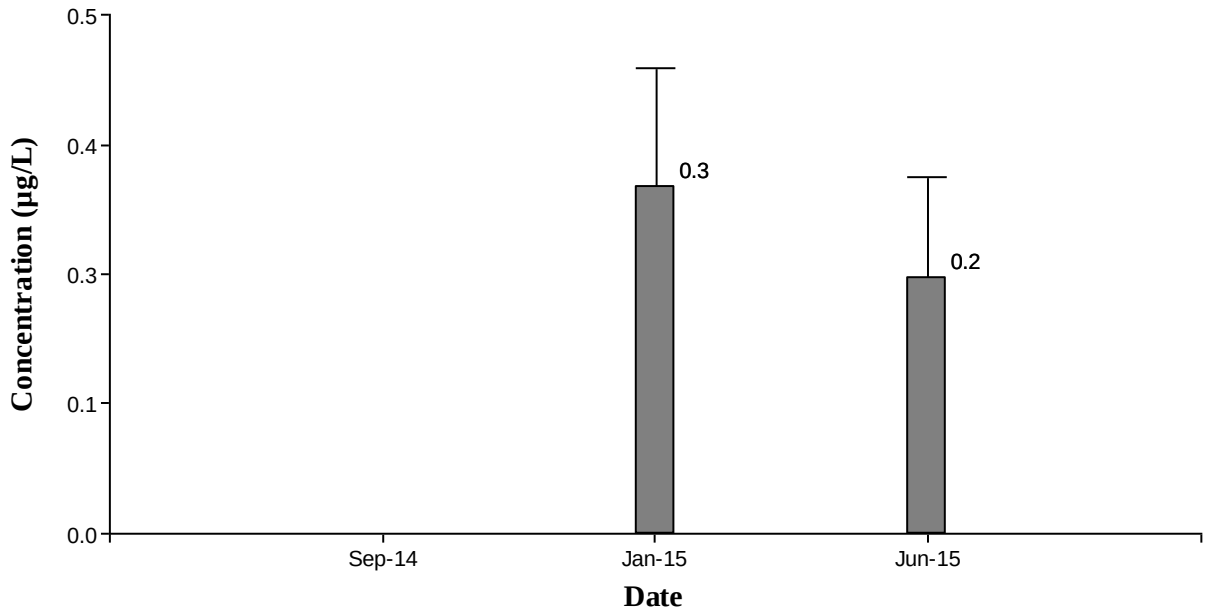


Figure 14 Average Blank Concentrations Found in the 1000-mL Samples Study per Experiment

Final recoveries for the 1000-mL sample tests, assumed a background DEHP concentration of 0.4 µg/L, which is the highest blanks concentration in these tests. Recoveries for the 1000-mL sample tests (Table 23) show a range from 2.9 to 57.4%. Similar to the 10-mL and 100-mL sample tests, recoveries are found to be directly related to the concentration of DEHP, having the lowest average recovery (19.6%) for the one of the highest concentration (75.4 µg/L) and the highest average recovery is (44.4%) for the lowest concentration (0.4 µg/L), respectively.

Table 23 Efficiencies for the 1000-mL Sample Study

Compound	Adjusted Concentration (C_o +HBG) (µg/L)	Range of Recovery (µg/L)	Average Recovery (µg/L)	Standard Deviation (µg/L)	Range of Percent Recovery (%)	Average of Percent Recovery (%)
DEHP	0.4	0.0 – 0.4	0.2	0.2	0 - 100	50.0
	5.4	1.6 – 3.1	2.4	0.6	29.6 – 57.4	44.4
	10.4	1.2 – 5.3	3.5	1.4	11.5 – 50.9	33.6
	50.4	5.4 – 27.4	12.4	7.7	10.7 – 54.4	24.6
	75.4	2.2 – 30.0	14.8	8.2	2.9 – 39.8	19.6
	100.4	10.2 – 31.2	22.4	8.9	10.2 – 31.1	22.3

C_o = Prepared concentration in water samples
HBG = Highest background concentration
Based on up to 9 replicate per concentration.

A comparison of C_{exp} vs C_{theo} slopes for the 10-, 100-, and 1000-mL sample tests (Figure 15) suggest 100-mL and 1000-mL sample extractions are more efficient that the 10-mL study. To assess if the slopes are significantly different among the tests, an analysis of covariance using a statistical program (SAS) is performed. In the analysis, the 1000-mL tests is used as the control because, it is the volume that EPA uses in their methods. Comparison of the 10-mL and 1000-mL studies, yield a p-value of 0.0004 indicating a significant difference between the slopes within a 95% of confidence interval. A p-value of 0.9758 is obtained when comparing the 100-mL and 1000-mL studies, indicating no significant difference. This suggests similar efficiencies for these tests. Table 24 shows the slopes, intercepts, linear distribution coefficient (R^2), and range of recoveries for each study. Despite sample variability, the linearity of the regressions (R^2) shows that measured concentrations vary linearly with theoretical concentrations. Although blanks background is considered in the recovery measurements, 100-mL samples study shows the highest range of percent recovery (12.1–95.9 %). Analysis of variance between percent recoveries of the different sample extraction volumes, show a p-value of 0.0001 and 0.0184 when comparing the 10-mL and 100-mL study with the 1000-mL study, respectively. This means that the 10 mL study recoveries are significantly different to the others two studies. Conversely, the 100 mL study and 1000 mL study, with a p-value of 0.09 are not significantly different. Therefore, although percent of recoveries for the 100 mL study seems to be different to the 1000 mL study in Table 24, statically they are not.

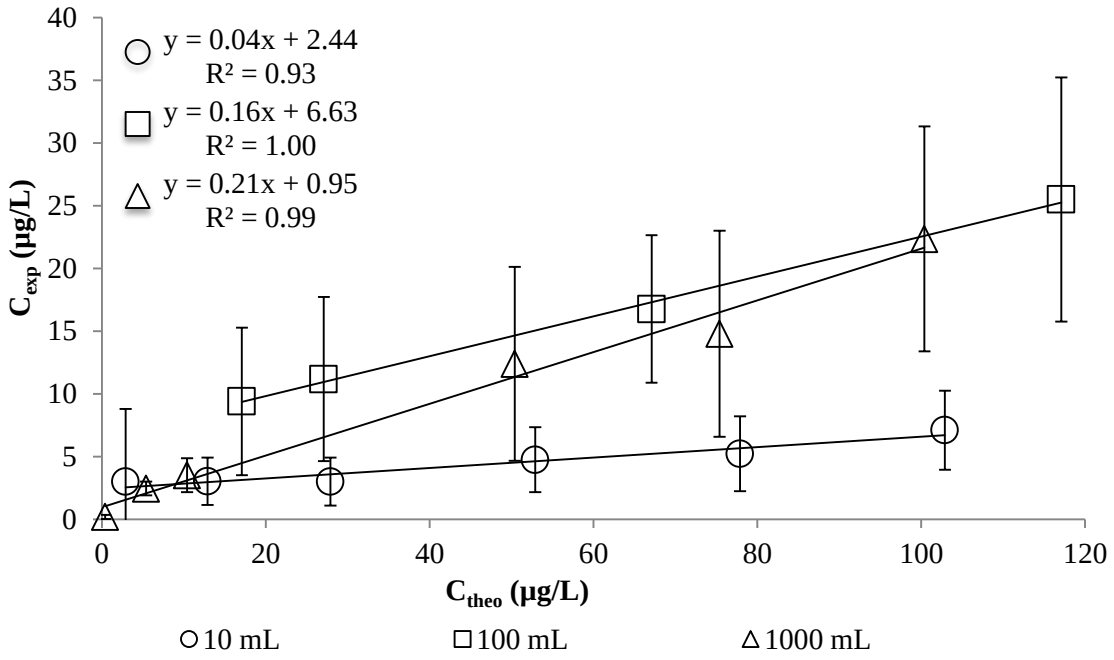


Figure 15 Linear Correlations between the Theoretical (C_{theo}) and Experimental (C_{exp}) Concentrations for Sample Extractions Studies. Error bars represent Standard deviation of estimates

Table 24 Summaries Linear Regression Parameters for C_{theo} vs C_{exp} Relationships and Average Percent Recoveries of Samples Extraction Studies

Sample Extraction Study	Slope	Intercept (µg/L)	R^2	Range Percent of Recovery (%)
10-mL	0.04	2.44	0.93	2.7 – 51.9
100-mL	0.16	6.63	1.00	12.1 – 95.9
1000-mL	0.21	0.95	0.99	2.9 – 57.4

4.1.1 CONCENTRATION AND SOLVENT EXCHANGE EFFICIENCY

Since the water extraction studies demonstrated low recoveries, an individual experiment was performed to assess the efficiency in the concentration (evaporation) and solvent exchange steps. A plot of experimental (C_{exp}) and theoretical (C_{theo}) concentrations (Figure 16) shows a positive linear tendency. A slope of almost one indicates high recoveries of the contaminant in

the concentration and solvent exchange steps. Blanks, which are supposed to be zeros, show a low detection in all replicates (1.4 - 3.3 µg/L).

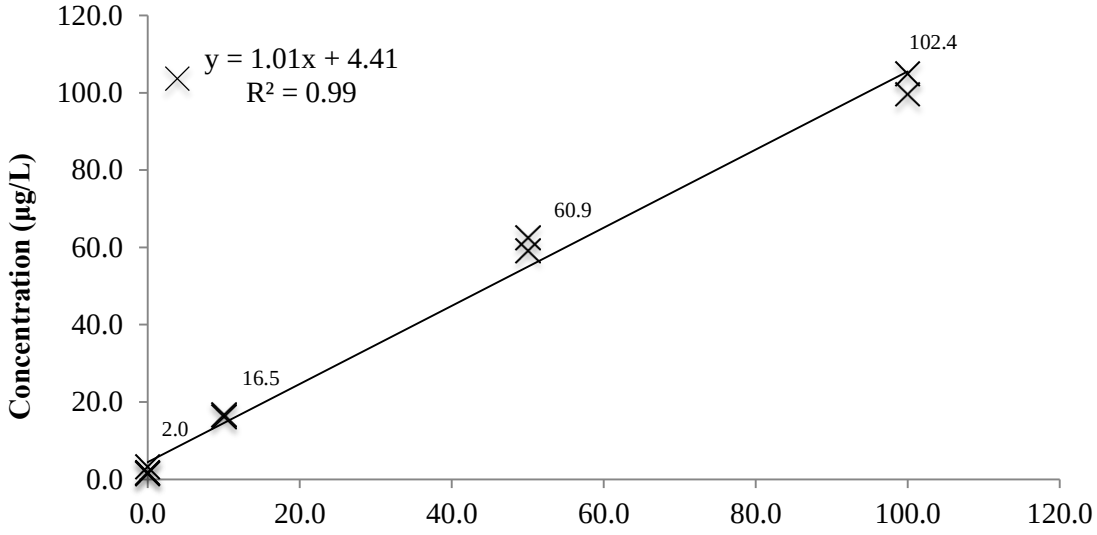


Figure 16 Linear Correlations between the Experimental (C_{exp}) and the Theoretical (C_{theo}) Concentrations for the Concentration (Evaporation) and Solvent Exchange Study. Number for each theoretical concentration represents average experimental concentrations.

Table 25 shows high average recoveries in all concentrations. Similar to the previous studies recoveries are found to be directly related to the concentration of DEHP. In this case, a lowest average recovery 102.4% is observed for the highest concentration (100.0), and a highest average recovery of 164.4% is observed for the lowest concentration (10.0 µg/L). Recoveries higher than 100% in the concentration and solvent exchange step suggest potential solvent contamination or may also result from solvent volume errors in the concentration step. However, recoveries indicate no losses in these steps. Therefore, it can be determined that the efficiency-limiting step of the methods is at the liquid-liquid extraction step.

Table 25 Efficiencies for the Concentration and Solvent Exchange Study per Concentrations

Compound	Concentration in DCM (µg/L)	Range of Recovery (µg/L)	Average Recovery (µg/L)	Average of Percent Recovery (%)
DEHP	0.0	1.4 – 3.3	2.4	-
	10.0	16.2 – 16.6	16.4	164.0
	50.0	59.2 – 62.5	60.9	121.8
	100.0	99.7 – 105.1	102.4	102.4

4.2 DEHP PARTITIONING COEFFICIENT BETWEEN DCM AND WATER

Concentration solvent exchange studies indicate that most of the losses in the procedure occur during the liquid-liquid extraction process, and that the contaminant does not transfer entirely to the solvent in the extraction process. As result this can be envisioned as a partitioning process in which the partition coefficient between water and DCM is given by equation 7. All calculations are made using adjusted initial concentrations (i.e., prepared concentration plus highest blanks background). A plot of C_{wf} versus C_s is built to predict the partitioning coefficient with the following regression (7):

$$C_s = K_{s,w} C_{wf} \tag{7}$$

where:

C_s is the DEHP concentration in the solvent after the extraction

C_{wf} is the remaining concentration of DEHP in water

$K_{s,w}$ is the partitioning coefficient of DEHP between DCM and water

Plots of C_{wf} vs C_s for the 10-mL sample experiments (n=4, Figure 17a), 100-mL sample experiments (n=4, Figure 17b), and 1000-mL sample experiments (n=3, Figure 17c) show linear behavior within experiments, with same variability among experiments. Average slopes

representing the K_{sw} for each experimental condition (Table 26) show a lower slope for the 10-mL samples (0.86 ± 0.43) than for 100-mL (1.46 ± 0.43), and 1000-mL (1.35 ± 0.51) sample experiments and suggest lower recoveries for the 10-mL samples.

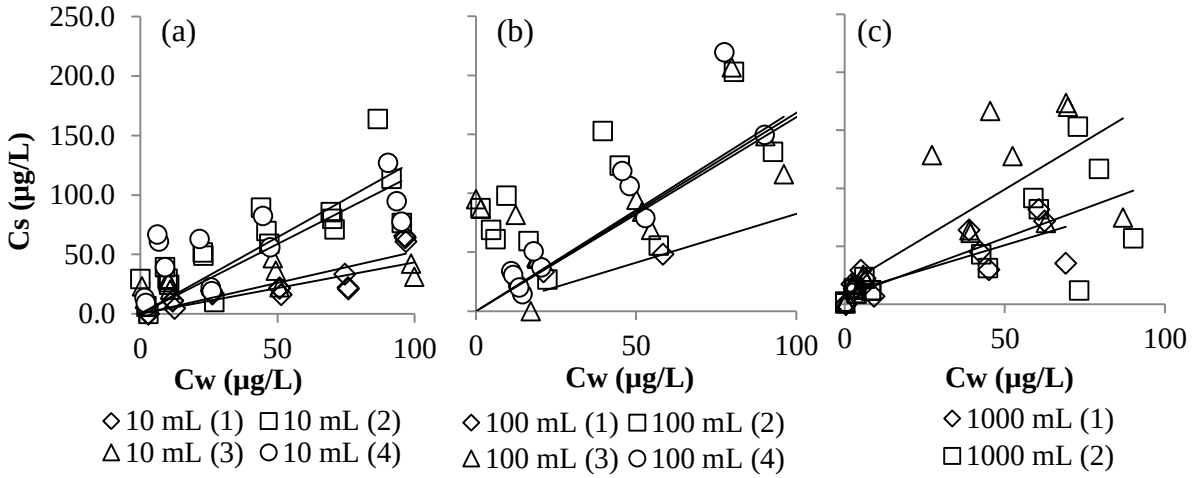


Figure 17 Plots of Equilibrium C_w vs C_s per experiment for: (a) 10-mL Sample Study; (b) 100-mL Sample Study; and (c) 1000-mL Sample Study. Lines Represent Linear Regressions Models Described in Table 26

Table 26 Average Partitioning Coefficients per Study

Study	Slope (K_{sw})	R^2	$\bar{K}_{sw}$ Average per Experiment	$\bar{K}_{sw}$ Standar Deviation
10-mL	0.54	0.8	0.86	0.43
	1.28	0.71		
	0.43	0.36		
	1.17	0.59		
100-mL	0.82	0.97	1.46	0.43
	1.64	0.22		
	1.71	0.42		
	1.68	0.6		
1000-mL	1.01	0.61	1.35	0.51
	1.11	0.67		
	1.94	0.58		

C_{wf} vs C_s plots of averages of all replicates per experimental sample volume (Figure 18) yield average slopes ($\overline{K}_{sw}$) that range within the values obtained from individual experiments (Table 26). Similar to the previous regressions (Figure 17) the standard deviations show a wide variability. A statistical analysis is, therefore, applied to compare the slopes among experimental conditions.

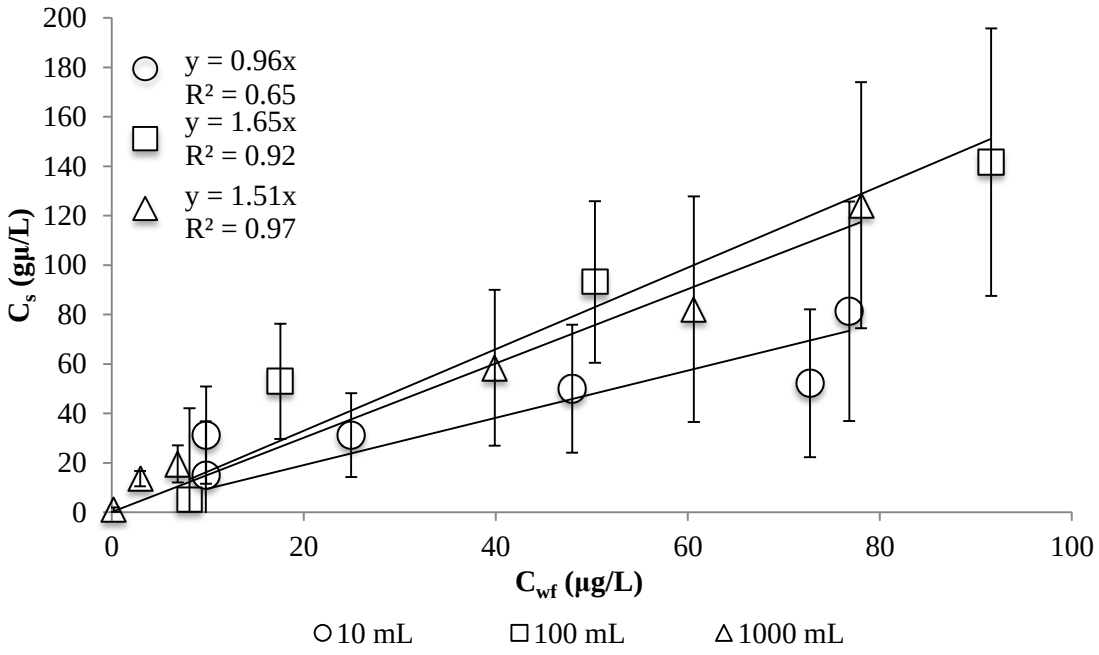


Figure 18 Plots and Linear Regressions of Averages C_{wf} vs C_s per Experimental Volume

To assess if a significant difference exists between the tests, an analysis of covariance in a statistical program (SAS) is performed. The 1000-mL study is used as the control because it is the volume that EPA uses in their methods (USEPA, 2014a). A comparison of 10- and 1000-mL studies yield a p-value of 0.0049, indicating significant difference between the slopes with a 95% confidence interval. A p-value of 0.2492 is obtained when the 100- and 1000-mL studies are compared, indicating no significant difference between the slopes. Because a comparison of the tests suggest that 100- and 1000-mL sample extractions are more efficient that the 10-mL

extraction and there is no significant difference between them, the DEHP partitioning coefficient between water and DCM is described using the averages values for the 100- and 1000-mL studies (Figure 19). This regression result in an overall partitioning coefficient of K_{sw} =1.59. Although this overall regression yields a strong linear model with a R^2 = 0.94, there is still a high variability within the average concentrations values, as shown by the error bars in Figure 19.

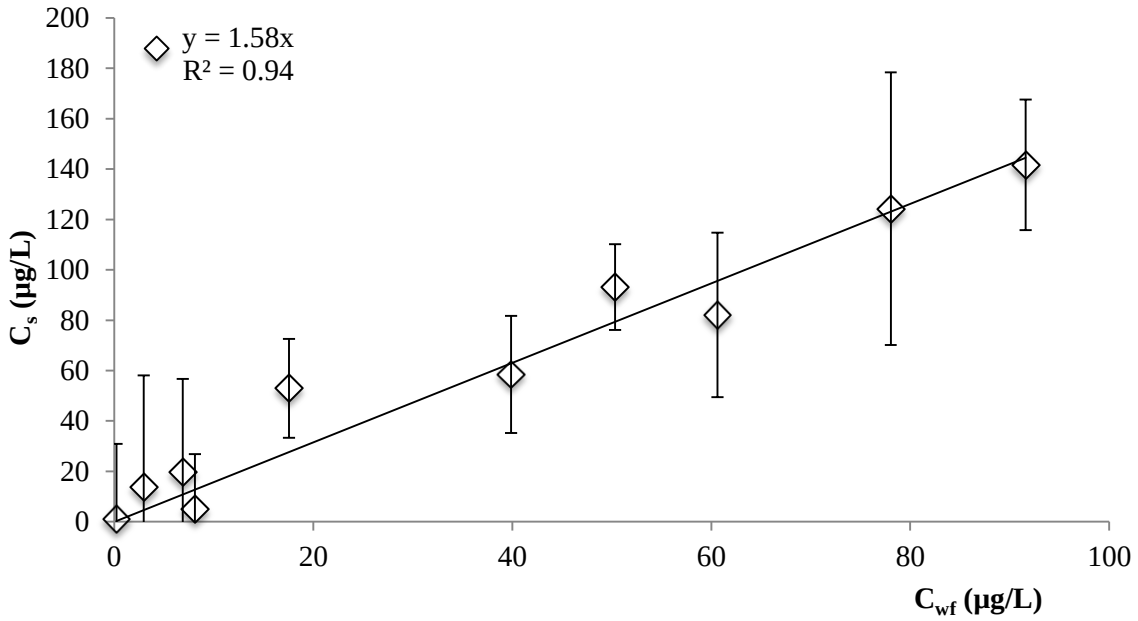


Figure 19 Plot and Linear Regression of Average C_{wf} vs C_s for 100- and 1000-mL Experimental Volumes

Since a partitioning coefficient of DEHP between water and DCM is not found in the literature, this research performed a comparison between the K_{sw} found in this study and the octanol/water partitioning coefficients (K_{ow}) found in the literature. In the literature review, the K_{ow} of DEHP varies by orders of magnitude, implying that the variability is very common in the phthalates studies (Stanely et al., 2003). Moreover, the partitioning coefficient found in this research, $\log K_{sw}$ = 0.20, is orders of magnitude lower that is the average $\log K_{ow} \approx 7.26$ found in the literature (Table 1). The much lower partition values for the DCM-water system is explained

by the lower compatibility of the DEHP with the DCM (related to octanol), and by cosolvency effects of the solvent in water.

DEHP is considered a hydrophobic compound (ATSDR, 2002) and would be more compatible with the less polar octanol than more polar DCM solvent. The cosolvency effect occurs when the presence of a solvent influences the solubility of a component in another solvent. Although DCM is considered immiscible in water, it is really a partially miscible organic solvent (PMOS) because it has a finite solubility in water (Pinal et al, 1990). According to Pinal et al. (1990), polar PMOSs have greater cosolvent effect, not because they are stronger solvents, but because they are present in greater concentrations in water as a result of their higher aqueous solubilities (~10^4mg/L or 1% volume fraction). Therefore, the higher the solubility of a PMOS, the greater its impact on the solubility of hydrophobic organic chemicals (HOC). In this case, DCM is a relative polar organic solvent with a water solubility of 1.3g/100mL at 20^o C, and has a specific gravity of 1.3. Hence, the percent of DCM in solubility is almost 1% per volume. It can be noted that the solubility of DCM in water is order of magnitudes higher than that of DEHP (~ 0.230 mg/L, Table 1). This suggests that a portion of the contaminant would be energetically favorable to stay in the water in the presence of the solvent. On the contrary, n-octanol has a very low solubility in water (0.003g/100mL @ 20^o C) despite it has an OH group, n-octanol is a big molecule mostly made up of hydrocarbons which is nonpolar. Since DEHP is a very hydrophobic organic chemical (i.e. water solubility ~0.2 mg/L) it would be more akin to octanol than DCM, which is a more polar organic solvent much more soluble in water.

4.3 GROUNDWATER AND TAP WATER DETECTIONS

This section describes the concentration ranges and statistics for phthalates and CVOCs in groundwater and tap water samples collected between 2011 and 2014. CVOCs analysis involves extracting 25 mL of water with 1.5mL of MTBE in the presence of 5mg of NaCl, and it is consistent throughout the sampling period. Analysis of phthalates, however, relied on two methods. The phthalates extraction method used before 2014 for samples analysis, both groundwater and tap water, applied the 10-mL water extraction method. The 100-mL water extraction method (K-D method) started at the beginning of 2014. Samples concentrations have not been yet corrected from extraction efficiencies.

4.3.1 DETECTION IN GROUNDWATER

Groundwater samples have been obtained from the karst region of northern Puerto Rico from 2011 to 2014. The samples include 22 wells and springs, which have been sampled up to 10 times. At least one phthalate have been detected in 96 of 253 samples (37.9%) and overall in 17 of 22 sampled wells and springs (77.3%). DBP is the most detected phthalate in groundwater, which is found in 16 of 22 wells and springs (72.7%) and in 22.5% of the samples. DEP and DEHP have been found in 11 and 12 of 22 sampled wells and springs (50.0% and 54.6%) and in 10.3% and 16.2% of de samples, respectively. The higher average concentrations of phthalates in wells are for DEP and DEHP (Figure 20a) with averages of 6.3 µg/L and 6.1 µg/L, respectively, followed by DBP with 3.8 µg/L. The median concentrations are, however, higher for DBP (3.2 µg/L) than for DEP (2.6 µg/L) and DEHP (2.1 µg/L) because of the large number of outliers found in the later two phthalates, with values reaching up to 36.6 µg/L and 74.0 µg/L, respectively (Figures 20b and 20c).

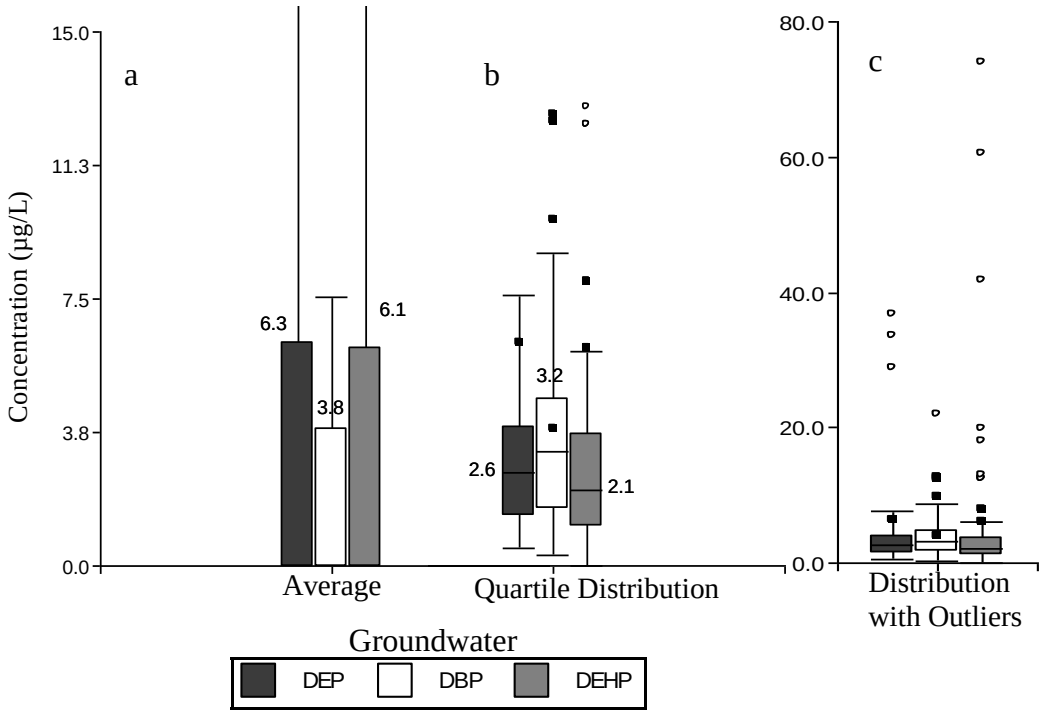


Figure 20 Concentrations of Phthalates in Groundwater: (a) Average Concentrations; (b) Quartile Distributions; (c) Distribution with Outliers

At least one detection of CVOCs has been found in 140 of 293 samples (47.8%) and overall in 18 of 22 sampled wells and springs (81.8%). TCM is the most common CVOC found in groundwater (72.7%) per wells and springs and 29.3% per samples, followed by PCE and TCE with 50.0% and 36.4% of detection per wells and springs and 23.8% and 10.6% per samples, respectively. Finally, CT is the less common CVOC in groundwater with 13.6% per wells and springs and 6.8% per samples. The highest average CVOC concentrations found in groundwater is for TCE, shown in Figure 20a, with an average concentration of 4.8 µg/L, followed by TCM with 4.1 µg/L, PCE with 1.0 µg/L, and finally CT with 0.4 µg/L. Although TCM seems to show similar concentrations to TCE in groundwater, TCM has a lower concentrations distribution than TCE (Figure 21b) with medians of 1.6 µg/L and 4.5 µg/L, respectively. A TCM outlier of 60.3 µg/L increases the average concentrations of TCM (Figure

21c). In summary, TCE has the higher concentrations of CVOCs in groundwater while CT has the lowest concentrations of sampling sites.

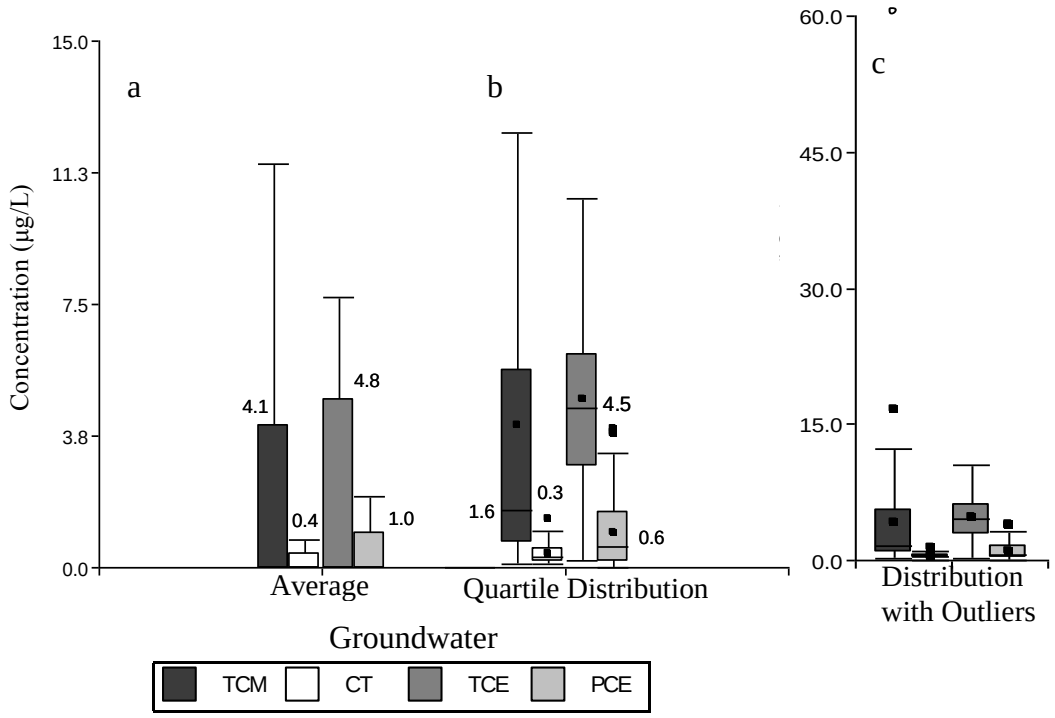


Figure 21 Concentrations of CVOCs in Groundwater: (a) Average Concentrations; (b) Quartile Distributions; (c) Distribution with Outliers

Most of phthalates and CVOCs found in groundwater have a Maximum Contamint Level (MCL) established by EPA, except for DEP and DBP (Table 27). Two of the seven contaminants found in groundwater have exceeded their MCL. These contaminants are DEHP and TCE. The MCL for DEHP is 6 µg/L and concentrations up to 74 µg/L have been found in groundwater for this contaminant. The MCL for TCE is 5 µg/L and concentrations up to 10 µg/L have been found in groundwater. The maximum concentrations found in groundwater per contaminant are show in Table 27.

Table 27 Summary of Minimum, Maximum and Average Concentrations of Detected CVOCs and Phthalates in Groundwater

Contaminant	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	*Average Concentration (µg/L)	Samples with Detection Above MCL	**MCL (µg/L)**
TCM	0.0	60.3	3.7	0/76	70
CT	0.0	1.4	0.2	0/19	5
TCE	0.0	10.0	4.3	15/36	5
PCE	0.0	3.9	0.6	0/73	5
DEP	0.0	36.6	3.6	0/25	-
DBP	0.0	21.8	2.4	0/55	-
DEHP	0.0	74.0	4.5	8/57	6

*Average concentrations are calculated just for samples with detection.

4.3.2 DETECTION IN TAP WATER

Tap water samples have been obtained for homes located in the karts region of northern Puerto Rico from 2011 to 2014. At least one phthalate have been found in 144 of 260 samples (55.4%) and overall in 87 of 130 houses (66.9%) being DEHP the most found phthalate in tap water (57 of 130 houses, 43.8% or 86 of 260 samples, 33.1%). DEP and DBP are detected in 26.1% and 30.0% of the houses, and in 16.9% and 21.5% of the samples, respectively. DEHP has the higher average concentration in tap water samples for phthalates (Figure 22a) with an average of 11.9 µg/L, followed by DBP with 2.9 µg/L and DEP with 1.9 µg/L. Although DEHP average concentration is 11.9 µg/L, the 75% of the DEHP concentrations are below 7.0 µg/L, indicating that the average DEHP is influenced by outliers (Figure 22c) with values up to 284 µg/L. Figure 22b shows a greater distribution and higher concentrations of DEHP than DEP and DBP in tap water.

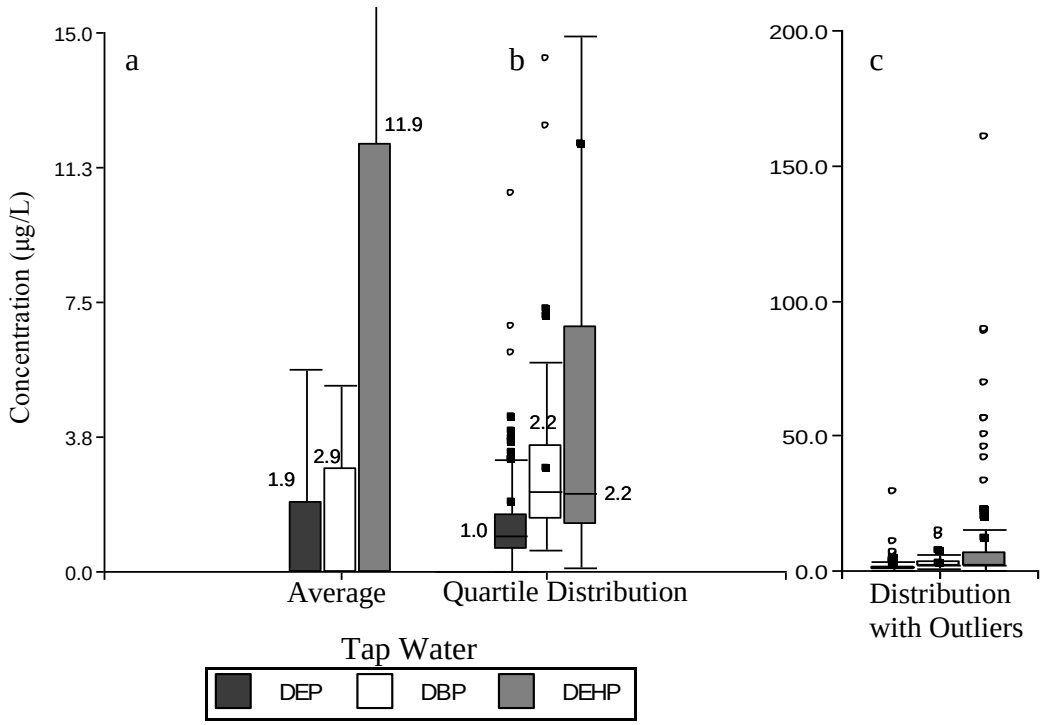


Figure 22 Concentrations of Phthalates in Tap Water: (a) Average Concentrations; (b) Quartile Distributions; (c) Distribution with Outliers

CVOCs are detected in 68.4% of the houses and 60.2 % of the samples where tap water samples are collected. This percent is almost entirely associated with detection of TCM in tap water (Figure 23a). The percent of houses with TCM detection is 66.1% (59.1% per samples), while for CT, TCE and PCE are 2.3, 0.7, and 5.4%, respectively. TCM is the contaminant with the higher concentration in tap water, with an average concentration of 12.2 µg/L, followed by PCE (0.6 µg/L), and finally CT (0.1 µg/L) and TCE (0.1 µg/L). Although 75% of the TCM concentrations are below 15.0 µg/L, it has been found in concentrations up to 63.0 µg/L in tap water. CT, TCE and PCE do not present outliers; therefore, averages and medians are almost the same (Figure 23).

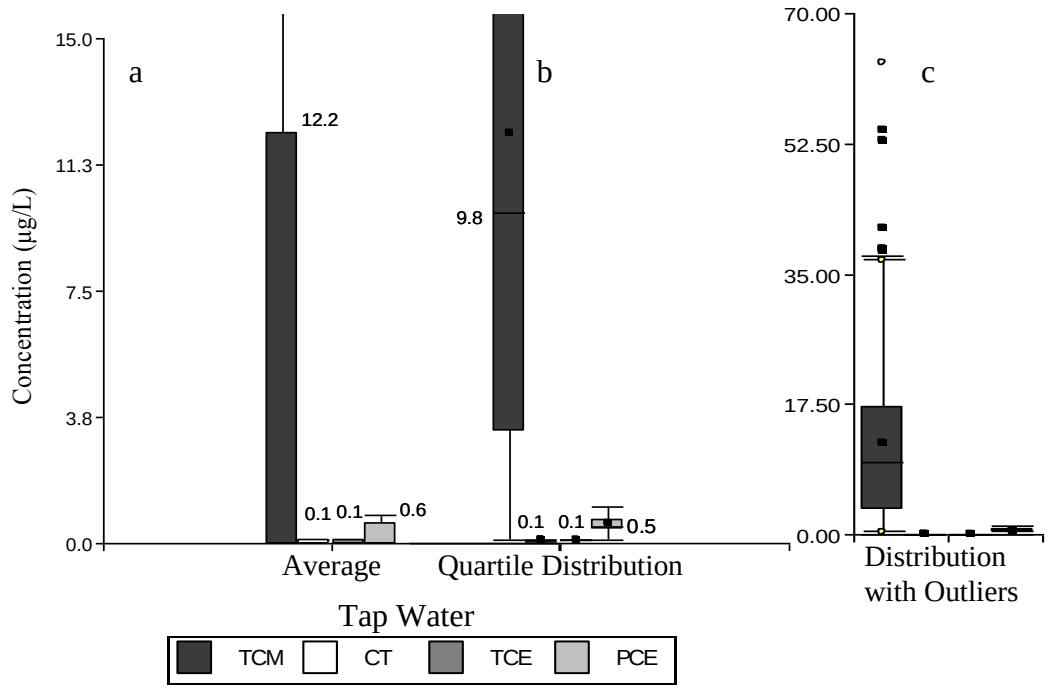


Figure 23 Concentrations of CVOCs in Tap Water: (a) Average Concentrations; (b) Quartile Distributions; (c) Distribution with Outliers

DEHP, the contaminant with the highest concentration in tap water, is the only one that has exceeded the MCL (Table 28) in these samples, with concentrations up 90 µg/L. However, with a 59.1 percent of detection, TCM is the most detected contaminant in tap water samples. Maximum, minimum, averages and MCLs concentrations are in Table 28.

Relative to groundwater samples, although it is important to point out that groundwater and tap water samples are not taken at the same time, tap water samples are detected to a slightly lower extent but higher concentrations range, than groundwater. The types of phthalates detected also vary, with DEHP most frequency found in tap water, and DBP in groundwater. CVOCs are generally detected in groundwater to a higher extent and, except for TCM, at higher concentrations than tap water. TCM is the most frequently found CVOC in both groundwater

and tap water. CVOC concentrations are higher for TCE in groundwater and tap water, but higher for TCM in tap water.

Table 28 Summary of Minimum, Maximum and Average Concentrations of detected CVOCs and phthalates in Tap Water

Contaminant	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)	*Average Concentration (µg/L)	Samples with Detection Above MCL	**MCL (µg/L)**
TCM	0.0	63.0	11.9	0/152	70
CT	0.0	0.1	0.1	0/5	5
TCE	0.0	0.1	0.1	0/2	5
PCE	0.0	1.1	0.6	0/14	5
DEP	0.0	29.1	2.1	0/67	-
DBP	0.0	14.2	3.0	0/69	-
DEHP	0.0	284.0	8.9	32/118	6

*Average concentrations are calculated just for samples with detection.

5. CONCLUSIONS AND RECOMMENDATIONS

This Chapter summarizes the major conclusions drawn from this study, and provides recommendations to address uncertainty and variability aspects of the study. These are described below.

5.1 CONCLUSIONS

The efficiency studies demonstrate that the modified extraction methods for phthalates are quantifiable and reproducible, although not efficient. The methods show higher extraction efficiencies for lower phthalates concentrations and higher extraction volumes. Recoveries higher than 100% in the concentration efficiency studies suggest potential solvent contamination. Although high variability is observed in all the measurements, statistical analysis indicates that the 100-mL and-1000 mL samples studies are more efficient than the 10-mL sample study, while a comparison between these methods does not reveal a significant difference. While it is true that the developed methods in this research for phthalates are not more efficient that the method used by EPA (1000-mL sample), it achieved a more practical and environmental friendly method (100-mL sample) with the same extraction efficiency. The new method uses less water sample, therefore, less extraction solvent (18mL DCM) compared with the EPA method that uses 180 mL DCM per sample. This fact make the modified method a more environmentally friendly that the 1000-mL water sample method since it produces less waste. The new method also is more practical than the 1000-mL sample method because by using less volume, the extractions consume less time and the necessary equipment (e.g. separatory funnels) is smaller and more manageable. Although the studies reflect that the water sample and solvent volumes affect sample extraction efficiency, this effect is lower for sample volumes greater than 100mL.

This research demonstrates that DEHP is distributed between water and DCM after the water extractions. Therefore, is clear that DEHP must have a partitioning coefficient among water and DCM. The partitioning coefficient found in this research, $\log K_{sw} = 0.20$, is orders of magnitude lower that is the average $\log K_{ow} \approx 7.26$. The much lower partition values for the DCM-water system is explained by the lower compatibility of the DEHP with the DCM (related to octanol), and by co-solvency effects of the solvent in water. As DCM is a PMOS, this solvent apparently produces a co-solvent effect that increases DEHP solubility in water. As results of the high concentrations of DCM in water (>1%), DEHP is more soluble in water and remains in the water phase to a greater extent than if DCM was not present in water at high concentrations.

Results from this study show the presence of CVOCs and phthalates in groundwater and tap water. Detected contaminants include TCM, CT, TCE, PCE, DEP, DBP and, DEHP. Samples analysis indicated that the detection frequency and concentration of CVOCs is higher for groundwater than tap water, except for chloroform, which is found at higher frequencies and concentrations in tap water. Phthalates are detected in both groundwater and tap water, indicating than water is a source of exposure for phthalates. The detection frequency of phthalates tends to increase in tap water more that groundwater, suggesting additional sources of contamination such as tap water pipes, water tanks, and filters, among others.

5.2 RECOMENDATIONS

To ensure the validity of the results other efficiencies studies are recommended, especially for 100-mL and 1000-mL samples, because they were the most efficient methods and did not get any significance different statistically. The background in blanks and the high variability made the samples analysis of phthalates very difficult at low concentrations. Therefore, it is extremely important to avoid the contamination in the cleaning step that can be

the more susceptible step of contamination, a more strict process of cleaning, that include drying the glassware in a furnace, is suggested. A cosolvency study can help to ascertain the behavior of phthalates in water in the presence of solvents such as DCM. Finally, since it is proven that DCM is not a very efficient extraction solvent, maybe a study of other solvents should be performed. Accuracy and precision studies for CVOCs, as well as their range of physicochemical properties, show little variability among measurements. For this reason, and the limitations, an efficiency study is not conducted for CVOCs. It is, however, recommended for future work.

REFERENCES

Agilent Thechnologies, Inc (2013) Agilent 5975 Series MSD: Operation Manual for masshunter. Manual Part Number G3170-90056. Retrieved September, 2015 from https://www.agilent.com/cs/library/usermanuals/public/5975_Op_Manual.pdf

Aschengrau A, Weinberg JM, Janulewicz PA, Romano ME, Gallagher LG, Winter MR, Martin BR, Viera VM, Webster TF, White RF, and Ozonoff DM (2012). Occurrence of mental illness following prenatal and early childhood exposure to tetrachloroethylene (PCE)-contaminated drinking water: a retrospective cohort study. Environmental Health Vol 11(2) doi: 10.1186/1476-069X-11-2

ASTM International (2013) Standard guide for sampling ground-water monitoring wells. Vol 11(04) doi: 10.1520/D4448-01R13.

ATSDR, Agency for Toxic Substances and Disease Registry (1997) Toxicological profile for chloroform. Retrieved September, 2015 from http://www.atsdr.cdc.gov/toxprofiles/tp6.pdf

ATSDR, Agency for Toxic Substances and Disease Registry (2002) Toxicological profile for di(2-ethylhexyl)phthalate (DEHP). Retrieved September, 2015 from http://www.atsdr.cdc.gov/toxprofiles/tp9.pdf

ATSDR, Agency for Toxic Substances and Disease Registry (2006) Toxicological profile for 1,1,1-trichloroethane Retrieved September, 2015 from http://www.atsdr.cdc.gov/toxprofiles/tp70.pdf

ATSDR, Agency for Toxic Substances and Disease Registry (2013) Summary data for 2013 priority list of hazardous substances. Retrieved September, 2015 from http://www.atsdr.cdc.gov/spl/

ATSDR, Agency for Toxic Substances and Disease Registry (2014) Toxicological profile for trichloroethylene. Retrieved September, 2015 from http://www.atsdr.cdc.gov/ToxProfiles/tp19.pdf

Barlow J, Brown K, Johnson JP, and Scofield L (2007) Early life exposure to phthalates and breast cancer risk in later years: Fact sheet on phthalates. Breast Cancer & The Environment Research Centers. Retrieved September, 2015 from http://www.bcerc.org/COTCpubs/BCERC.FactSheet_Phthalates.pdf

Behrman RE, Butler AS (2007) Preterm Birth: Causes, Consequences, and Prevention. National Academies Press (US) Retrieved September, 2015 from https://iom.nationalacademies.org/~/media/Files/Report%20Files/2006/Preterm-Birth-Causes-Consequences-and-Prevention/Preterm%20Birth%202006%20Report%20Brief.pdf

Berthod A, and Carda-Broch S (2004) Determination of liquid–liquid partition coefficients by separation methods. Journal of Chromatography Vol 1037 (1-2): 3-14 doi:10.1016/j.chroma.2004.01.001

Blencowe H, Cousens S, Oestergaard MZ, Chou D, Moller A, Narwal R, Adler A, Vera-García C, Rohde S, Say L, and Lawn JE (2012) National, regional and worldwide estimates of preterm birth rates in the year 2010 with time trends since 1990 for selected countries: a systematic analysis and implications. The Lancet Vol 379 (9832): 2162-2172 doi:10.1016/S0140-6736(12)60820-4

Cai YQ, Jiang GB, Liu JF, and Zhou QX (2003) Multi-walled carbon nanotubes packed cartridge for the solid-phaseextraction of several phthalate esters from water samples and theirdetermination by high performance liquid chromatography. Analytica Chimica Acta Vol 494 (1-2): 149-156 doi:10.1016/j.aca.2003.08.006

Calò F, and Parise M (2009) Waste management and problems of groundwater pollution in karst environments in the context of a post-conflict scenario: The case of Mostar (Bosnia Herzegovina). Habitat International Vol 33 (1): 63–72 doi:10.1016/j.habitatint.2008.05.001

CDC, Center for Disease Control and Prevention (2005) Third national report on human exposure to environmental chemicals. Retrieved September, 2015 from http://www.jhsph.edu/research/centers-and-institutes/center-for-excellence-in-environmental-health-tracking/Third_Report.pdf

CERHR, Center for Evaluation of Risks of Human Reproduction (2006). NTP-CERHR monograph on the Potential Human Reproductive and Development Effects of Di(2-Ethylhexyl) Phthalate (DEHP) NIH Publication No. 06-4476 Retrieved September, 2015 from http://ntp.niehs.nih.gov/ntp/ohat/phthalates/dehp/dehp-monograph.pdf

CHRP, Commitee on the Health Risks of Phthalates (2008) Phthalates and cumulative risk assessment: The Tasks Ahead. The Nationa Academy of Sciences. Retrieved September, 2015 from http://dels.nas.edu/resources/static-assets/materials-based-on-reports/reports-in-brief/phthalates_final.pdf

Clark KE, David RM, Guinn R, Kramarz KW, Lampi MA, and Staples CA (2011) Modelling human exposure to phthalate esters: A comparison of indirect and biomonitoring estimation methods. Human and Ecological Risk Assessment Vol 17(4): 923-965 doi: 10.1080/10807039.2011.588157

Clark K, Cousins I, Mackay D, and Yam K (2003) Observed concentrations in the environment. The Handbook of Environmental Chemistry: Phthalate Esters Vol 3Q: 125-177 doi:10.1007/b11465

Colón I, Caro D, Bourdony CD, and Rosario O (2000) Identification of phthalate esters in the serum of young Puerto Rican girls with premature breast development. Environ Health Perspectives Vol 108(9): 895–900

Compton J, Ackerman L, Quinones A, and Cosgrove B (2007) Standard operating procedures for surface water sampling. US Environmental Protection Agency Region 4: Science and Ecosystems Report No. SESDPROC-201-R1 Replaced by SESDPROC-201-R3 Retrieved September, 2015 from http://www.epa.gov/region4/sesd/fbqstp/Surfacewater-Sampling.pdf

Cordero JF (2013) Risk factors for preterm births in Puerto Rico: from health disparities to endocrine disruptors. Society for the Study of Reproduction Diversity Symposium Grand Rapids, Michigan. Retrieved September, 2015 from http://www.northeastern.edu/protect/assets/CorderoSSR.July2014.FINAL_.pdf

Cousins IT, Mackay D, and Parkerton TF (2003) Physical-chemical properties and evaluative fate modelling of phthalate esters. The Handbook of Environmental Chemistry: Phthalate Esters Vol 3Q: 57-84 doi: 10.1007/b11463

Cruz de Oliveira E, MullerI E, Abad F, Dallarosa J, Adriano C (2010) Internal standard versus external standard calibration: an uncertainty case study of a liquid chromatography analysis. Qímica Nova Vol 33(4): 984-987 http://dx.doi.org/10.1590/S0100-40422010000400041

David F, Sandra P, Tienpont B, Vanwalleghem F, and Ikonomou M (2003) Analytical Methods Review. The Handbook of Environmental Chemistry: Phthalate Esters Vol 3Q: 9-56 doi: 10.1007/b11461

Dumitrașcu I (2012) Determination of Phthalates from Bottled Water by GC-MS. Air and Water Components of the Environment: 337-343

Einsiedl F, Radke M, and Maloszewski P (2010) Occurrence and transport of pharmaceuticals in a karst groundwater system. Journal of Contaminant Hydrology Vol 117 (1-4): 26–36 doi: 10.1016/j.jconhyd.2010.05.008

EWG, Environmental Working Group (2009) National Drinking Water Database. Retrieved September, 2015 from http://www.ewg.org/tap-water/

Forand S, Lewis-Michl E, and Gomez M (2012) Adverse birth outcomes and maternal exposure to trichloroethylene and tetrachloroethylene through soil vapor intrusion in new york state. Environmental Health Perspectives Vol 120(4): 616-621 doi: 10.1289/ehp.1103884

Ford D, and Williams P (2007) Karst hydrogeology and geomorphology. Vol 2 doi: 10.1002/9781118684986

Godwin A (2010) Uses of phthalates and other plasticizers. ExxonMobil Chemical Company. Retrieved September, 2015 from https://www.cpsc.gov/PageFiles/126379/godwin.pdf

Göppert, and Goldscheider (2008) Solute and colloid transport in karst conduits under low- and high-flow conditioner. Groundwater Vol 46(1): 61-68 doi: 10.1111/j.1745-6584.2007.00373.x

Graening G, and Brown A (1999) Cavefish population status and environmental quality in cave springs cave. Arkansas Water Resources Center: Publication No. 276: 36 Retrieved September, 2015 from http://cavespringskarststudy.com/wp-content/ftp_listing/OULs%20Bibliography%20Reference%20Material/Graening/GraeningBrown1999_ANHC1999Report.pdf

Green R, Painter S, Sun A, and Wort S (2006) Groundwater contamination in karst terranes. Water, Air and Soil Pollution Vol 6(1-2): 157-170 doi: 10.1007/s11267-005-9004-3

Guzmán-Ríos S, García R, and Avilés A (1986) Reconnaissance of volatile synthetic organic chemicals at public water supply wells throughout Puerto Rico, November 1984-May 1985. US Geological Survey Publication Open-File Report: 86-63

Guzzella L, Pozzoni F, and Giuliano G (2005) Herbicide contamination of surficial groundwater in Northern Italy. Environmental Pollution Vol 142(2): 344-353 doi:10.1016/j.envpol.2005.10.037

Ha E, and Cho I (2002) Parental exposure to organic solvents and reduced birth weight. Arch Environment Health Vol 57(3): 207-214 doi: 10.1080/00039890209602938

Hamilton BE, Martin JA, and Ventura SJ (2012) Births: preliminary data for 2011. Centers for Disease Control and Prevention Vol 61(5) Available at Retrieved September, 2015 from http://www.cdc.gov/nchs/data/nvsr/nvsr61/nvsr61_05.pdf

Herrmann R (2001) Chemical and biotic processes affecting the fate and transport of trace organic contaminants in municipal landfills: a discussion. Journal of Hydrology Vol 40(1): 43-57

Holadová K, Prokůpková G, Hajšlová J, and Poustka J (2007) Headspace solid-phase microextraction of phthalic acid esters from vegetable oil employing solvent based matrix modification. Analitica Chimica Acta Vol 582(1): 24-33 doi:10.1016/j.aca.2006.09.005

Holt BD, Sturchio NC, and Abrajano TA (1997) Conversion of Chlorinated Volatile Organic Compounds to Carbon Dioxide and Methyl Chloride for Isotopic Analysis of Carbon and Chlorine. Analytical Chemistry Vol 69(14): 2727-2733 doi: 10.1021/ac961096b

Huang B, Lei C, Wei C, Zeng G (2014) Chlorinated volatile organic compounds (Cl-VOCs) in environment - sources, potential human health impacts, and current remediation technologies. Environment International Vol 71: 118-138 doi.org/10.1016/j.envint.2014.06.013

Hunter JM and Arbona S (1995) Paradise Lost: An introduction to the geography of water pollution in Puerto Rico. Social Science and Medicine Vol 40(10): 1331-1355 doi: 10.1016/0277-9536(94)00255-R

IEPA, Illinois Environmental Protection Agency (2009) Sample Collector's Handbook Retrieved September, 2015 from http://www.epa.state.il.us/water/compliance/drinking-water/collectors-handbook/sample-collectors-handbook.pdf

Khattak S, K-Moghtader G, McMartin K, Barrera M, Kennedy D, and Koren G (1999) Pregnancy outcome following gestational exposure to organic solvents: a prospective controlled study. Jama Vol 281(12): 1106-1109 doi:10.1001/jama.281.12.1106

Irizarry C (2014) Historical assessment of chlorinated volatile organic compounds (CVOCs) and phthalates contamination in the northern karst aquifer of Puerto Rico using GIS. Master of Engineering in Civil Engineering. University of Puerto Rico, Mayagüez

Koterba M, Wilde FD, and Lapham WW (1995) Groundwater data collection protocols and procedures for the national water-quality assessment program: collection and documentation of water quality samples and related data. US Geological Survey Publication Open-File Report: 95-399

Latini G, De Felice G, Presta C, Del Vecchio G, Paris A, Ruggieri F, and Mazzeo P (2003) In utero exposure to di-(2-ethylhexyl)phthalate and duration of human pregnancy. Environmental Health Perspectives Vol 111(14): 1783-1785 doi: 10.1289/ehp.6202

Lawrence SJ (2006) Description, properties, and degradation of selected volatile organic compounds detected in ground water—a review of selected literature. US Geological Survey Publication Open-File Report: 2006-1338

Li J, Cai Y, Shi Y, Mou S, and Jiang G (2008) Analysis of phthalates via HPLC-UV in environmental water samplesafter concentration by solid-phase extraction using

ionicliquid mixed hemimicelles. Talanta Vol 74(4): 498-504 doi:10.1016/j.talanta.2007.06.008

Liang P, Xu J, and Li Q (2008) Application of dispersive liquid–liquid microextraction and high-performance liquid chromatography for thedetermination of three phthalate esters in water samples. Analytica Chimica Acta Vol 609(1): 53-58

Lipscomb JA, Fenster L, Wrensch M, Shusterman D, and Swan S (1991) Pregnancy outcomes in women potentially exposed to occupational solvents and women working. Journal of Occupational Environmental Medicine Vol 33(5): 597-604

Loraine JA, and Pettigrove ME (2006) Seasonal variations in concentrations of pharmaceutical and personal care products in drinking water and reclaimed wastewatrer in southern California. Environmental Science and Technology Vol 40: 687-695 doi: 10.1021/es051380x

Luks-Betleja K, Popp P, Janoszka B, and Paschke H (2001) Solid-phase microextraction of phthalates from water. Journal of Chromatography A Vol 938(1-2): 93-101 doi:10.1016/S0021-9673(01)01363-2

Marín A, Andreo B, and Mudarra M (2010) Importance of evaluating karst features in contamination vulnerability and groundwater protection assessment of carbonate aquifers. The case study of Alta Cadena (Southern Spain). Zeitschrift für Geomorphologie Vol 54(2): 179–194 doi: 10.1127/0372-8854/2010/0054S2-0010

MDH, Minnesota Department of Health (2015) VOCs in private drinking water wells. Retrieved September, 2015 from http://www.health.state.mn.us/divs/eh/hazardous/topics/vocs.html

Meeker JD (2012) Exposure to environmental endocrine disruptors and child development. Archives of Pediatrics & Adolescent Medicine. Vol 166(6): E1-7 doi: 10.1001/archpediatrics.2012.241

Meeker JD, Hu H, Cantonewine DE, Lamadrid-Figueroa H, Calafat AM, Ettinger AS, Hernandez-Avila M, Loch-Caruso R, Téllez-Rojo MM (2009) Urinary phthalate metabolites in relation to preterm birth in mexico city. Environmental Healt Perspective Vol 117(10): 1587-1592 doi: 10.1289/ehp.0800522

Metcalfea CD, Beddows PA, Gold-Bouchot GG, Metcalfe TL, Li H, and Van-Lavieren H (2010) Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico. Environmental Pollution Vol 159 (4): 991-997 doi:10.1016/j.envpol.2010.11.031

Mohan S, Danimon K, and Vairavamoorthy K (2004) Development of GIS based contamination risk assessment in water distribution systems. 30th WEDC International Conference,

Vientiane, Lao PDR, 2004: 483-490 Retrieved September, 2015 from http://wedc.lboro.ac.uk/resources/conference/30/Mohan.pdf

Molina-Rivera WL (1996) Puerto Rico water-use program: public water use and wastewater disposal during 1990. US Geological Survey Fact Sheet: 098-96

Molina-Rivera WL (1997) Ground-water use from the principal aquifers in Puerto Rico during calendar year 1990. US Geological Survey Fact Sheet: FS-188-96

Molina-Rivera WL, and Goméz-Goméz F (2008) Estimated water use in Puerto Rico, 2005. US Geological Survey Open-File Report: 2008-1286

Munch DJ, and Hautman DP (1995) EPA Method 551.1: Determination of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron-capture detection (GC/ECD). Retrieved September, 2015 from https://www.o2si.com/docs/epa-method-551.1.pdf

Nathan VR (2006) Drinking water in Michigan: source, quality, and contaminants. Journal of Water and Health Vol 04:67-73 doi: 10.2166/wh.2005.041

NRDC, Nature Resources Defense Council (2013) Study finds safety of drinking water in U.S. cities at risk. Retrieved September, 2015 from http://www.nrdc.org/water/drinking/uscities.asp

Padilla IY, Irizarry C, and Steele K (2011) Historical contamination of groundwater resources in the north coast karst aquifer of Puerto Rico. National Institutes of Health Vol 3(7-12): 1-15

Padilla IY, Rivera VL, and Irizarry C (2015) Spatiotemporal response of CVOC contamination and remedial actions in eogenetic karst aquifers. 14th Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst, Rochester, Minnesota October 5-9, 2015

Parise M, and Pascali V (2003) Surface and subsurface environmental degradation in the karst of Apulia (southern Italy). Environmental Geology Vol 44: 247–256 doi: 10.1007/s00254-003-0773-6

Patnaik P (2010) Organic volatile compounds. Handbook of Environmental Analysis Chemical Pollutants in Air, Water, Soil, and Solid Wastes. Second Edition: 445–463

Peterson DR, and Stapples CA (2003) Degradation of phthalates in the environment. The Handbook of Environmental Chemistry: Phthalate Esters. Vol 3Q: 85-124 doi: 10.1007/b11464

Pinal R, Rao PSC, Lee LS, and Cline PV (1990) Cosolvency of partially miscible organic solvents on the solubility of hydrophobic organic chemicals. Environmental Science and Technology Vol 24(5): 639-647 doi: 10.1021/es00075a004

Pitkänen T, Miettinen IT, Nakari UM, Takkinen J, Nieminen K, Siitonen A, Kuusi M, Holopainen A, and Hänninen ML (2008) Faecal contamination of a municipal drinking water distribution system in association with Campylobacter jejuni infections. Journal of Water and Health Vol 6(3): 365-376 doi: 10.2166/wh.2008.050

PRoTECT, Puerto Rico Testsite for Exploring Contamination Threats (2013) About PRoTECT. Retrieved September, 2015 from www.northeastern.edu/protect/about-protect/

Schwarz K, Gocht T, and Grathwohl P (2011) Transport of polycyclic aromatic hydrocarbons in highly vulnerable karst systems. Environmental Pollution Vol 159(1): 133-139 doi: 10.1016/j.envpol.2010.09.026

Schwarzenbach RP, Gschwend PM, and Imbodem, DM (2003) Environmental Organic Chemictry Second Edtition. Chapter 5: Activity Coefficient and Solubility in Water: 165-172

Serôdio P, and Nogueira JMF (2006) Considerations on ultra-trace analysis of phthalates in drinking water. Water Research Vol 40(13): 2572-2582 doi:10.1016/j.watres.2006.05.002

Shailaja S, Venkata Mohan S, Rama Krishna M, and Sarma PN (2008) Degradation of di-ethylhexyl Phthalatae (DEHP) in bioslurry phase reactor and identification of metabolites by HPLC and MS. International Biodeterioration and Bidegradation Vol 62(2): 143-152 doi:10.1016/j.ibiod.2008.01.002

Shen HY (2004) Simultaneous screening and determination eight phthalates in plasticproducts for food use by sonication-assisted extraction/GC–MS methods. Talanta Vol 66(3): 734-739 doi:10.1016/j.talanta.2004.12.021

Sonnenfeld N, Hertz-Picciotto I, and Kaye WE (2001) Tetrachloroethylene in drinking water and birth outcomes at the US Marine Corps Base at Camp Lejeune, North Carolina. American Journal of Epidemiology Vol 154(10): 902-908

Stanely MK, Robillard KA, and Staples (2003) Introduction. The Handbook of Environmental Chemistry: Phthalate Esters Vol 3.Q: 1-7 doi: 10.1007/b11460

Steele-Valentín, KM, Padilla IY (2009) Assessment of Potential Exposure Pathways in Karst Groundwater Systems in Vega Alta, Puerto Rico using Geographic Information Systems 7th Latin American and Caribbean Conference for Engineering and Technology

Retrieved September, 2015 from http://www.laccei.org/LACCEI2009-Venezuela/p223.pdf

Tienpont B (2004) Determination of phthalates in environmental, food and biomatrices-an analytical challenge. Thesis Degree of Doctor in Science. Department of Organic Chemistry, Ghent University. Deparment of Organic Chemistry Ghent University.

Tobin B, and Weary D (2004) Digital engineering aspects of karst map: a GIS version of Davies WE, Simpson JH, Ohlmacher GC, Kirk WS, and Newton EG, 1984, engineering aspects of karst. US Geological Survey Open-File Report: 2004-1352 Retrieved September, 2015 from http://pubs.usgs.gov/of/2004/1352/data/USA_karst.pdf

Torres N, Padilla IY, Mudarra M, Cordero J, and Meeker J (2013) Assessment of Changes in Potential Contamination Exposure in a Karst Aquifer Using GIS and Temporal Analysis, Abstract RP084, SETAC North America 34th Annual Meeting, Nashville, TN, November 17-21, 2013

USEPA, US Environmental Protection Agency (1994) Method 8250A: Semivolatile organic compounds by gas chomatography/mass spectrometry (GC/MS). Retrieved September, 2015 from http://legismex.mty.itesm.mx/secc_inter/SW-846/8250a.pdf

USEPA, US Environmental Protection Agency (1996a) Method 3510C: Separatory funnel liquid-liquid extraction. Retrieved September, 2015 from http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3510c.pdf

USEPA, US Environmental Protection Agency (1996b) Method 3520C: Continuous liquid-liquid extraction. Retrieved September, 2015 from http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3520c.pdf

USEPA, US Environmental Protection Agency (1996c) Method 606: Methods for organic chemical analysis of municipal and indutrial wastewater: phthalate esters (GC/ECD). Retrieved September, 2015 from http://water.epa.gov/scitech/methods/cwa/organics/upload/2007_07_10_methods_method_organics_606.pdf

USEPA, US Environmental Protection Agency (1996d) Method 8061A: Phthalate esters by gas chromatography with electron capture detection (GC/ECD). Retrieved September, 2015 from http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/8061a.pdf

USEPA, US Environmental Protection Agency (1996e) Method 8260B: Volatile organic compounds by gas chromatography/ mass spectrometry (GC/MS). Retrieved September, 2015 from http://www3.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/8260b.pdf

USEPA, US Environmental Protection Agency (1996f) Method 5032: Volatile organic compounds by vacuum distillation. Retrieved September, 2015 from http://www3.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/5032.pdf

USEPA, US Environmental Protection Agency (1996g) Soil Screening Guidance: Technical Background Document Table of Contents. Part 5 Chemical-Specific Parameters EPA/540/R-95/128: 133-160 Retrieved September, 2015 from http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part_5.pdf

USEPA, US Environmental Protection Agency (2003a) Method 5030C: Purge-and-trap for aqueous samples Retrieved September, 2015 from http://www3.epa.gov/epawaste/hazard/testmethods/pdfs/5030c.pdf

USEPA, US Environmental Protection Agency (2003b) Method 5021A: Volatile organic compounds in various sample matrices using equilibrium headspace analysis. Retrieved September, 2015 from http://www3.epa.gov/epawaste/hazard/testmethods/pdfs/5021a_r1.pdf

USEPA, US Environmental Protection Agency (2006) EPA says more landfills in Puerto Rico must be addressed. EPA Region 2 Newsroom. Retrieved 2015, from http://yosemite.epa.gov/opa/admpress.nsf/354ac96cb31f0a9a852572a00065683b/cd3e8ea00ad81f7e852571cb0055580d!OpenDocument

USEPA, US Environmental Protection Agency (2007a) Method 3500C: Organic extraction and sample preparation. Retrieved September, 2015 http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3500c.pdf

USEPA, US Environmental Protection Agency (2007b) Method 3535: Solid-Phase Extraction (SPE). Retrieved September, 2015 http://www.caslab.com/EPA-Methods/PDF/EPA-Method-3535.pdf

USEPA, US Environmental Protection Agency (2007c) Phthalates: TEACH chemical summary. Toxicity and Exposure Assessment for Children's Health. Retrieved September, 2015 http://www.epa.gov/teach/chem_summ/phthalates_summary.pdf

USEPA, US Environmental protection Agency (2009) STORET data warehouse access. Retrieved 2015, from http://www.epa.gov/storet/dbtop.html

USEPA, US Environmental Protection Agency (2013) TOXMAP: Environmental Health e-Maps. Retrieved September, 2015 from http://toxmap.nlm.nih.gov/toxmap/superfund/identifyAll.do

USEPA, US Environmental Protection Agency (2014a) Method 8270D: Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). Retrieved September, 2015 from http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/8270d.pdf

USEPA, US Environmental Protection Agency (2014b) Method 8021B: Aromatic and halogenated volatiles by gas chromatography using photoionization and/or electrolytic conductivity detectors. Retrieved September, 2015 from http://www3.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/8021b.pdf

USEPA, US Environmental Protection Agency (2015) SW-846: What is SW-846? Retrieved September 2015 from http://www.epa.gov/wastes/hazard/testmethods/sw846/

USGS, US Geology Survey (2009) Water quality samples for Puerto Rico. Retrieved September, 2015 from http://nwis.waterdata.usgs.gov/pr/nwis/qwdata

Veni G, DuChene H, Crawford CN, Groves CG, Huppert GN, Kastning EH, Olson R, and Wheeler BJ (2001). Living with karst: a fragile foundation. US Geological Survey: AGI Environmental Awareness Series, 4 Retrieved September, 2015 from http://www.americangeosciences.org/sites/default/files/karst.pdf

Veve TD, and Taggart BE (1996) Atlas of Ground-Water Resources in Puerto Rico and the U.S. Virgin Islands US Geological Survey: Water Resources Investigations Report 94-4198

Weschlera CJ, and Nazaroffc WW (2008) Semivolatile organic compounds in indoor environments. Atmospheric Environment Vol 42(40): 9018–9040 doi:10.1016/j.atmosenv.2008.09.052

Wilde FD (2010) National Field Manual for the Collection of Water-Quality Data. US Geological Survey Techniques of Water-Resources Investigations: Book 9-Chapter A6: Field Measurements Retrieved September, 2015 from https://water.usgs.gov/owq/FieldManual/Chapter6/final508ChapterA6.pdf

Willmott CJ, and Matsuura K (2005) Advantages of the mean absolute error (MAE) over the root mean square error (RMSE) in assessing average model performance. Climate Research Vol 30(1): 79–82 http://doi.org/10.3354/cr030079

Xu J, Liang P, and Zhang T (2007) Dynamic liquid-phase microextraction of three phthalate esters from water samples and determination by gas chromatography. Analytical Chimica Acta Vol 597(1): 1-5 doi:10.1016/j.aca.2007.06.047

Yu X, Ghasemizadeh R, Padilla IY, Irizarry C, Kaeli D, and Alshawabkeh A (2015) Spatiotemporal changes of CVOC concentrations in karst aquifers: analysis of three decades of data from Puerto Rico. Science of the Total Environment Vol 511: 1–10 doi:10.1016/j.scitotenv.2014.12.031.

Zack A, Rodriguez-Alonso T, and Romas-Mas A (1987) Puerto Rico Groundwater Quality. US Geological Survey Open File Report: 87-0749

Zia AI, Rahman MSA, Mukhopadhyay SC, Yu PL, Gooneratne CP, Kosel J, and Liao TS (2013) Technique for rapid detection of phthalates in water and beverages. Journal of Food Engineering Vol 116(2): 515–523 doi:10.1016/j.jfoodeng.2012.12.024

Zogorki JS, Carter JM, Ivahnenko T, Lapham WW, Moran MJ, Rowe BL, Squillace PJ, and Toccalino PL (2006) The Quality of Our Nation's Waters: Volatile Organic Compounds in the Nation's Ground Water and Drinking-Water Supply Well. US Geological Survey Circular 1292

APPENDIX

APPENDIX A: DEHP PARTITIONING COEFFICIENTS

APPENDIX B: VARIANCE ANALYSES

APPENDIX C: COVARIANCE ANALYSES

APPENDIX A

DEHP PARTITIONING COEFFICIENTS

Appendix A contains the performed linear regressions to obtain the DEHP partitioning coefficients for a mixture of DCM and Water of each study (i.e. 10mL, 100 mL and 1000 mL samples)

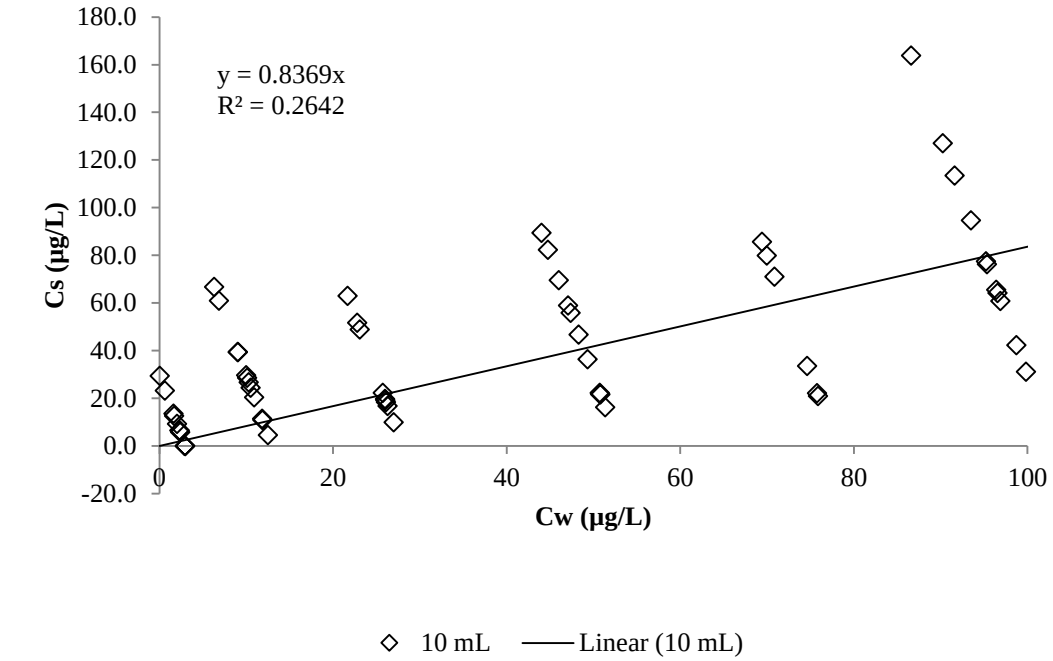


Figure A1: DEHP partitioning coefficient for the 10 mL samples study

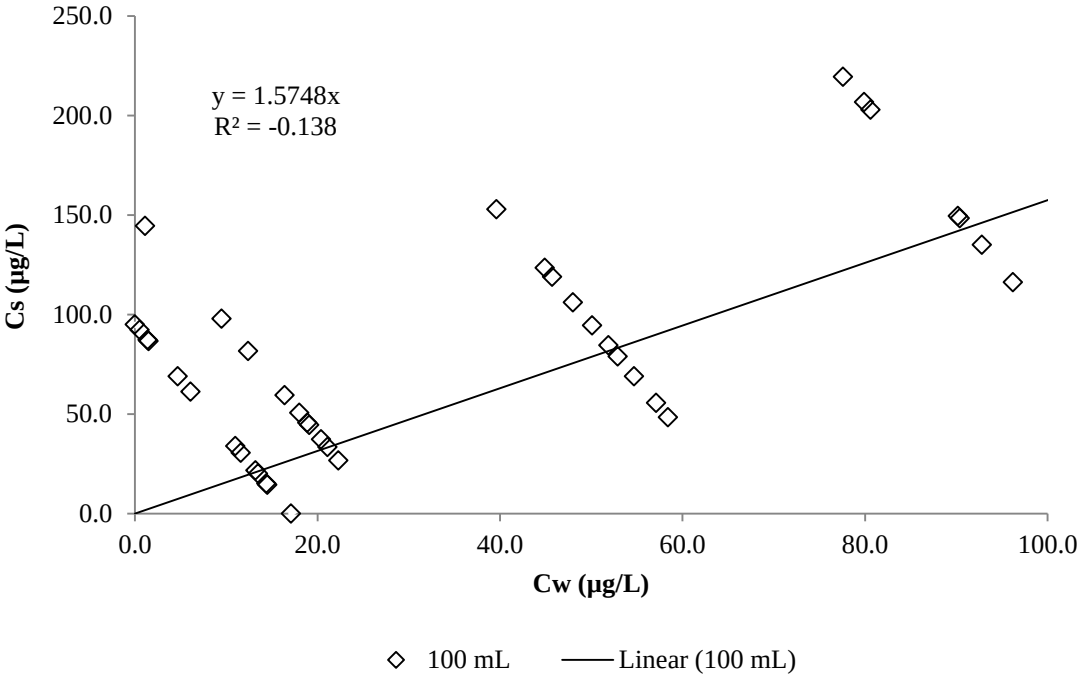


Figure A2: DEHP partitioning coefficient for the 100 mL samples study

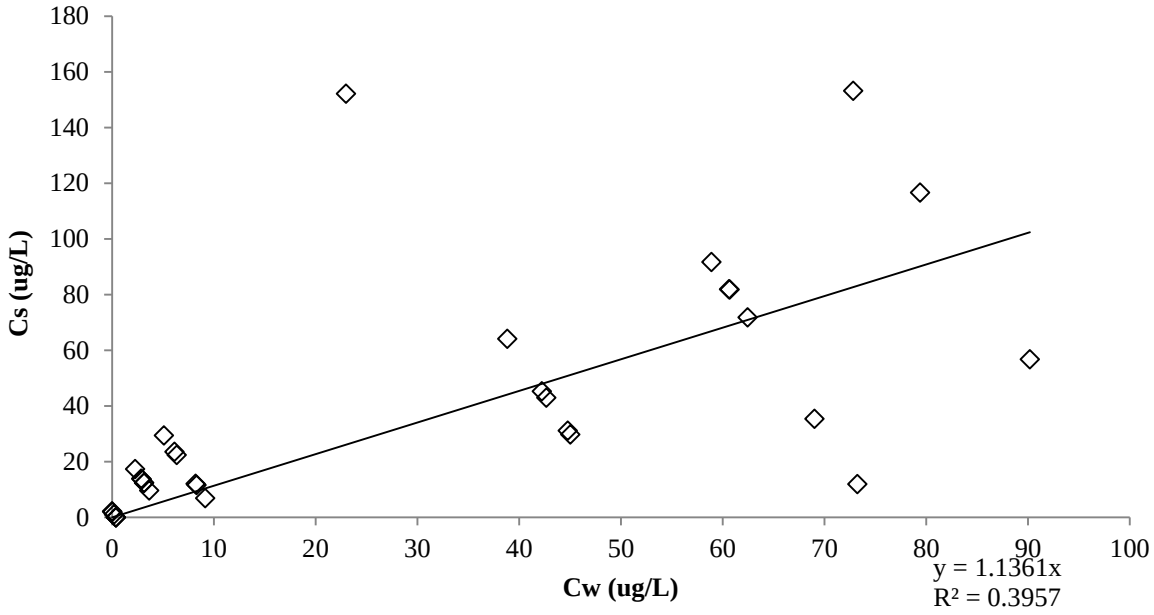


Figure A3: DEHP partitioning coefficient for the 1000 mL samples study

APPENDIX B

VARIANCE ANALYSES (INFO STAT)

Appendix B contains the variance analyses performed to compare the linear regression of each efficiency study (i.e. 10mL 100 mL and 1000 mL samples).

B1: Variance Analysis between 10 mL and 100 mL Samples Studies

B2: Variance Analysis between 10 mL and 1000 mL Samples Studies

B3: Variance Analysis between 100 mL and 1000 mL Samples Studies

B1: Variance Analysis between 10 mL and 100 mL Samples Studies

Análisis de la varianza

Variable	N	R^2	R^2 Aj	CV
%Recovery	142	0.13	0.12	90.16

Cuadro de Análisis de la Varianza (SC tipo III)

F.V.	SC	gl	CM	F	p-valor
Modelo.	10278.65	2	5139.32	10.25	0.0001
EXP	10278.65	2	5139.32	10.25	0.0001
Error	69707.52	139	501.49		
Total	79986.17	141			

Contrastes

EXP	Contraste	E.E.	SC	gl	CM	F	p-valor
Contraste1	-19.80	4.43	10015.45	1	10015.45	19.97	<0.0001
Total			10015.45	1	10015.45	19.97	<0.0001

Coeficientes de los contrastes

EXP	Ct.1
10 mL	1.00
100 mL	-1.00
1000 mL	0.00

Test:LSD Fisher Alfa=0.05 DMS=9.22942

Error: 501.4930 gl: 139

EXP	Medias	n	E.E.		
10 mL	16.01	63	2.82	A	
1000 mL	27.18	36	3.73		B
100 mL	35.81	43	3.42		B

Medias con una letra común no son significativamente diferentes (p > 0.05)

B2: Variance Analysis between 10 mL and 1000 mL Samples Studies

Análisis de la varianza

Variable	N	R^2	R^2 Aj	CV
%Recovery	142	0.13	0.12	90.16

Cuadro de Análisis de la Varianza (SC tipo III)

F.V.	SC	gl	CM	F	p-valor
Modelo.	10278.65	2	5139.32	10.25	0.0001
EXP	10278.65	2	5139.32	10.25	0.0001
Error	69707.52	139	501.49		
Total	79986.17	141			

Contrastes

EXP	Contraste	E.E.	SC	gl	CM	F	p-valor
Contraste1	-11.16	4.68	2853.30	1	2853.30	5.69	0.0184
Total			2853.30	1	2853.30	5.69	0.0184

Coeficientes de los contrastes

EXP	Ct.1
10 mL	1.00
100 mL	0.00
1000 mL	-1.00

Test:LSD Fisher Alfa=0.05 DMS=9.22942

Error: 501.4930 gl: 139

EXP	Medias	n	E.E.		
10 mL	16.01	63	2.82	A	
1000 mL	27.18	36	3.73		B
100 mL	35.81	43	3.42		B

Medias con una letra común no son significativamente diferentes (p > 0.05)

B3: Variance Analysis between 100 mL and 1000 mL Samples Studies

Análisis de la varianza

Variable	N	R^2	R^2 Aj	CV
%Recovery	142	0.13	0.12	90.16

Cuadro de Análisis de la Varianza (SC tipo III)

F.V.	SC	gl	CM	F	p-valor
Modelo.	10278.65	2	5139.32	10.25	0.0001
EXP	10278.65	2	5139.32	10.25	0.0001
Error	69707.52	139	501.49		
Total	79986.17	141			

Contrastes

EXP	Contraste	E.E.	SC	gl	CM	F	p-valor
Contraste1	8.64	5.06	1461.45	1	1461.45	2.91	0.0900
Total			1461.45	1	1461.45	2.91	0.0900

Coeficientes de los contrastes

EXP	Ct.1
10 mL	0.00
100 mL	1.00
1000 mL	-1.00

Test:LSD Fisher Alfa=0.05 DMS=9.22942

Error: 501.4930 gl: 139

EXP	Medias	n	E.E.		
10 mL	16.01	63	2.82	A	
1000 mL	27.18	36	3.73		B
100 mL	35.81	43	3.42		B

Medias con una letra común no son significativamente diferentes (p > 0.05)

APPENDIX C

COVARIANCE ANALYSES (SAS)

C1: Efficiencies Studies

C2: Partitioning Coefficients

C1: Efficiencies Studies

Class Level Information		
Class	**Levels**	**Values**
EXP	3	1 2 3

Number of Observations Read	161
Number of Observations Used	160

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	7183.50388	1436.70078	46.43	<.0001
Error	154	4764.84911	30.94058		
Corrected Total	159	11948.35298			

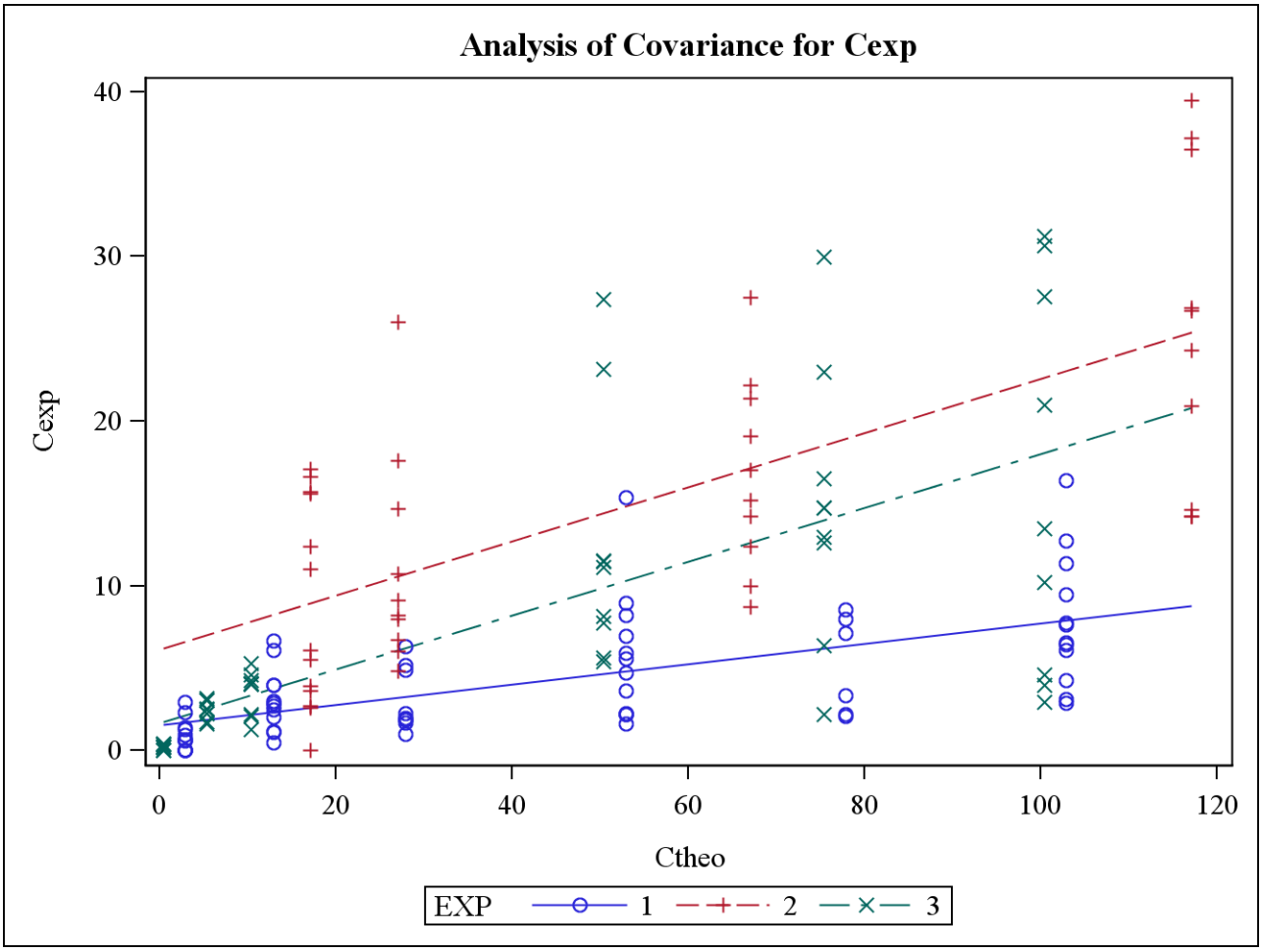
R-Square	Coeff Var	Root MSE	Cexp Mean
0.601213	65.41194	5.562426	8.503686

Source	DF	Type I SS	Mean Square	F Value	Pr > F
EXP	2	2989.215826	1494.607913	48.31	<.0001
Ctheo	1	3647.337264	3647.337264	117.88	<.0001
Ctheo*EXP	2	546.950786	273.475393	8.84	0.0002

Source	DF	Type III SS	Mean Square	F Value	Pr > F
EXP	2	237.775068	118.887534	3.84	0.0235
Ctheo	1	3813.530507	3813.530507	123.25	<.0001
Ctheo*EXP	2	546.950786	273.475393	8.84	0.0002

Parameter	Estimate		Standard Error	t Value	Pr > |t|
Intercept	1.653504447	B	1.10528581	1.50	0.1367
EXP 1	-0.146564666	B	1.55932951	-0.09	0.9252
EXP 2	4.479253460	B	1.82050674	2.46	0.0150
EXP 3	0.000000000	B	.	.	.
Ctheo	0.163363781	B	0.01993586	8.19	<.0001
Ctheo*EXP 1	-0.101201247	B	0.02769769	-3.65	0.0004
Ctheo*EXP 2	0.000894092	B	0.02937609	0.03	0.9758
Ctheo*EXP 3	0.000000000	B	.	.	.

Note The X'X matrix has been found to be singular, and a generalized inverse was used to solve the normal equations. Terms whose estimates are followed by the letter 'B' are not uniquely estimable.



The GLM Procedure

EXP=1

Number of Observations Read	63
Number of Observations Used	63

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	323.3767127	323.3767127	39.22	<.0001
Error	61	502.9289912	8.2447376		
Corrected Total	62	826.3057039			

R-Square	Coeff Var	Root MSE	Cexp Mean
0.391352	67.59787	2.871365	4.247715

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Ctheo	1	323.3767127	323.3767127	39.22	<.0001

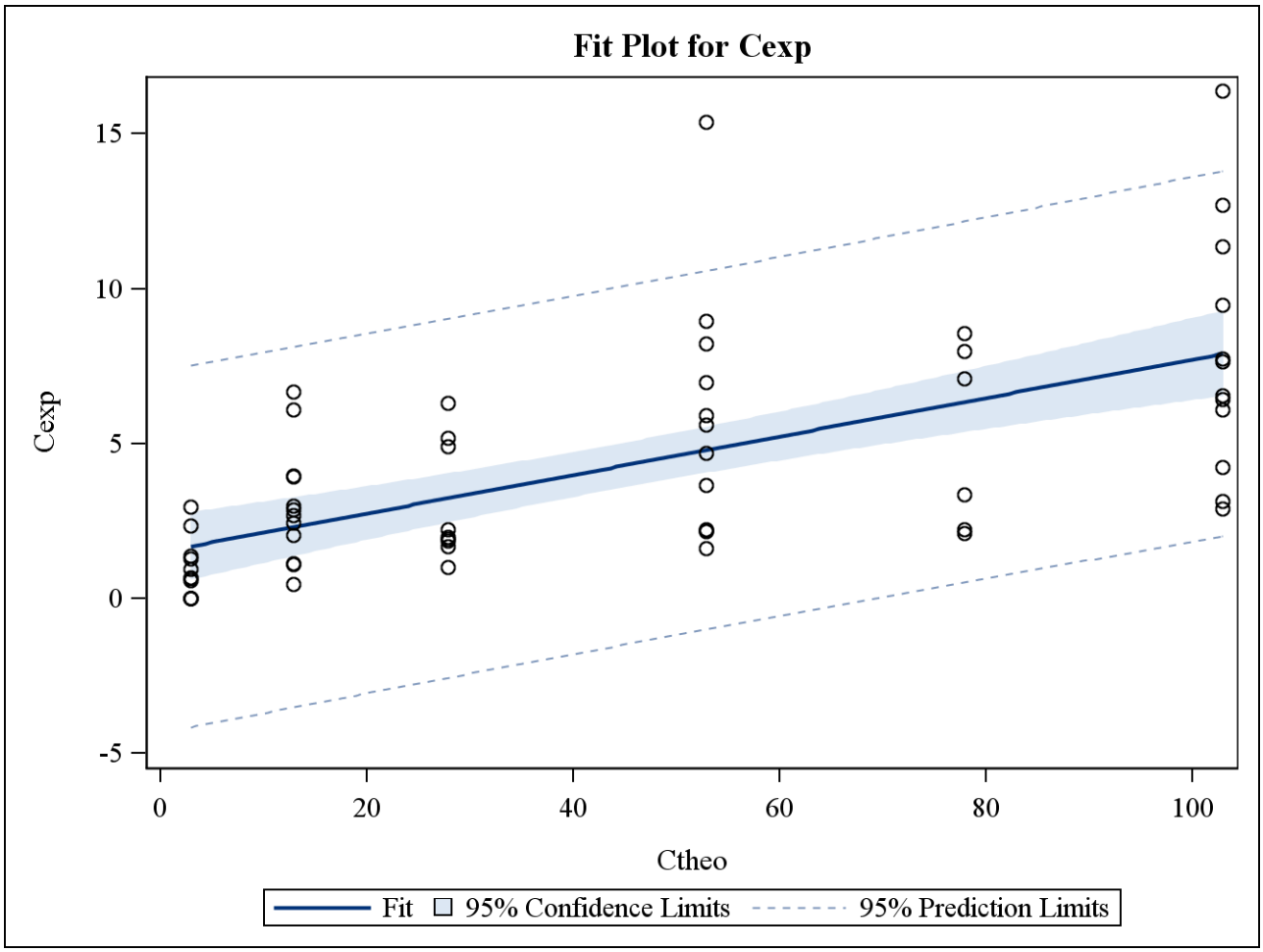
Source	DF	Type III SS	Mean Square	F Value	Pr > F
Ctheo	1	323.3767127	323.3767127	39.22	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > |t|
Intercept	1.506939781	0.56779333	2.65	0.0101
Ctheo	0.062162534	0.00992574	6.26	<.0001

The GLM Procedure

Dependent Variable: Cexp

EXP=1



Number of Observations Read	43
Number of Observations Used	43

The GLM Procedure

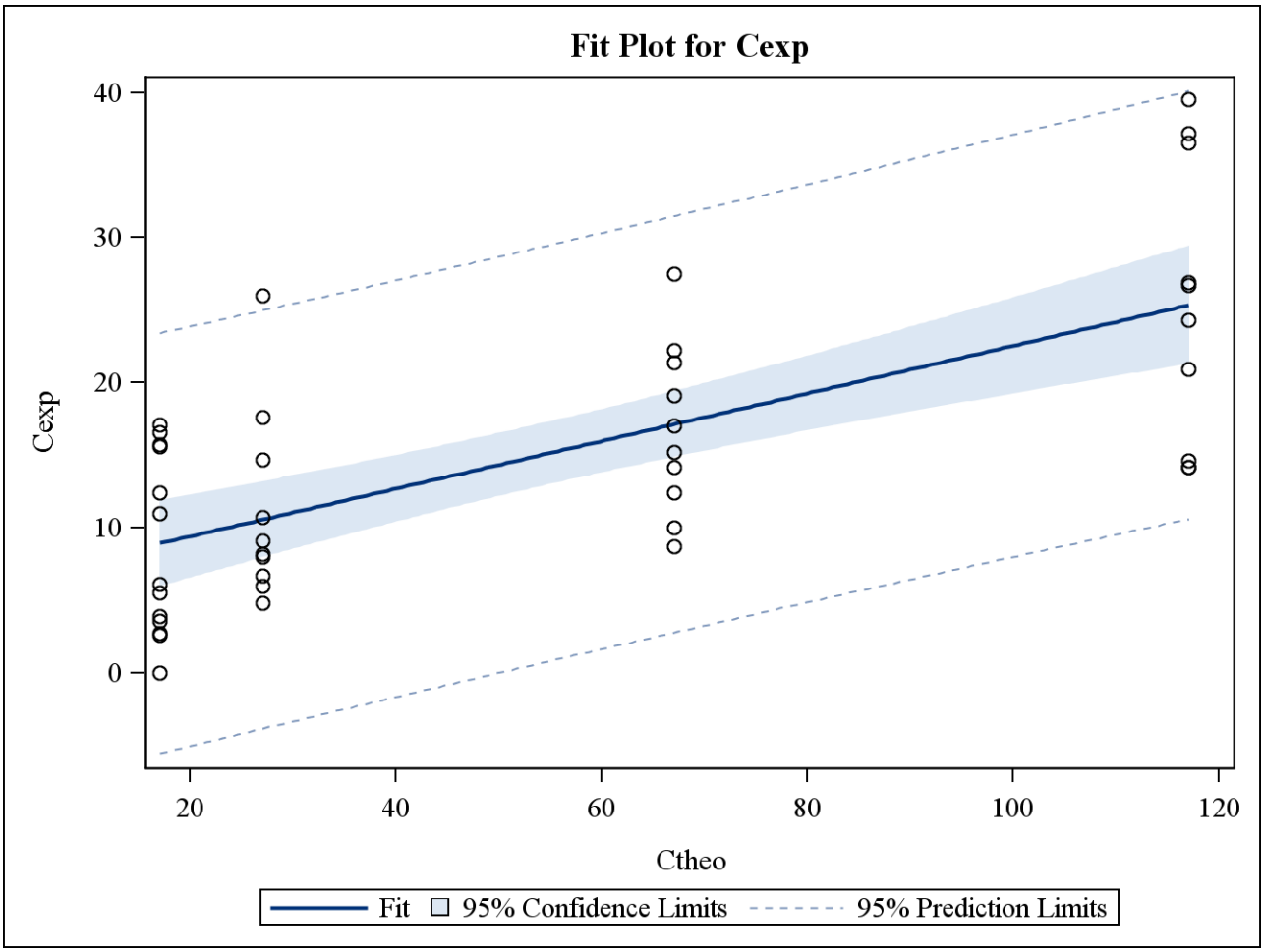
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	1793.271955	1793.271955	36.42	<.0001
Error	41	2018.755022	49.237927		
Corrected Total	42	3812.026977			

R-Square	Coeff Var	Root MSE	Cexp Mean
0.470425	46.61361	7.016974	15.05349

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Ctheo	1	1793.271955	1793.271955	36.42	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Ctheo	1	1793.271955	1793.271955	36.42	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > |t|
Intercept	6.132757908	1.82485155	3.36	0.0017
Ctheo	0.164257873	0.02721780	6.03	<.0001


Fit Plot for Cexp
Cexp
Ctheo
40
30
20
10
0
20
40
60
80
100
120
Fit
95% Confidence Limits
95% Prediction Limits

C2: Partitioning Coefficients

Class Level Information		
Class	**Levels**	**Values**
EXP	3	1 2 3

Number of Observations Read	154
Number of Observations Used	152

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	174692.3081	34938.4616	29.07	<.0001
Error	146	175490.7749	1201.9916		
Corrected Total	151	350183.0831			

R-Square	Coeff Var	Root MSE	Cs Mean
0.498860	64.95951	34.66975	53.37132

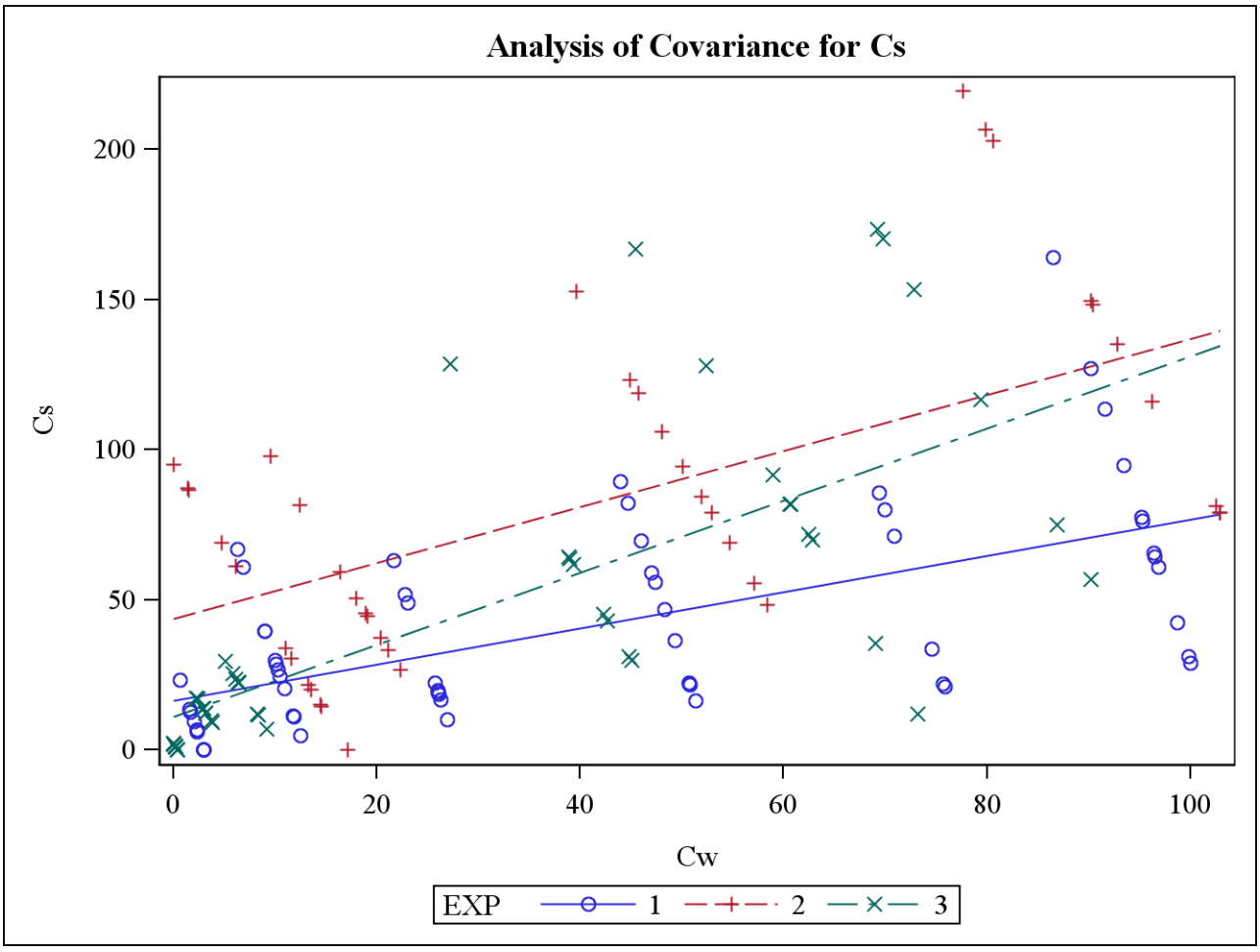
Source	DF	Type I SS	Mean Square	F Value	Pr > F
EXP	2	46332.4456	23166.2228	19.27	<.0001
Cw	1	118200.7922	118200.7922	98.34	<.0001
Cw*EXP	2	10159.0703	5079.5352	4.23	0.0164

Source	DF	Type III SS	Mean Square	F Value	Pr > F
EXP	2	11387.7011	5693.8505	4.74	0.0102
Cw	1	127078.4900	127078.4900	105.72	<.0001
Cw*EXP	2	10159.0703	5079.5352	4.23	0.0164

Parameter	Estimate		Standard Error	t Value	Pr > |t|
Intercept	11.00569241	B	6.81373298	1.62	0.1084
EXP 1	5.46889023	B	9.66657492	0.57	0.5724
EXP 2	32.59635271	B	10.98156678	2.97	0.0035
EXP 3	0.00000000	B	.	.	.
Cw	1.20120336	B	0.16619688	7.23	<.0001
Cw*EXP 1	-0.60015514	B	0.21024917	-2.85	0.0049
Cw*EXP 2	-0.26918213	B	0.23266271	-1.16	0.2492
Cw*EXP 3	0.00000000	B	.	.	.

Dependent Variable: Cs

Note: The X'X matrix has been found to be singular, and a generalized inverse was used to solve the normal equations. Terms whose estimates are followed by the letter 'B' are not uniquely estimable.



Number of Observations Read	61
Number of Observations Used	61

Dependent Variable: Cs

EXP=1

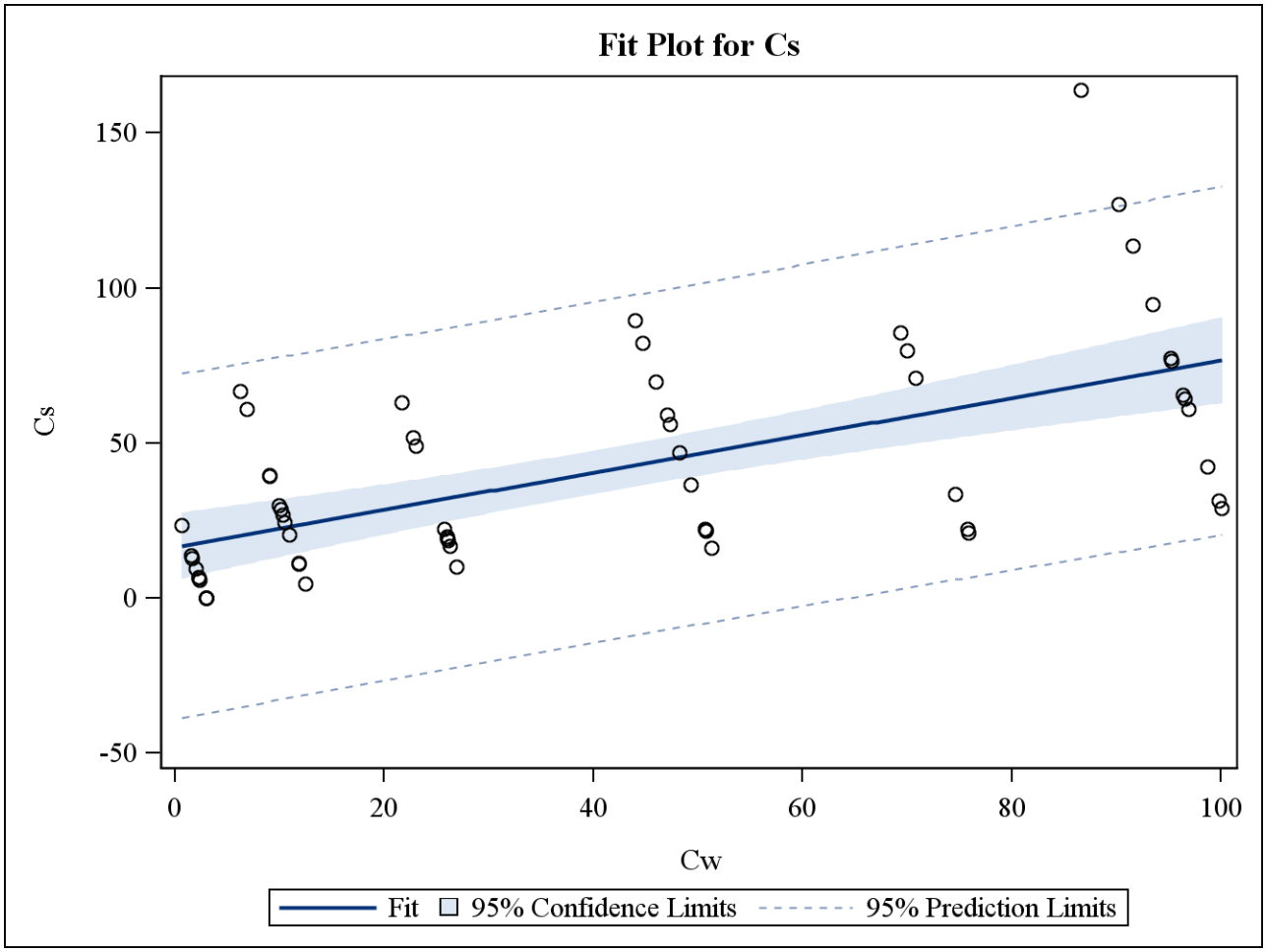
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	26184.77277	26184.77277	35.32	<.0001
Error	59	43737.73834	741.31760		
Corrected Total	60	69922.51111			

R-Square	Coeff Var	Root MSE	Cs Mean
0.374483	66.62498	27.22715	40.86628

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Cw	1	26184.77277	26184.77277	35.32	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Cw	1	26184.77277	26184.77277	35.32	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > |t|
Intercept	16.47458264	5.38484185	3.06	0.0033
Cw	0.60104822	0.10113164	5.94	<.0001


Fit Plot for Cs
150
100
50
0
-50
Cs
0
20
40
60
80
100
Cw
Fit
95% Confidence Limits
95% Prediction Limits

EXP=2

Number of Observations Read	41
Number of Observations Used	41

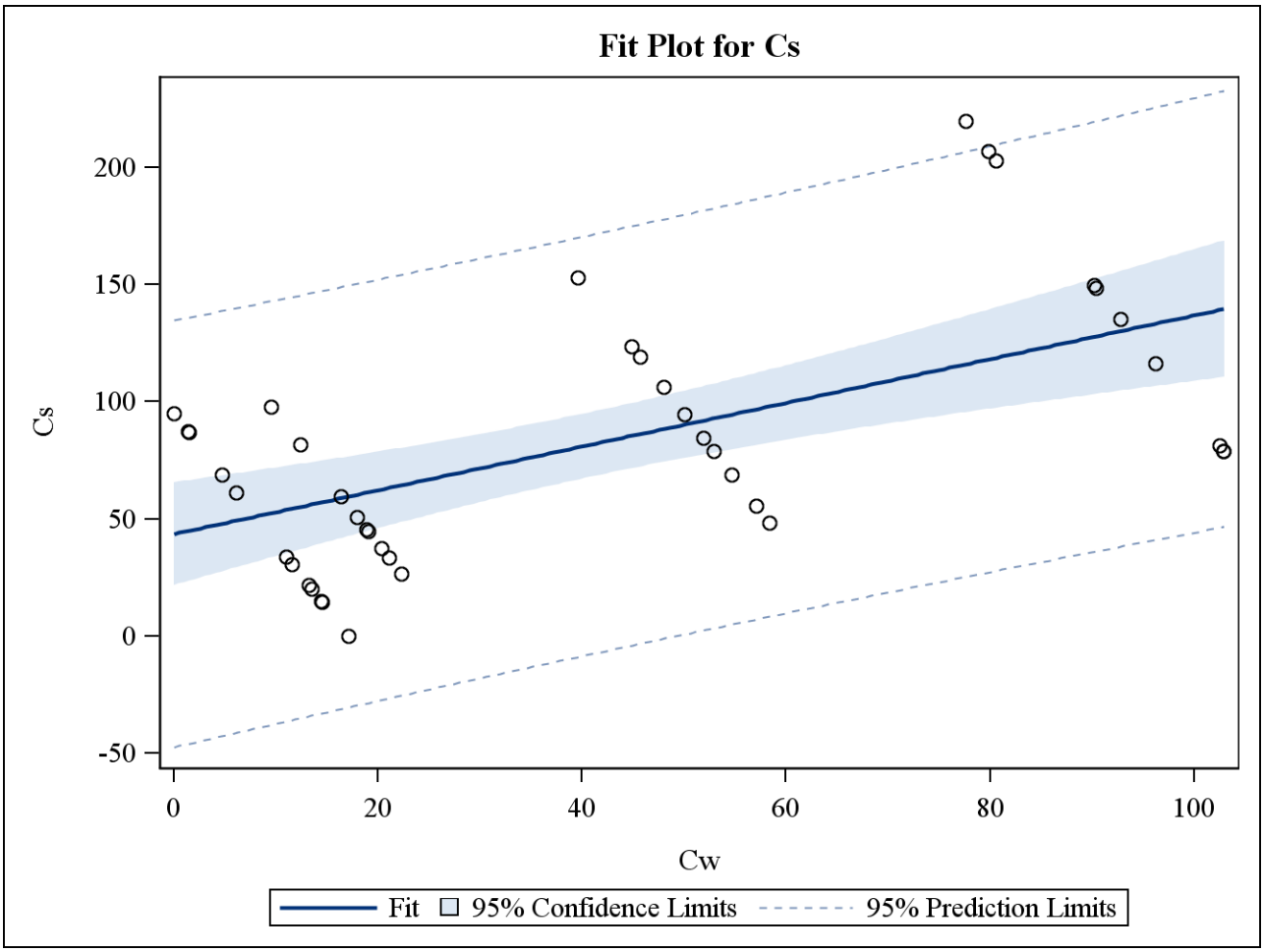
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	39385.3353	39385.3353	20.65	<.0001
Error	39	74380.1721	1907.1839		
Corrected Total	40	113765.5074			

R-Square	Coeff Var	Root MSE	Cs Mean
0.346198	53.29822	43.67132	81.93767

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Cw	1	39385.33526	39385.33526	20.65	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Cw	1	39385.33526	39385.33526	20.65	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > |t|
Intercept	43.60204512	10.84809346	4.02	0.0003
Cw	0.93202123	0.20509488	4.54	<.0001


Fit Plot for Cs
Cs
200
150
100
50
0
-50
0
20
40
60
80
100
Cw
Fit
95% Confidence Limits
95% Prediction Limits