EVALUATING A SOLID-PHASE EXTRACTION METHOD WITH NOVEL POROUS CYCLODEXTRIN POLYMERS

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Chenjun Li

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ABSTRACT

Organic micropollutants (MPs) occur ubiquitously in the aquatic environment at trace concentrations, which presents great challenges for environmental monitoring. Solid-phase extraction (SPE) is a widely-used sample preparation procedure that concentrates MPs in environmentally derived water samples. SPE relies on columns packed with an adsorbent material that captures MPs from water samples. Loaded SPE adsorbents can then be eluted with organic solvents to release the captured MPs. The conventional adsorbent used for SPE is a hydrophilic-lipophilic balanced material available from a variety of commercial vendors, often referred to as HLB. These HLB adsorbents feature stability at extreme pHs and high retention of polar and apolar organic MPs. The primary disadvantage of HLB adsorbent materials is price, which often makes sample preparation the most expensive step in an environmental monitoring workflow. In this research, novel porous β-cyclodextrin polymers (P-CDP) were evaluated as an alternative SPE adsorbent. Cyclodextrins are sustainably produced macrocycles of glucose, featuring a hydrophobic interior cavity that forms host-guest complexes with thousands of organic molecules. P-CDP is a polymer of cyclodextrin and is synthesized in one-step, making it relatively inexpensive to produce. The objective of this research was to develop an SPE procedure using P-CDP and compare its performance to a conventional SPE procedure using HLB. A set of 189 MPs were included in the study and the P-CDP method was optimized to maximize efficiency in MP capture and MP release. The optimized P-CDP method exhibits moderate absolute recovery ($\geq$60%) for 135 (75%) MPs and high absolute recovery ($\geq$80%) for 121 (67%) MPs. The conventional HLB method exhibits moderate absolute recovery for 130 (72%) MPs and high absolute recovery for 109 (61%) MPs. The results of this research demonstrate that P-CDP could be used as a cost-effective SPE adsorbent.

BIOGRAPHICAL SKETCH

Chenjun Li was born in Maanshan, China in 1992. She graduated from Shanghai Jiao Tong University with a Bachelor degree in Environmental Science and Engineering in 2014. In college, she served as the director of the Secretariat of College Students' Union and organized some Environmental Forums within the department. Her experiences in the Environmental Engineering field include a one-month internship as an assistant technician in the Second Monitoring Station of Minhang District (China), a four-month internship as an assistant engineer in the HSE department of AkzoNobel (China) Ltd., and a two-year lab research on electro-photocatalysis in the Jia research group in Shanghai Jiao Tong University. In August 2015, she entered Cornell University. In April 2016, she joined Dr. Damian Helbling's research group and continued her study towards the M.S. Degree in Environmental Engineering.

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CHAPTER 1: INTRODUCTION

1.1 Micropollutants (MPs)

Good water quality is an important precondition for human health. With the increasing consumption of chemical products, waters are increasingly contaminated with organic substances and their residues, such as pharmaceuticals, personal care products (PCPs), household chemicals, and pesticides (Margot et al., 2015).

These so-called organic micropollutants (MPs), or "trace contaminants", have become a major environmental issue for wastewater treatment facilities and water utilities. With a broad range of sources, MPs enter water bodies through different flow paths, including transport from agricultural land, runoff from contaminated surface and ground waters, discharge from sewage systems (sewer overflow or leaking sewers), and untreated wastewaters (Eggen et al., 2014; Musolff et al., 2010). Although most of these MPs are measured at trace concentrations, ranging from ng L^{-1} to μg L^{-1}, many MPs may still cause adverse environmental effects. For example, some industrial chemicals (bis (2-ethylhexyl) phthalate) and hormones (estrone) are confirmed endocrine disrupters (Ahel et al., 1994; Schwarzenbach et al., 2006). Some antibiotics which have been widely used in personal hygiene products for several decades, such as triclosan, are suspected to have the potential of enhancing bacterial resistance. In fact, triclosan was regarded as a safe antibacterial agent previously (Bedoux et al., 2012; McMurry et al., 1998), but in 2016 the U.S. Food and Drug Administration (FDA) issued a final rule and banned its usage in many personal care products (U.S. FDA, 2016). The U.S. Environmental Protection Agency (EPA) is also currently reviewing the risk of triclosan exposure to humans (Beyond Pesticides, 2016). Besides, some other emerging contaminants appearing in water resources have increasing environmental concerns. One group of closely watched emerging contaminants are the perfluoroalkyl substances

(PFASs), which have potential negative impacts for human health. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are the two most intensely used PFAS chemicals during many industrial processes. Studies conducted by the U.S. EPA showed that PFOA and PFOS could cause reproductive and immunological problems on lab animals, indicating its potential of having negative impacts on the immune system of humans, as well as the potential of contributing to cancer and thyroid disruption. Therefore, the U.S. EPA recently issued a human health advisory level for PFOA and PFOS at a combined concentration of 70 ng L^{-1} in drinking water (US EPA; Water Research Foundation, 2016). The level is quite low and could hardly be detected by current instruments directly without some sample concentration steps.

Emerging concern over MPs occurring in water resources has motivated a number of monitoring studies focused on characterizing MP occurrence in groundwater, surface water, wastewater, and drinking water (Benner et al., 2013; Gilliom, 2007; Kolpin and Meyer, 2002; Pochodylo and Helbling, 2016). However, there are unique challenges associated with environmental monitoring for MPs. In the following sections, I will describe some of the important considerations for sample preparation and sample analysis with respect to MP monitoring.

1.2 Sample Preparation

Some of the biggest challenges for environmental monitoring of MPs are their occurrence at low concentrations, their occurrence in complex matrices, the large diversity of chemical structures, and the variability in mobilization from different sources. Therefore, careful sample collection and sample preparation techniques are required to enable robust analysis and detection. The conventional sample preparation workflow for MP analysis includes sample collection, sample handling (filtration, acidification, or basification) and sample clean-up (extraction, elution,

evaporation and reconstitution if necessary) (Comerton et al., 2009). Each of these steps will be discussed in the following.

Sample collection. Representative samples are important for obtaining reliable data for decision making. Large sampling errors and sampling biases may contribute to the improper interpretation of collected data, and further lead to wrong conclusions. Appropriate sampling mode, sampling frequency, sample distributions, and sample numbers all help reduce errors and biases. First, the variations of flow determine the sampling mode. If the variations have a fixed pattern, some sampling time points with proper frequency could be selected; while if the variations have some rapid changes or are totally random, continuous sampling is a more suitable sampling mode (Ort, C., Lawrence, M. G., Rieckermann, J., and Joss, 2010). Second, the concentration variations of target MPs is the determining factor for choosing the sampling frequency. The frequency of changes of the concentrations must be carefully investigated beforehand, with the help of some online automatic instruments. The sampling intervals for collecting a 24-hour average sample largely depends on the frequency of changes of concentrations of the target MPs. Since many MPs exist in waters at very low concentrations and could not be detected directly by online instruments, a high frequency of sampling is usually adopted to ensure the representativeness of samples (Ort, C., Lawrence, M. G., Rieckermann, J., and Joss, 2010). Besides, the distribution of sampling locations is selected according to the field situation and MPs of interest, usually three replicates are needed to ensure the precision of collected data. The total number of samples are calculated based on the total area or the total load required for monitoring. Water samples are usually collected using trace clean preservative bottles. Some acids, bases, or other preservatives are often necessary for stabilizing different kinds of target compounds or preventing bacterial activity.

Samples are usually stored under 4 ℃ before handling for no longer than 48 hours (U.S. EPA, 2005).

Sample handling. Environmental samples usually first need filtration to remove large particles or interferences like natural organic matter (NOM), otherwise clogging could happen during the following clean-up steps or the analysis procedures. Cellulose and glass fiber filters are typically used to minimize adsorption of organic MPs (Comerton et al., 2009). Besides, the pH of the water sample is one of the key factors that may have impacts on analysis. pH can determine the speciation of target analytes and change the ionic strength of water samples, which may lead to different interactions with analytes and sorbents in the following clean-up steps. For example, some acidic drugs favor low pH (around 2.5) to achieve undissociated forms and high recoveries during extraction (Hartig et al., 1999). In addition, for complicated environmental samples such as lake waters or wastewaters, some field "spike" samples are used to measure the loss or gain of analytes due to degradation and water-matrix characteristics. These "spike" samples are achieved by adding labelled standards at certain predetermined concentrations into samples collected in field. The "spike" samples help determine the bias and reflect the actual concentration of analytes expressed as the ratio of the amount spiked (Myers, 2006). After handling, some clean-up steps are conducted before analysis, so that the instrumental analysis of target analytes could be more sensitive and precise.

Sample clean-up. Sample clean-up usually refers to extraction and concentration. This step is the most important part of the overall sample preparation workflow. During clean-up processes, analytes will be extracted from water samples, the complexity of the matrix will be reduced, and the consequent analytical interferences will be minimized.

Generally speaking, classical liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are the two major methods for sample extraction and concentration. LLE uses the differences of relative solubility of target analytes in two solvents as a means to separate analytes. Enrichment happens when solutes transfer from one solvent to another. Analytes in the feed solution (solvent containing analytes of interest) will gradually partition into another solvent. Many optimized LLE methods were widely used in clinical analysis, food analysis, and pharmaceutical bioseparation for decades (Silvestre et al., 2009; Xu et al., 2001). However, LLE is difficult to automate and cannot achieve high recoveries for polar compounds (Cabaleiro et al., 2013; Silvestre et al., 2009), therefore it is seldom used for environmental water sample enrichment.

Conventional SPE uses specific or mixed solid adsorbents to retain analytes from liquid samples; target analytes can be concentrated after desorbing from solid adsorbents into a small amount of solvent. SPE has many advantages over LLE for analyzing MPs in water samples. For example, target compounds adsorbed onto solid adsorbents can be stored for some period of time under proper conditions of handling and storage, with concentration or components unchanged. Further, reproducibility is largely improved with the stable solid adsorbents relative to LLE (Green and Pape, 1987). Besides, SPE generally requires a smaller volume of organic solvent than LLE, and is easier to automate for high sample throughput, therefore is more energy-saving and cost-effective (Ahadi and Partoazar, 2011). Another important feature of SPE is that it can extract a wide range of organic analytes from complex matrices with portable configurations (Andrade-Eiroa et al., 2016a). SPE has also made remarkable progress in terms of solvents, and therefore has advantages specifically for the retention of polar drugs and metabolites compare to LLE (Ahadi and Partoazar, 2011; Cabaleiro et al., 2013; Saar et al., 2009; Titato and Lanças, 2005), which is very desirable for environmental monitoring and analysis for emerging contaminants. Recently,

SPE has been accepted in many EPA methods for analysis of organic pollutants in waters. For example, Method 1964 suggested conducting SPE with HLB cartridges to analyze personal care products (PCPs) and pharmaceuticals in waters (EPA, 2007).

Choice of SPE adsorbents is the key point for the overall SPE procedure because different adsorbents have various selectivity, affinity and capacity (Pavlović et al., 2007). Conventional SPE adsorbents include chemically bonded silica with C18, ion-exchange materials, polymeric materials, and molecularly-imprinted polymers (MIPs). Many of those adsorbents are relatively limited to some certain kinds of target analytes (Gros et al., 2006a; Pavlović et al., 2007; Pichon, 2000). Currently, hydrophilic-lipophilic balanced adsorption materials (HLB) remain the most popular SPE adsorbents for a wide range of organic compounds because it is pH stable and exhibits high capacity and good recoveries for many organic chemicals. Many multi-residue analytical methods aiming to quantify the occurrence of hundreds of MPs have been developed with HLB used for sample extraction and concentration (Cazorla-Reyes et al., 2011; Gros et al., 2006a, 2006b; Huntscha et al., 2012; Robles-Molina et al., 2014; Subedi et al., 2014; Zhang and Zhou, 2007). Although HLB has many advantages as an SPE adsorbent, the major disadvantage is the high unit price, which makes sample preparation one of the most expensive parts of the overall analytical workflow.

1.3 Sample Analysis

During the sample preparation step, target analytes are concentrated to detectable ranges and subsequently can be measured on a variety of analytical instruments directly. Two common analytical techniques are gas chromatography mass spectrometry (GC-MS) and liquid chromatography mass spectrometry (LC-MS). These analytical procedures include two parts. The

first step is the separation of target analytes, which is achieved by chromatography. With mass spectrometry, analytes can be detected and quantified.

1.3.1 Gas Chromatography Mass Spectrometry (GC-MS)

GC-MS is an analytical technique used for decades and has been most typically applied for analyzing volatile or non-polar compounds. The stationary phase of GC is a layer of inert fluid and the mobile phase is an inert gas, usually helium or nitrogen. During the operation, concentrated samples are injected into the instrument, and the carrier gas (mobile phase) carries samples to the analytical column, a division tube. Different analytes would be separated in the column based on different physiochemical properties and relating interactions (Pravallika, 2016). GC-MS is still being adopted in environmental laboratories as a reliable analytical technique. However, polar analytes with GC sometimes need to be converted to less polar analogues to achieve higher thermal stability and volatility (Radjenović et al., 2007). Therefore, GC is not a suitable analytical technique for analyzing MPs in waters, especially for more polar compounds such as acidic pharmaceuticals and pesticides.

1.3.2 Liquid Chromatography Mass Spectrometry (LC-MS)

LC-MS is the most popular analytical technique for analyzing environmental water samples for MPs. LC-MS usually applies to non-volatile, polar compounds such as the more polar pharmaceuticals and pesticides (Gómez et al., 2006; Gros et al., 2006b; Sargent et al., 2013). LC-MS also employs a mobile phase, in this case an organic solvent, and a stationary phase, an analytical column packed with a solid material. Separation of analytes occurs on the analytical column as mobile phase passes through the column. In reversed-phase chromatography, polar compounds elute at short retention times and under highly aqueous mobile phase and apolar compounds elute at longer retention times and under highly organic mobile phase. LC-MS is more

favorable for organic micropollutants in the explicit identification of the analytes. Even with the same molecular mass, LC-MS can still separate and identify the unique peak of several analytes based on different product ions as well as molecular fragments (Comerton et al., 2009). The major drawback of LC-MS is the matrix effect of water samples, but with internal standards, matrix effects could be minimized. In this research, LC-MS was used as the final sample analysis method for detecting and quantifying a variety of MPs, covering a broad range of polarity.

1.4 Research Objective

Among the overall environmental monitoring workflow, sample preparation is the most expensive part, but it is also essential for generating reliable results. As mentioned in the preceding section, currently HLB is the universal SPE adsorbent used for analyte extraction and concentration with high unit price. Cheaper but also broadly effective adsorbents would be very desirable, and can provide significant value for MP monitoring.

In this research, a novel porous β-cyclodextrin polymer (P-CDP) was adopted as the alternative SPE adsorbent. The unit price of P-CDP is estimated to be one thousand times cheaper than HLB (Alsbaiee et al., 2016), and has been regarded as an effective adsorbent for the removal of a wide range of MPs in water (Ling et al., 2017). It was also demonstrated that P-CDP has the potential of releasing certain MPs with easy rinsing steps (Alsbaiee et al., 2016). Therefore, the objective of this research was *to develop and evaluate a solid-phase extraction method for a wide range of micropollutants with P-CDP as the adsorbent*. I hypothesized that P-CDP will outperform leading SPE materials (HLB) for the enrichment of micropollutants in aqueous samples. To test this hypothesis, (1) a conventional SPE method was adapted from the literature and the procedure was replicated using an HLB material and a mixture of 189 micropollutants, (2) the performance of the P-CDP material was compared to the HLB material using the previously described

conventional SPE method, and (3) the SPE method was systematically optimized to improve the performance of P-CDP as an SPE material. The result of this work is an optimized SPE method that uses P-CDP and outperforms conventional SPE methods that utilize HLB materials.

CHAPTER 2: EVALUATING A SOLID-PHASE EXTRACTION METHOD WITH NOVEL POROUS CYCLODEXTRIN POLYMERS

Abstract

Organic micropollutants (MPs) occur ubiquitously in the aquatic environment at trace concentrations, which presents great challenges for environmental monitoring. Solid-phase extraction (SPE) is a sample preparation procedure used for bringing concentrations of MPs to detectable levels. The conventional adsorbent used for SPE is a hydrophilic-lipophilic balanced material, often referred to as HLB. However, its high unit price makes sample preparation one of the most expensive parts of the overall environmental monitoring workflow. In this research, a novel β-cyclodextrin polymer (P-CDP) was studied as a potential SPE adsorbent and its performance was compared to HLB. Absolute recovery rates for 189 target MPs were first evaluated for P-CDP and HLB using conventional SPE conditions previously optimized for HLB (180 mg adsorbent, loading at pH 6, 5 mL methanol elution). Under these conditions, P-CDP performed rather poorly as an SPE material. The SPE conditions were then systematically optimized to improve the absolute recovery rate of MPs on P-CDP. These optimization steps included evaluation of adsorbent mass, sample loading pH, and volume and composition of elution solvent. After optimization (500 mg adsorbent, loading at pH 3, 15 mL salt-assisted methanol elution), the P-CDP method exhibited moderate absolute recovery ((≥60%) for 135 (75%) MPs and high absolute recovery (≥80%) for 121 (67%) MPs. The conventional HLB method exhibited moderate absolute recovery for 130 (72%) MPs and high absolute recovery for 109 (61%) MPs. The results of this research demonstrate that P-CDP could be used as a cost-effective SPE adsorbent.

2.1 Introduction

During the last few decades, there has been increasing concerns over the occurrence of organic micropollutants (MPs) in the aquatic environment (Eggen et al., 2014; Geissen et al., 2015; Petrie et al., 2014; Sorensen et al., 2015). MPs consist of a broad range of both anthropogenic compounds and natural substances including pharmaceuticals, personal care products, industrial chemicals, and pesticides (Luo et al., 2014). Sources of MPs are diverse and include industrial wastewater, domestic wastewater, landfill leachates, and runoff from agriculture or urban landscapes (Barbosa et al., 2016). Conventional WWTP processes are not specifically designed for eliminating MPs, and the majority of MPs will appear in vital aquatic environments such as surface water, ground water, or even in drinking water (Mompelat et al., 2009; Ternes et al., 2015; Tijani et al., 2013). Although these MPs exist in waters at trace concentrations, mainly observed from several ng L^{-1} to a few μg L^{-1} (Petrie et al., 2014), their presence may cause negative ecological impacts to aquatic ecosystems (Carbajo et al., 2014; Eggen et al., 2014; Etchepare and van der Hoek, 2015; Haddad et al., 2015; Tijani et al., 2013).

The very low concentrations of MPs and the broad range of sources complicate environmental monitoring. Although analytical instrumentation has developed rapidly, many MPs still cannot be detected at environmentally relevant concentrations using instruments directly such as with liquid-chromatography coupled to a mass spectrometer (LC-MS). In addition, environmental waters are complex and usually contain a lot of natural and anthropogenic chemical constituents. Sample preparation works are necessary for extracting, isolating and concentrating target analytes with certain characteristics from complex matrices (Kataoka, 2003). Sample pretreatment steps are of importance, and the quality of sample pretreatment is the key factor for determining the success of analysis. With proper sample enrichment methods, potential interferes in complex matrices could be removed so that reproducible analytical methods could be set up and target analytes could be enriched and

stabilized to provide more sensitive and precise analysis. Besides, tailored preparation works help increase the potential for automated monitoring (Pavlović et al., 2007).

Recently, some sample enrichment methods have been developed to bring the concentration of MPs into detectable ranges and to extract target compounds from various matrices. Solid-phase extraction (SPE) is one of the most useful methods for effectively extracting organic compounds. It largely replaced the older techniques, such as liquid-liquid extraction (LLE), and has been widely used in biological analysis, environmental sample enrichment, and clinical treatments (Andersson, 2000; Andrade-Eiroa et al., 2016b; Cai et al., 2003; Gómez et al., 2006; Lindsey et al., 2001). SPE uses solid adsorbents to extract target compounds from water samples, and is mostly used to prepare liquid samples and extracts of non-volatile or semi-volatile analytes (Pavlović et al., 2007). It also has great tolerance for extracting polar compounds, and therefore fits the extraction of emerging contaminants well.

One universal adsorbent for general use in SPE is HLB. HLB stands for hydrophilic-lipophilic balance, the polymeric adsorbent has a poly (divinylbenzene-co-N-vinylpyrrolidone) skeleton with a nominal pore size of 8 nm and a specific surface area of about 800 $m^2 g^{-1}$ (Dias and Poole, 2002). Within the structure, the imbedded hydrophilic groups (pyrrolidone) provide good wettability and enhance retention for some polar compounds, while lipophilic groups promote interactions with more hydrophobic organic compounds (Fanali et al., 2017). HLB has very high capacity because of its high specific surface area and usually requires low elution volumes due to the small bed mass used in SPE cartridges. It is also pH stable and compatible with a broad range of organic solvents. Compared to some regular silica-based adsorbents, HLB has larger enrichment factors and permits more selective elution (Robles-Molina et al., 2014). Its chemical structure and a picture of the solid form is shown in Figure 1. Many adapted HLB-based SPE procedures have been applied for the analysis of pesticides, metabolites, pharmaceuticals, and other emerging pollutants in waters (Heavner et al., 2005; Liu et al., 2006;

Zhang and Zhou, 2007). However, the unit price of HLB ranges from $13 to $31 per gram (Sigma-Aldrich, 2017; Waters, 2017), which also makes current sample preparation works one of the most expensive parts of the overall environmental monitoring workflow. Therefore, cheaper but also broadly effective SPE adsorbents are desirable.

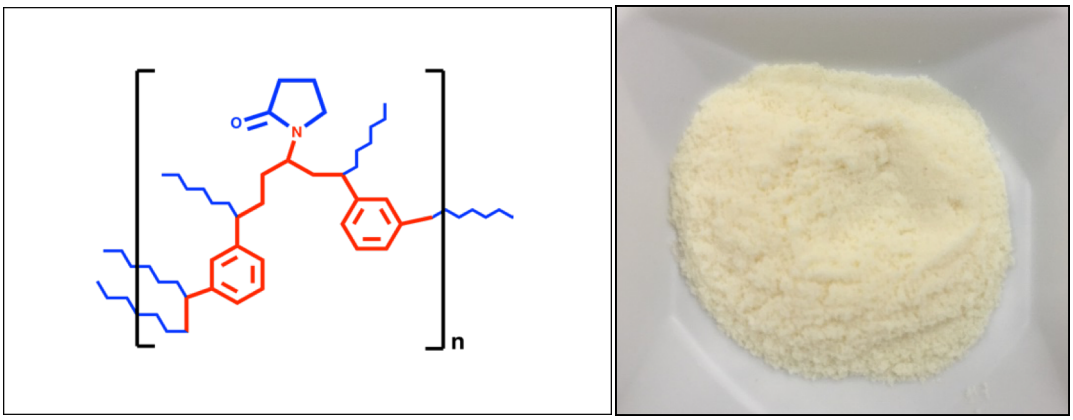


Figure 1. Oasis HLB in its chemical form (left) and in its solid form (right).

Last year, our research group reported the discovery of a novel porous β-cyclodextrin polymer (P-CDP), an inexpensive, sustainably produced macrocycle of glucose (Alsbaiee et al., 2016). β-cyclodextrin polymers form host-guest complexes with thousands of organic compounds, and have already been applied in biological and environmental related applications (Gidwani and Vyas, 2014; Jambhekar and Breen, 2016; Morin-Crini and Crini, 2013; Raoov et al., 2014). The basic shape of the cyclodextrin monomer is like a cup, which consists of a hydrophobic cavity and hydrophilic exterior. Similar to HLB, the hydrophobic cavity of P-CDP could provide interactions with organic compounds, and the hydroxyl groups make P-CDP contact thoroughly with water. Networked with proper cross-linkers, P-CDP remains stable in water. The chemical structure and the photo of its solid form is shown in Figure 2.

The newly made P-CDP material has high water uptake rate due to its porous surface, and has outperformed conventional adsorbents like activated carbon in both batch and flow-through experiments, suggesting great ability of extracting a broad range of MPs in waters (Ling et al., 2017). In addition, adsorbed bisphenol A could be released by simply rinsing the

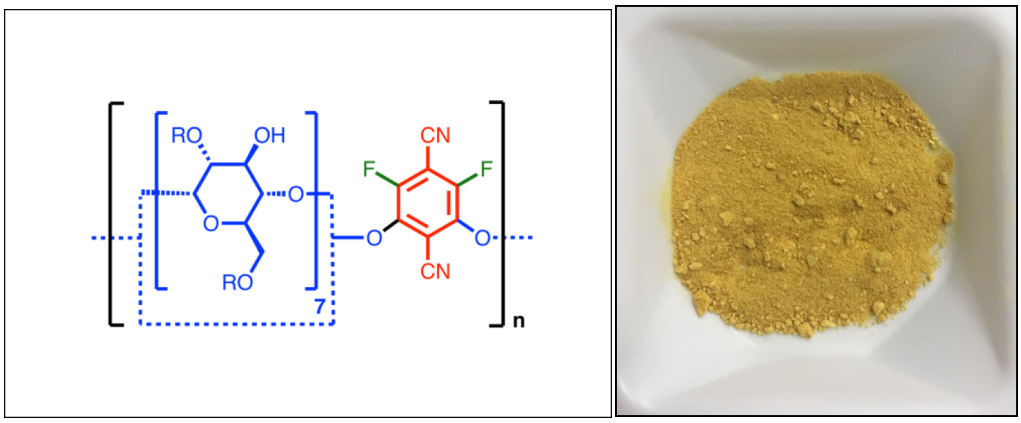


Figure 2. P-CDP in its chemical form (left) and solid form (right).

polymer with methanol at room temperature, indicating P-CDP has the potential for facile recovery of polar compounds (Alsbaiee et al., 2016). Therefore, P-CDP has great potential to capture and release MPs at environmentally relevant concentrations. The unit price of P-CDP is around $11 per kilogram based on pilot scale, which is more than one thousand times cheaper than HLB (Alsbaiee et al., 2016). I expect that P-CDP could be a useful or alternative SPE adsorbent. Therefore, the objective of this research was *to develop and evaluate a solid-phase extraction method for a wide range of micropollutants with P-CDP as the adsorbent*. I hypothesized that P-CDP will outperform leading SPE materials (HLB) for the enrichment of micropollutants in aqueous samples. To test this hypothesis, (1) a conventional SPE method was adapted from the literature and the procedure was replicated using an HLB material and a mixture of 189 micropollutants, (2) the performance of the P-CDP material was compared to the HLB material using the previously described conventional SPE method, and (3) the SPE method was systematically optimized to improve the performance of P-CDP as an SPE material. The result of this work is an optimized SPE method that uses P-CDP and outperforms conventional SPE methods that utilize HLB materials.

2.2 Materials and Methods

2.2.1 Standards and Reagents

A total of 242 compounds were selected for the evaluation and optimization of a conventional solid-phase extraction procedure. These compounds are representative of seven groups of chemicals based on usage including pharmaceuticals (47%), pesticides (36%), industrial chemicals (7%), lifestyle chemicals (3%), hormones (3%), natural chemicals (3%), and illicit drugs (1%). These compounds were also selected based on their varied physicochemical properties including their size (McGowan volume), their pK_a (and resulting charge state at pH 3 and pH 6), and their hydrophobicity ($logK_{ow}$ and logD). A summary of all 242 compounds including name, CAS number, supplier, chemical formula, usage category, and physicochemical properties is provided in Table A1 in Appendix A. Stock solutions of each compound and 44 isotope-labelled internal standards (ILIS) were prepared in appropriate solvents at a concentration of 1 g L^{-1} or 0.1 mg L^{-1} (depending on the solubility characteristics of the compound). An experimental mixture containing all 242 compounds was prepared in Milli-Q water at a concentration of 5 mg L^{-1} and a mixture of the ILISs was prepared in Milli-Q water at a concentration of 10 mg L^{-1}. All stock solutions and the experimental mixture were stored in a freezer at -20 ℃ until usage. Information on the solvents used for preparing the stock solutions is provided in Table A2 in Appendix A and information on the ILISs is provided in Table A3 in Appendix A.

2.2.2 Solid-Phase Extraction

The general solid-phase extraction (SPE) procedure was adapted from a previously reported study (Vogler, 2013). Synthetic water samples consisting of Milli-Q water spiked with the experimental mixture of compounds were used to validate the procedure using a conventional hydrophilic-lipophilic balance (HLB) SPE material (Oasis, Waters) and to

optimize the procedure for a novel porous cyclodextrin polymer (P-CDP) material synthesized as previously described (Alsbaiee et al., 2016).

Sample preparation. Five 1 L water samples were prepared for each SPE test and labelled as the blank sample, the calibration sample, and three recovery samples (R1 – R3). A volume of 100 µL of the 5 mg L^{-1} experimental mixture was spiked into each of the three recovery samples to yield a concentration of 500 ng L^{-1} of each of the 242 compounds. The five prepared samples were then filtered through glass microfiber filters (GF/F Circles, 47 mm, Whatman™; Nalgene filter) under vacuum to remove unwanted particles; recovery samples were filtered after the blank and calibration samples. Then, 1 mL of 1 M ammonium acetate buffer was added to each sample and the pH was adjusted to around 6 using 20% formic acid and a 1.4 N ammonia solution.

Solid phase extraction. For each SPE test, five solid-phase extraction cartridges (PP, 6 mL, Supelco) were filled with a fixed mass (180 mg in the base case, higher masses during the optimization steps) of SPE material (either HLB or P-CDP) sandwiched between two porous frits (PE, 20 µm, Supelco). The SPE procedure was performed on a 12 port SPE vacuum manifold (Phenomenex). The cartridges were first conditioned with a mixture of 5 mL of pure methanol and 10 mL of Milli-Q water to remove residues and then loaded with the prepared 1 L samples. The loading speed was controlled at 1~3 drops per second by adjusting the vacuum condition; the total loading period lasted from 5.5 hours to 7.5 hours. To evaluate compound capture, samples were taken from the effluent of the cartridges during the loading step and stored at 4 ℃ prior to analysis. After the loading step, all cartridges were dried under vacuum and were stored in a refrigerator overnight at 4 ℃. The next day, cartridges were removed from the refrigerator and warmed to ambient temperature (around 25 ℃) before elution. Elution was achieved by passing a fixed volume (5 mL in the base case, higher volumes during optimization) of organic solvent (methanol in the base case, other solvents or amendments during

optimization) over each cartridge and collecting the eluate in a centrifuge tube (15 mL, VWR). A volume of 100 µL of the 5 mg L^{-1} experimental mixture was spiked into the eluate from the calibration sample. A volume of 20 µL of the 10 mg L^{-1} ILIS mixture was spiked into the eluate of all five samples. Collected eluates were then evaporated under a gentle flow of high purity nitrogen gas until dry. The dried eluates were reconstituted in 100 µL of methanol and 900 µL of Milli-Q water and mixed with a vortex mixer (Fisher Scientific) for a few seconds. The reconstituted eluate was then transferred into a plastic syringe, filtered with 4 mm syringe filters (0.45 µm, VWR) into 2 mL amber vials, and stored in a freezer at -20°C before analysis.

2.2.3 Analytical Methods

Quantification of analytes was by means of high-performance liquid chromatography (HPLC) coupled to a quadrupole-orbitrap mass spectrometer (MS) (QExactive, ThermoFisher Scientific). For concentrated samples (offline method), the analytical method was adapted from a previous study reporting the screening of transformation products of organic micropollutants by means of high-performance liquid chromatography (HPLC) coupled with high-resolution mass spectrometry (Helbling et al., 2010; Pochodylo and Helbling, 2016). Briefly, for the reconstituted SPE eluate, a volume of 30 µL of each sample was injected onto a 20 µL sample loop and separated on a reversed-phase analytical column (XBridge^{TM} C18 column; 3.5 µm; 2.1 mm × 50 mm). The mobile phase consisted of HPLC grade water (A) and methanol (B) both acidified with 0.1 vol% formic acid and was delivered to the analytical column by a gradient pump at flowrate of 0.2 mL min^{-1}. The mobile phase gradient started at 90% A and decreased linearly to 50% A over 4 mins and then to 5% A ever the next 13 minutes where the gradient was held constant for 8 minutes before switching back to 90% A to equilibrate the analytical column prior to injection of the next sample. The overall analysis for each sample lasted for 29 minutes. For the capture samples collected during SPE cartridge loading (online method), the analytical method was adapted from a previous study reporting the ultra-trace

level screening of polar and semi-polar organic chemicals (Huntscha et al., 2012; Ling et al., 2017). Briefly, samples were injected at 5 mL volumes and were loaded onto an XBridge (Waters) C-18 Intelligent Speed (2.1 mm × 20 mm; particle size 5 μm) trap column with a loading pump delivering 98% A at 2 mL min^{-1}. Elution from the trap column and onto the analytical column (XBridge^{TM} C18 column; 2.1 mm × 50 mm; particle size 3.5 μm) was performed using a gradient pump delivering 0.2 mL min^{-1} of mobile phase as described in the preceding. The HPLC-MS was operated with electrospray ionization (ESI) in positive and negative polarity modes. The MS acquired full-scan MS data within a mass-to-charge range of 100-1,000 for each sample followed by a data-dependent acquisition of product ion spectra (MS/MS). Analytes from concentrated samples (offline method) were quantified based on the area ratio of the analyte to ILIS area response; analytes from capture samples (online method) were quantified based on the analyte response and external calibration standards. Limits of detection (LOD) for each analyte were determined as the lowest point of an external calibration curve in which at least 5 spectra could be observed at a certain intensity (greater than 10^5) with clear isotopic signatures and the most intense MS/MS fragments were still detected. All 242 compounds were carefully examined, and 189 compounds with a LOD (offline method) less than 500 ng L^{-1} were selected as a final set of compounds for this study. Exact molecular masses, ionization behavior, retention times, the most intense MS/MS fragments, and limits of detection of each analyte are provided in Table B1 in Appendix B.

2.2.4 Data Analysis

To evaluate the performance of the two SPE materials (HLB and P-CDP), the absolute recovery rate, the capture recovery rate, and the relative recovery rate of each target compound was calculated.

Absolute Recovery Rate. Absolute recovery rate (AbsRec) of each compound represents the overall SPE performance of the SPE materials. Because ILISs were spiked into the recovery

samples prior to evaporation and reconstitution, losses during these steps or due to matrix suppression are accounted for. The absolute recovery rate for each target compound is determined as the ratio of the recovered/actual concentration to the theoretical concentration, and was calculated as:

$$\text{AbsRec}\ (\%) = \frac{Area\ Ratio\ of\ Recovery\ Sample - Area\ Ratio\ of\ Blank\ Sample}{Area\ Ratio\ of\ Calibration\ Sample - Area\ Ratio\ of\ Blank\ Sample} \times 100\%$$

Equation (1)

In final optimized SPE recovery tests (salt-assisted elution SPE tests), we could only detect and report 180 out of 189 target compounds with low offline LODs (< 500 ng L^{-1}) limited by current instrumental analytical method.

Absolute Capture Rate. Absolute capture rate (AbsCap) of each compound is used to express the capture efficiency of the SPE materials during the loading step. For capture samples, no ILIS was added because the concentration of each compound was very low. The absolute capture rate for each target compound is determined as the ratio of the differences of the peak areas, and was calculated as:

$$\text{AbsCap}\ (\%) = (1 - \frac{Area\ of\ Influent\ Sample - Area\ of\ Effluent\ Sample}{Area\ of\ Influent\ Sample - Area\ of\ Blank\ Sample}) \times 100\%$$

Equation (2)

Because the online method used for measuring the absolute capture rate has a higher LOD than the offline method, we could only report absolute capture rates for 159 of the 189 target compounds with online LODs of <100 ng L^{-1}.

Relative Recovery Rate. Relative recovery rate (R/C Ratio) of each compound is used to describe the recovery potential of each SPE material for each compound during the elution step. A higher R/C ratio means the compound can be more easily released from the SPE material by the eluent, and therefore can be more efficiently recovered. The R/C ratio considers only the

rate of release of the mass of each compound that was captured, allowing us to more carefully study the release of captured compounds. The R/C Ratio was calculated as:

$$R/C \text{ Ratio } (\%) = \frac{Absolute\ Recovery\ Rate\ (AbsRec)}{Absolute\ Capture\ Rate\ (AbsCap)} \times 100\%$$

Equation (3)

Because the R/C ratio includes measurements made with both the online and offline methods which have different LODs, we could only report relative recovery rates for 159 of the 189 target compounds which have low offline (< 500 ng L^{-1}) and online (< 100 ng L^{-1}) LODs.

All recovery data are reported as the average of triplicate or duplicate measurements and error bars represent the minimum and maximum measurement. All capture data are reported as the average of six or nine replicate measurements and error bars represent the standard deviations.

2.3 Results and Discussion

The evaluation of P-CDP as a potential SPE material included three parts. First, a conventional SPE method was adapted from the literature and the procedure was replicated using an HLB SPE material and a mixture of 242 micropollutants (only 189 of the MPs could be detected with our analytical method). The results of replicated experiment was compared with the literature reported results for the 115 overlapping compounds and confirmed good agreement. Second, the performance of the P-CDP material was compared to the HLB material using the previously described conventional SPE method. The results showed that the performance of the P-CDP as an SPE material was rather poor under the conditions of the conventional SPE method that had been developed and optimized for HLB materials. Third, the SPE method was systematically optimized to improve the performance of P-CDP as an SPE

material. The result of this work is an optimized SPE method that uses P-CDP and outperforms conventional SPE methods that utilize HLB materials.

2.3.1 Adaption of conventional SPE method

The conventional SPE method was adapted from a previously described study which presents the development of a multilayer SPE method for polar organic compounds (Vogler, 2013). The author of this study also reports absolute recovery rates for 418 environmentally relevant compounds with a single layer SPE method using Oasis® HLB as the adsorbent. I first aimed to replicate this SPE procedure with the 242 compounds included in my test mixture. Some minor changes were made to the method, based on availability of SPE materials. Briefly, HLB was provided by a different producer and the mass used was 180 mg instead of the 200 mg used in the previous study. Additionally, a one-step elution process with just 5 mL of methanol was employed instead of the three-step elution process described in the previous work. All other steps were controlled to be as described in the conventional SPE method including loading speed and pH adjustment to 6.3.

Absolute recovery rates were calculated for the 189 compounds in my test mixture that could be detected using Equation (1). A comparison of the absolute recovery rates among 115 compounds that were included in the previous study and my study are presented in Figure 3. The error bars on the data collected in the present work reflect the minimum and maximum values of triplicate measurements. A total of 103 of the compounds (90%) had minimum or maximum

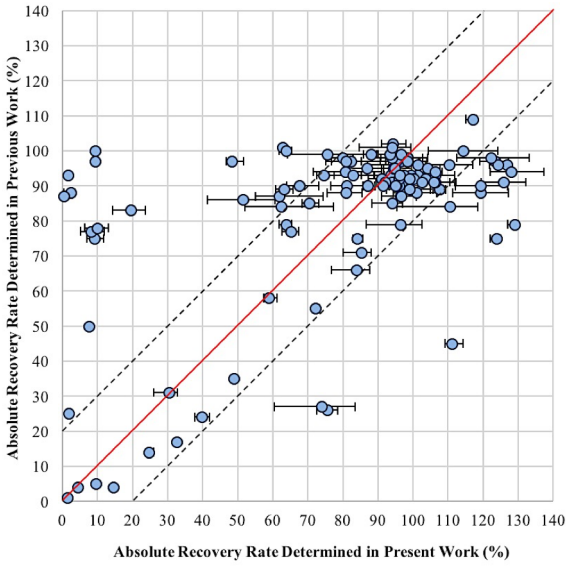


Figure 3. Comparison of absolute recovery rates for 115 compounds from a previously reported experiment and a new experiment with HLB as the SPE adsorbent. Error bars represent minimum and maximum of triplicate measurements.

values within 10% of the average value, reflecting the accuracy and precision of the triplicate measurements. The red line represents the situation in which the absolute recovery rate is the same when comparing the present work to the previous work and the dashed lines represent a 20% deviation between the experiments. A total of 83 of the compounds (72%) had less than a 20% deviation between the experiments. Considering the differences in the producer of the HLB materials, the masses of HLB material used in each of the studies, and the simplified step used for elution, these results reflect similar performances of the HLB materials between the experiments and provide evidence that my SPE experiments could reproduce previously reported data. The absolute recovery rates for each of the 189 compounds and the 115 overlapping compounds are provided in Table C1 in Appendix C.

2.3.2 Comparison of P-CDP to HLB as SPE materials

2.3.2.1 Modification of SPE cartridge packing procedure

The SPE cartridge packaging procedure for HLB involves filling each cartridge with a fixed mass of HLB sandwiched between two porous frits with a pore size of 20 µm. However, the average particle size of P-CDP (~15 µm) is much smaller than Oasis® HLB (55 µm), and in preliminary experiments I observed that some P-CDP particles can leak into the eluent when SPE cartridges are packed with P-CDP in this way, introducing a light yellow color to the eluate. This is not an ideal situation, as leaking adsorbents can capture compounds in the eluent, leading to overestimation of capture potential and underestimation of recovery potential of P-CDP materials. Therefore, several options were explored for packing SPE

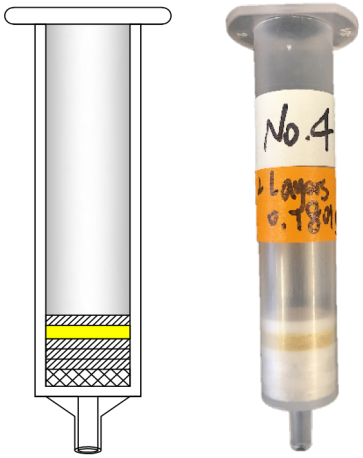


Figure 4. Modified packaging method used in P-CDP SPE tests.

cartridges with P-CDP materials to eliminate material leaking. The final configuration utilizes 0.2 grams of glass wool (8 µm porosity) (Yavuz et al., 2013) and two additional frits at the bottom of each cartridge, as shown in Figure 4. This configuration eliminated the yellow color observed in the eluents and was considered adequate for our P-CDP method.

2.3.2.2 Evaluation of overall performance of P-CDP as an SPE material

I next aimed to apply the previously described SPE procedure that was designed for HLB materials with P-CDP materials used as the adsorbents. The only change to the method was in the way the cartridges were packed, as described in the preceding section. The test mixture of 242 compounds was used and all other process variables were controlled. The only noticeable difference between the experiments was in the pressure required to maintain the desired flowrate through the SPE cartridges; the vacuum pump was pulling a vacuum of 13 inches of mercury to maintain a 2-3 drop per minute flowrate through the P-CDP materials whereas only 4 inches of mercury were required to meet the same flowrate through HLB materials. The difference can be attributed to the new packing configuration, the smaller size of the P-CDP materials, and the broader particle size distribution of the P-CDP materials, which allows fine particles to fill void spaces.

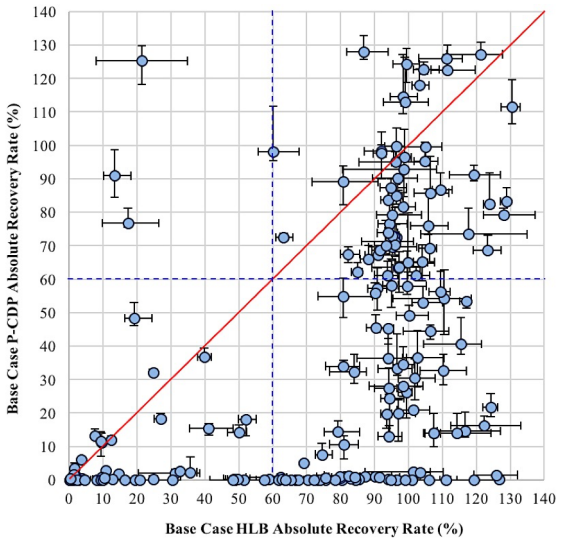


Figure 5. Comparison of absolute recovery rates of 189 targeted compounds with P-CDP vs HLB as adsorbent; error bars represent the minimum and maximum of triplicate measurements.

Absolute recovery rates for each of the 189 compounds that could be detected were calculated using Equation (1) and are compared to the absolute recovery rates measured using HLB materials in Figure 5. The error bars in Figure 5 reflect the minimum and maximum

values of triplicate measurements. The red line represents the situation in which the absolute recovery rate measured for HLB is the same as the absolute recovery rate measured for P-CDP, and data plotted above the red line would reflect a situation in which that compound exhibited greater recovery on P-CDP than HLB. Considering the previously reported observations of nearly instantaneous uptake of a diverse set of polar organic compounds on the P-CDP (Ling et al., 2017) and facile regeneration with methanol (Alsbaiee et al., 2016), the expectation for this comparison was that much of the data would fall along the red line or above the red line. However, only 27 of the compounds (14%) could be recovered better when P-CDP is used as the SPE material under these conditions. If 60% is selected as the criterion to describe a "moderate or good" absolute recovery rate (Cazorla-Reyes et al., 2011; Raoov et al., 2014; Vogler, 2013), then only 60 compounds (32%) could be recovered well using P-CDP as an adsorbent under these conditions, while 137 compounds (72%) could be recovered well with HLB. The absolute recovery rates for each of the 189 compounds on P-CDP under these conditions are provided in Table C1 in Appendix C.

The absolute recovery rates of most compounds were relatively poor for P-CDP under the experimental conditions that have been optimized for HLB materials (Jeong et al., 2017; Mazzella et al., 2008; Robles-Molina et al., 2014; Tavengwa et al., 2016; Vogler, 2013). However, there are two parts to absolute recovery; there is compound capture by the SPE material and there is compound release from the SPE material. It is not clear if the poor performance of the P-CDP material was due to deficiencies in compound capture during loading or compound release during elution or both. In the following sections, experiments were designed for addressing the question of whether deficiencies in capture during loading or release during elution or both are contributing to the poor absolute recovery performance of P-CDP. Capture ability is assessed by measuring the absolute capture rate as described in

Equation (2) and the release potential is assessed by calculating the relative recovery rate as described in Equation (3).

2.3.2.2 Evaluation of capture ability of P-CDP vs HLB

To measure the absolute capture rate, a series of experiments were conducted where effluent were collected from SPE cartridges during compound loading at three different time points (1 hour, 3 hour, and 5 hour). These experiments were conducted with SPE cartridges loaded with either HLB or P-CDP materials and in duplicates. Because the concentration of many compounds was very low after capture by the SPE materials, samples were measured by means of the online method described in the preceding, which had suitable LODs for 159 of the compounds in my test mixture.

Absolute capture rates for each compound were calculated for each SPE material using Equation (2) and are compared in Figure 6. The error bars in Figure 6 reflect the standard deviation of six measurements derived from the three samples collected from duplicate experiments. These data show that under the conditions optimized for HLB, absolute capture of the 159 compounds on P-CDP is relatively poor. I selected 80% as the criterion to describe "moderate or good" absolute capture rates. Only 86 compounds (54%) could be captured well using P-CDP as adsorbent under these conditions, while 146 compounds (92%) could be captured well with HLB. The efficacy of HLB under these conditions was further evidenced by an accounting of compounds that were "perfectly captured"

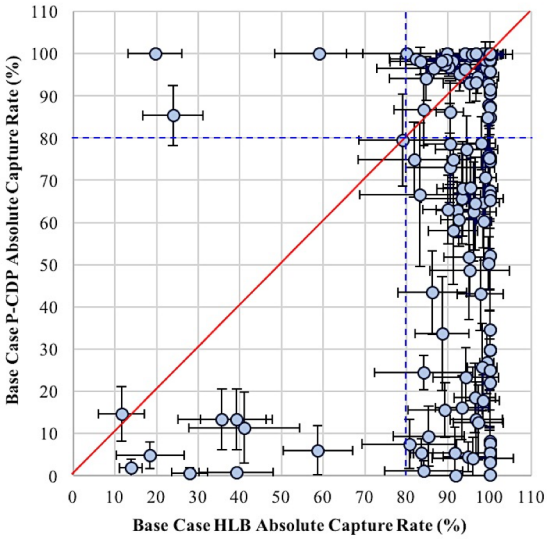


Figure 6. Comparison of absolute capture rates of the 159 compounds with P-CDP and HLB as adsorbents; error bars represent the standard deviation of six measurements.

with absolute capture rates greater than 95%. Based on this criterion, only 69 compounds (43%) were perfectly captured by P-CDP whereas 104 compounds (65%) could be perfectly captured with HLB. The poor absolute capture performance of P-CDP could partly explain the poor absolute recovery performance, though a careful evaluation of compound release is also warranted. The absolute capture rates for each of the 159 compounds on HLB and P-CDP are provided in Table C2 in Appendix C.

2.3.2.3 Evaluation of release potential of P-CDP vs HLB

To measure the release potential, the data from the absolute recovery rate experiments and absolute capture rate experiments were used to calculate the relative recovery ratio (R/C ratio) as provided in Equation (3). The R/C ratio can be interpreted as the rate at which captured compounds are released during the elution step of the SPE method. Perfect elution of captured compounds would result in an R/C ratio of one; values less than one can be interpreted as a situation where some of the captured compound remains on the adsorbent following the elution step. Because data from the capture experiments are needed to calculate the R/C ratio, the R/C ratio for the 159 compounds detected in the capture study were calculated.

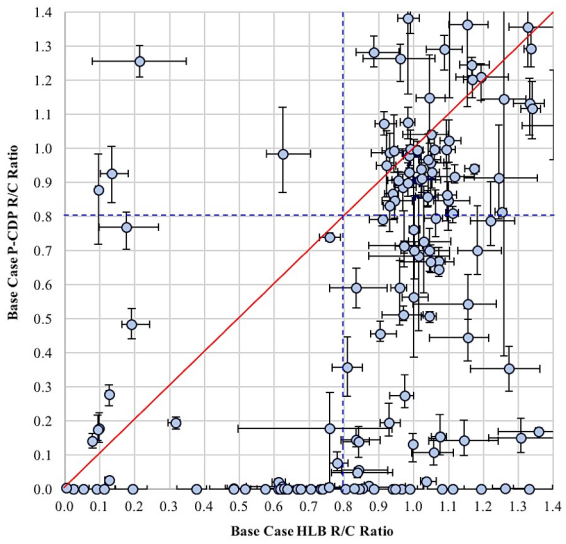


Figure 7. Comparison of relative recovery rates (R/C ratio) of 159 target compounds with P-CDP and HLB as adsorbents; error bars represent the minimum and maximum of triplicate measurements.

The R/C ratios for each compound were calculated using Equation (3) and are compared for each SPE material in Figure 7. There are several notable observations in these data. First, the majority of the compounds exhibit R/C ratios near one for HLB. A total of 117 compounds (74%) had an R/C ratio greater than 0.80 for HLB, reflecting the potential for

compounds to be easily released from HLB with 5 mL of methanol. Second, relatively few compounds had an R/C ratio near one for P-CDP. Only 67 compounds (42%) had an R/C ratio greater than 0.80 for P-CDP, reflecting that the majority of the compounds that are captured by P-CDP are incompletely released with 5 mL of methanol. Finally, it is notable that many compounds have a R/C ratio of zero for P-CDP, indicating that they were captured but not released at all with 5 mL of methanol. The poor R/C ratios calculated for compounds on P-CDP further suggest that release potential may also partly explain the poor absolute recovery performance. Careful steps to optimize capture and release will be required prior to using P-CDP as an SPE material. The R/C ratios for each of the 159 compounds on HLB and P-CDP are provided in Table C2 in Appendix C.

2.3.3 Optimization of P-CDP Based SPE Procedure

I determined that the performance of P-CDP as an SPE material is relatively poor when compared to HLB, under experimental conditions that had been optimized for HLB. However, there are several notable properties of P-CDP that could be exploited to improve either the capture ability or the release potential of compounds on P-CDP. First, based on the thermodynamics of equilibrium of adsorbents, the uptake of target compounds should be increased when more adsorbents are added (Benjamin and Lawler, 2013). Therefore, increasing the mass of P-CDP materials in each cartridge may enhance the capture rates of target compounds. Second, P-CDP has many hydroxyl groups at the outside of its cyclodextrin monomers, as well as fluorine-containing cross-linkers; these functional groups might impart some charge selectivity to adsorbate uptake. Indeed, pH-dependent uptake was observed in removal of MPs in aqueous samples using P-CDP (Ling et al., 2017) and other fluorinated polymer networks (Byun et al., 2016). P-CDP adopted in this research showed positively charged favorable property during adsorption tests while no such charge favorable property has been observed for HLB (Jeong et al., 2017; Zhang and Zhou, 2007). Since pH will influence

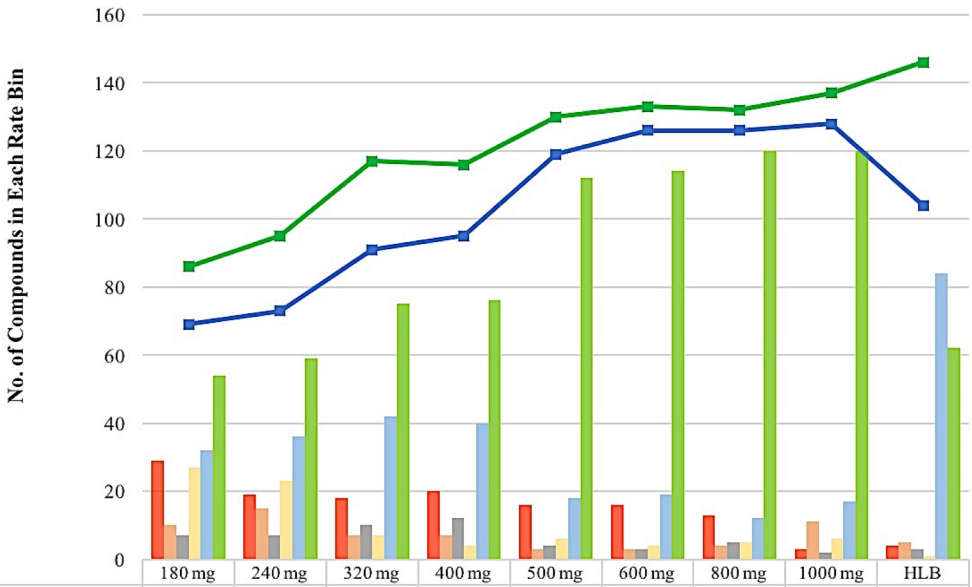
the ionic forms of many target compounds, lowering the pH of water samples might turn neutral or negatively charged compounds to more positively charged state, which might help improve the capture performance of P-CDP materials. As for potential recovery ability, the type and volume of elution solvent are important factors that should be considered during elution (Andrade-Eiroa et al., 2016c; He and Blaney, 2015). Considering the pH-dependent observation of preferential uptake of positively charged molecules, the pH and ionic strength of the elution solvents may have impacts on the potential recovery ability of P-CDPs.

2.3.3.1 Optimization of capture ability (Mass Study)

One of the major advantages of P-CDP as an SPE adsorbent is their price relative to HLB. Rough estimates suggest that P-CDP could be produced at prices that are several orders of magnitude less than those for which HLB is currently commercially available (Alsbaiee et al., 2016; Waters, 2017). Therefore, increasing the mass of P-CDP used in each SPE cartridge could be explored as an economically viable means to improve the absolute capture rate.

A series of experiments were conducted in which SPE cartridges were packed with increasing masses of P-CDP ranging between 180 mg and 1000 mg. Samples of the effluent were collected during the loading step to measure the absolute capture rate as described in the preceding. The resulting data were distributed into bins that represent different levels of absolute capture rates (AbsCap<20; 20%≤AbsCap<40%; 20%≤AbsCap<40%; 40%≤AbsCap<60%; 60%≤AbsCap<80%; 80%≤AbsCap<99%; AbsCap≥99%) among the experiments. An accounting of the number of compounds that were assigned to each bin for each experiment is presented in Figure 8. The bars presented in Figure 8 represent the number of compounds assigned to each bin, and the lines in Figure 8 represent the cumulative number of compounds with absolute capture rates above 80% (green) and 95% (blue). The data for HLB are provided as a means for comparison.

There are clear performance gains as P-CDP mass is added to the SPE cartridges. From 100 mg to 500 mg, there is a clear increase in the number of compounds with absolute capture rates greater than 99% and a concomitant decrease in the number of compounds with absolute capture rates less than 20%. This proves that added mass improves the capture ability of P-CDP materials, likely for thermodynamic reasons as a new equilibrium situation is established (Huang et al., 2013; Liu et al., 2011). Interestingly, the performance gains diminish rather markedly between 500 mg and 1000 mg, where only incremental gains in performance are noted. This may be the result of having achieved an infinite dilution condition at 500 mg of P-CDP, with added mass not changing the thermodynamics of the situation considerably (Jambhekar and Breen, 2016). Most notably, the absolute capture rate of P-CDP at 500 mg is superior to the performance of HLB at 180 mg. One would naturally expect that the perforamnce of HLB would also increase if the mass of HLB increased by a factor of almost



	180 mg	240 mg	320 mg	400 mg	500 mg	600 mg	800 mg	1000 mg	HLB
AbsCap <20%	29	19	18	20	16	16	13	3	4
20%≤ AbsCap <40%	10	15	7	7	3	3	4	11	5
40%≤ AbsCap <60%	7	7	10	12	4	3	5	2	3
60%≤ AbsCap <80%	27	23	7	4	6	4	5	6	1
80%≤ AbsCap <99%	32	36	42	40	18	19	12	17	84
AbsCap ≥99%	54	59	75	76	112	114	120	120	62
AbsCap ≥80%	86	95	117	116	130	133	132	137	146
AbsCap ≥95%	69	73	91	95	119	126	126	128	104

Figure 8. Distribution of absolute capture rates for compounds with different mass of P-CDP as adsorbent.

three, though the cost of HLB precludes that as an option. Based on these results, I defined 500 mg of P-CDP as the optimal mass for the P-CDP SPE method.

With the new values of absolute capture rate estimated at a mass of 500 mg of P-CDP, a revised comparison of the absolute capture rates for each compound and for each SPE material is presented in Figure 9. The error bars reflect the standard deviation of six measurements derived from the three samples collected from duplicate experiments. These data show that the absolute capture rates of many of the compounds improved significantly with additional P-CDP mass. The number of compounds with a "moderate or good" absolute capture rate increased from 86 compounds (54%) to 130 compounds (82%), and the number of compounds that were "perfectly captured" increased from 69 compounds (43%) to 119 compounds (75%). Nevertheless, there remain 19 compounds (12%) that have absolute capture rates of less than 40%, which indicates that further optimization of capture ability will be required. The absolute capture rates for each of the 159 compounds on 500 mg of P-CDP are provided in Table C3 in Appendix C.

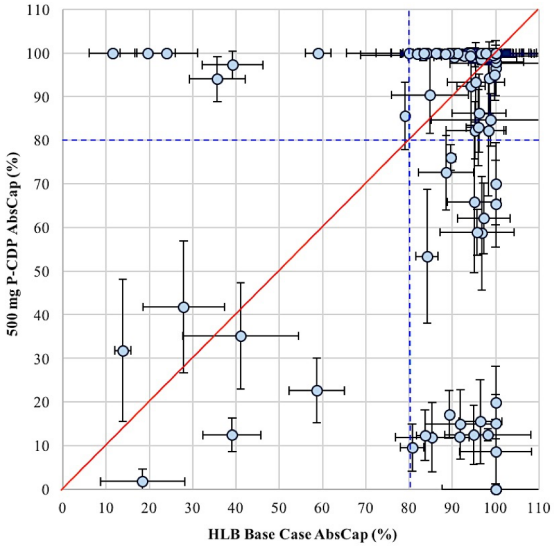


Figure 9. Distribution of absolute capture rates of 159 target compounds with P-CDP (500 mg per cartridge) and HLB as adsorbents; error bars represent standard deviations of six measurements.

2.3.3.2 Optimization of capture ability (pH Study)

I next aimed to examine the physicochemical properties of each of the compounds included in my test mixture to determine whether any compound property contributed to either excellent capture ability or poor capture ability. Particular attention was paid to the McGowan Volume (MV, molecular size) and charge state of the compound based on previous reports on

the influence of these parameters on adsorption of polar organic compounds on cyclodextrin polymers (Crini, 2003; Hu et al., 2014; Huang et al., 2013; Ling et al., 2017; Pan et al., 2010; Yang et al., 2015). The logD (charge-dependent lipophilicity) which is often used to describe the adsorption of organic compounds onto hydrophobic surfaces was also examined (Kadar et al., 2010; Kah and Brown, 2007). Based on an examination of these properties, I found that the charge state of the compound was an important determinant of compound capture ability on P-CDP. This agrees with the previously reported study that charge state plays an important role in the selectivity of MPs for P-CDP during adsorption (Ling et al., 2017). This observation is detailed in Figure 10, where the comparison of the absolute capture rates for each compound and for each SPE material as a function of charge state of the compound at pH 6 is presented. Interestingly, every compound that is positively charged at pH 6 is "perfectly captured" (AbsCap≥95%) by P-CDP. To the contrary, neutral compounds and compounds that are negatively charged are captured to varying extents. The majority of the compounds with the poorest absolute capture rates (AbsCap < 20%) were negatively charged compounds. Also important to note, no such charge exclusivity was observed for capture by HLB. Based on these observations, I hypothesized that lowering the pH of the water during the SPE loading step will improve compound capture due to the changing charge state of the compounds.

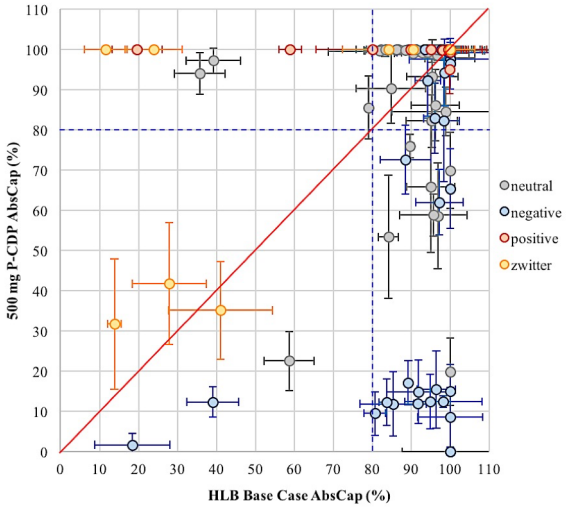
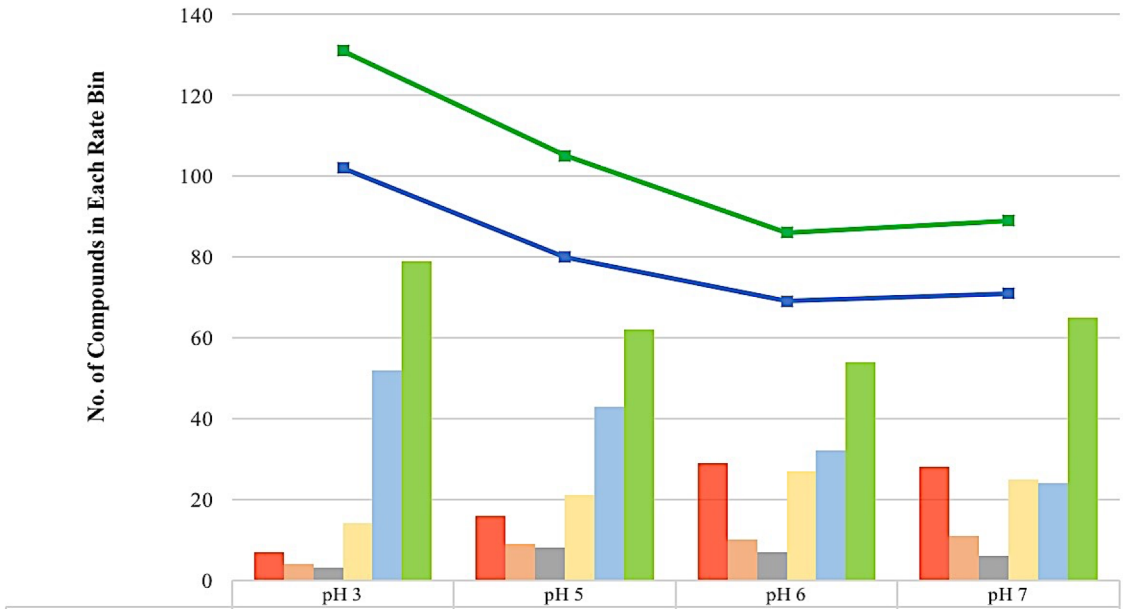


Figure 10. Distribution of absolute capture rates of 159 target compounds with P-CDP (500 mg per cartridge) and HLB as adsorbents; error bars represent standard deviations of six measurements; charge states are estimated at pH 6 from Marvin.

A series of experiments were conducted in which the pH of the water samples used for compound loading were adjusted to between pH 3 and pH 7 using 10% formic acid or a 0.7 N

ammonia solution. A mass of 180 mg of P-CDP was used and samples of the effluent were collected during the loading step to measure the absolute capture rate. The resulting data were distributed into bins as described in the preceding and an accounting of the number of compounds that were assigned to each bin and for each experiment is presented in Figure 11. The bars presented in Figure 11 represent the number of compounds assigned to each bin, and the lines in Figure 11 represent the cumulative number of compounds with absolute capture rates above 80% (green) and 95% (blue).



	pH 3	pH 5	pH 6	pH 7
AbsCap <20%	7	16	29	28
20%≤ AbsCap <40%	4	9	10	11
40%≤ AbsCap <60%	3	8	7	6
60%≤ AbsCap <80%	14	21	27	25
80%≤ AbsCap <99%	52	43	32	24
AbsCap ≥99%	79	62	54	65
AbsCap ≥80%	131	105	86	89
AbsCap ≥95%	102	80	69	71

Figure 11. Distribution of absolute capture rates for target compounds with different loading pHs.

Whereas the distribution of the compounds among the removal groups was relatively stable in the range of pH 5 to pH 7, there is a clear performance gain at pH 3. This can be explained by the pK_a values of the 159 compounds included in this analysis; the majority of the compounds have pK_a values between 3 and 5, meaning that those compounds that become

neutral or positively charged at lower values of pH will only respond to pH below 5. Because only a few compounds had a pK_a below 3, I did not consider lower pHs in this study.

Based on the optimization of P-CDP mass and the pH of the waters used for compound loading, an optimal method combining 500 mg of P-CDP and a loading condition of pH 3 was selected. An experiment to evaluate this optimized condition was performed and a comparison of the optimized absolute capture rates on P-CDP to the absolute capture rates previously measured on HLB is presented in Figure 12. The error bars reflect the standard deviation of nine measurements derived from the three samples collected from triplicate experiments. These data show that the absolute capture rates of many of the compounds improved even more under the conditions of optimal mass and pH. The number of compounds with a "moderate or good" absolute capture rate increased to 147 compounds (92%), and the number of compounds that were "perfectly captured" increased to 141 compounds (89%). Only 5 compounds (3%) have absolute capture rates of less than 40%. These five compounds were metolachlor ESA, propachlor ESA, propachlor OXA, hexamethylphosphoramide, and sucralose. After examining the properties of these five compounds, I hypothesized that the charge state, the logD, and unique functional groups contributed to this result. First, compounds with a negative charge *and* high hydrophilicity are poorly captured by P-CDP. Metolachlor ESA and propachlor ESA are the only two compounds that are negatively charged at pH 3 and have negative values of logD. Propachlor OXA has a pK_a close to 3, indicating that half of the compound is negatively

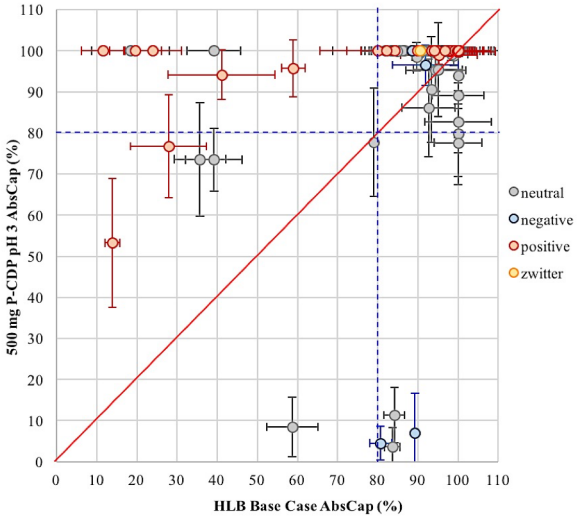


Figure 12. Distribution of absolute capture rates for 159 target compounds with P-CDP (500 mg per cartridge at pH 3) and HLB; error bars represents standard deviations of nine measurements. Charge states are estimated at pH 3 from Marvin.

charged at a pH of 3, and it also has a negative logD value. No other compounds included in this study have a similar combination of acidity and hydrophilicity. Second, some unique functional groups may explain the poor capture of hexamethylphosphoramide (HMPA) and sucralose. HMPA is a special compound with a phosphoric triamide structure. The P-O bond in its structure is highly polar with a significant partial negative charge residing on the oxygen atom. This unique functional group along with its small molecular volume (Ling et al., 2017) likely contributes to its poor capture ability. Sucralose is a neutral molecule at pH 3 and pH 6, but is very hydrophilic and has a negative logD value. Sucralose also is a cyclic aliphatic containing five hydroxyl groups, rendering it very polar. As such, sucralose is a poor adsorbate with P-CDP. The optimized absolute capture rates for each of the 159 compounds are provided in Table C3 in Appendix C.

Finally, an absolute recovery test was performed based on the optimized capture procedure to determine whether there was any improvement relative to the base case presented in Figure 5. The absolute recovery rates for each compound were calculated and are compared with HLB in Figure 13. Whereas there was some clear improvement in the absolute recovery of some compounds compared to the base case, the absolute recovery of most compounds on P-CDP remained relatively poor; only 68 (36%) of the compounds could be recovered moderately (AbsRec ≥ 60%) with P-CDP. This suggests that further optimization of the method will be required, with focus now on optimization of the release potential. The optimized

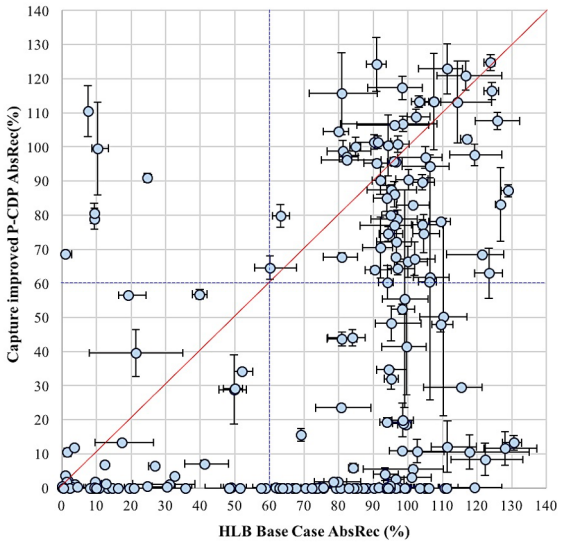


Figure 13. Distribution of absolute recovery rates for 189 target compounds with P-CDP (with optimized loading condition) and HLB as adsorbents; error bars represent the minimum and maximum of triplicate measurements.

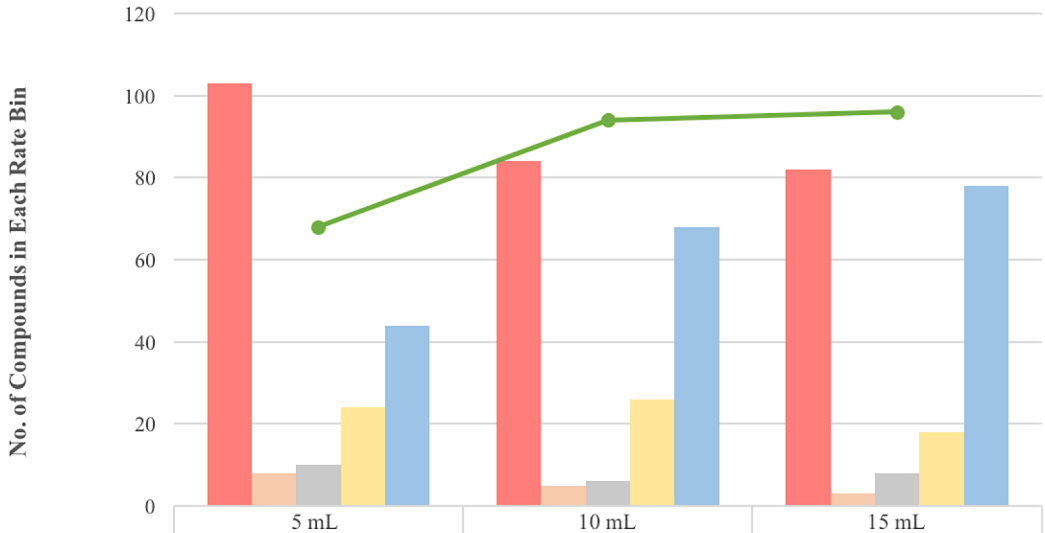
absolute recovery rates for each of the 189 compounds that were detected are provided in Table C4 in Appendix C.

2.3.3.3 Optimization of release potential (Volume Study)

Capture ability could only partly explain the overall poor absolute recovery of adsorbates on P-CDP. Therefore, the optimization of the recovery step was performed by considering the type of elution solvent, the volume of the elution solvent, and chemical amendments to the elution solvent.

Selection of a proper elution solvent is one of the most important parameters for adsorbate recovery in SPE. some preliminary recovery tests were conducted in advance using some conventional elution solvents including methanol, ethanol, acetone, acetonitrile, and ethyl acetate (Bhaskar et al., 2004; Huck and Bonn, 2000; Maldaner and Jardim, 2012; Moon et al., 2008; Yu et al., 2003). Interestingly, acetone, acetonitrile, and ethyl acetate could not pass through the P-CDP, apparently due to swelling of the material, since the thin top layer of polymers became darker after contacting those organic solvents. Both methanol and ethanol passed through the P-CDP adequately and both produced similar recovery results. Therefore, I decided to use methanol as the elution solvent for the P-CDP based SPE method.

I next examined whether the volume of methanol was an important determinant of adsorbate recovery. The base case applied for the HLB materials used 5 mL of methanol, and here I also conducted recovery experiments using 10 mL and 15 mL of methanol. The resulting data were distributed into bins as described in the preceding and an accounting of the number of compounds that were assigned to each bin and for each experiment is presented in Figure 14. The bars presented in Figure 14 represent the number of compounds assigned to each bin, and the green line is the cumulative number of compounds that have “moderate or good” absolute recovery rates.



	5 mL	10 mL	15 mL
AbsRec <20%	103	84	82
20%≤ AbsRec <40%	8	5	3
40%≤ AbsRec <60%	10	6	8
60%≤ AbsRec <80%	24	26	18
AbsRec ≥80%	44	68	78
AbsRec ≥60%	68	94	96

Figure 14. Distribution of absolute recovery rates for compounds using different volume of methanol as elution solvents.

There are clear performance gains as the volume of methanol used for elution is increased from 5 mL to 15 mL, with an increase in the number of compounds with absolute recovery rates greater than 80% and a concomitant decrease in the number of compounds with absolute capture rates less than 20%. This proves that increasing the volume of methanol used for elution can improve absolute recovery rates. However, the total volume of methanol that could be used was limited due to the size of the centrifuge tubes available for eluate capture and the size of the SPE manifold. It is likely that further increases in eluent volume may lead to further gains in absolute recovery rates. Interestingly, the distribution of absolute recovery rates among the compounds when using 15 mL methanol as the eluent is rather extreme, with nearly half of the compounds recovered well and the other half of the compounds rather poorly recovered (AbsRec<20%). This suggests that the increase in volume of the eluent enhances the

removal of some types of compounds (likely those undergoing hydrophobic interactions) but has no effect on other types of compounds (likely those undergoing electrostatic interactions). Based on these results and practical considerations, I defined 15 mL of methanol as the optimal volume for the P-CDP SPE method.

With the new values of absolute recovery rate estimated with 15 mL of methanol as the eluent, a revised comparison of the absolute recovery rates for each compound and for each SPE material is presented in Figure 15. The error bars reflect the standard deviation of six measurements derived from the minimum and maximum values of triplicate experiments. These data show that the absolute recovery rates of many of the compounds improved significantly with additional methanol volume. However, even with the increased volume of methanol, many compounds still are not recovered well from the P-CDP; only 96 (51%) of the compounds were recovered moderately (AbsRec≥60%) using P-CDP compared to 137 (72%) using HLB. Nevertheless, many of the target compounds had similar absolute recovery rates using P-CDP and HLB as adsorbents, whereas some compounds are still distributed along the x-axis in Figure 15, indicating no recovery at all. The absolute recovery rates of each of 189 compounds using 15 mL of methanol as the eluent are provided in Table C4 in Appendix C.

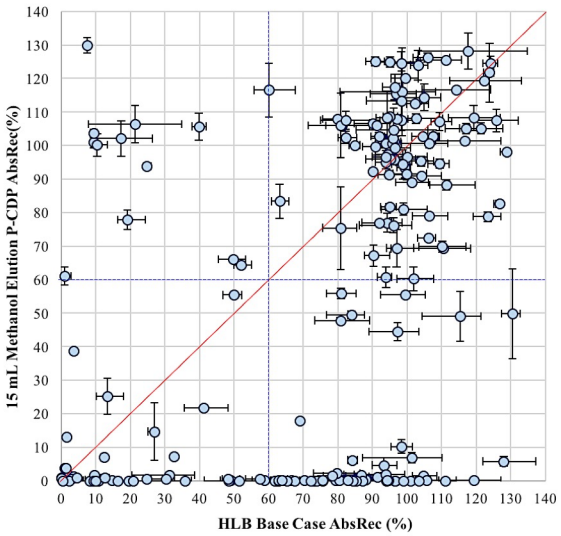


Figure 15. Distribution of absolute recovery rates of 189 target compounds with P-CDP (15 mL methanol elution) and HLB; error bars represent the minimum and maximum of triplicate measurements.

2.3.3.4 Optimization of release potential (Salt Study)

Analogous to my approach in evaluating capture performance, I next examined the physicochemical properties of each of the compounds included in my test mixture to determine whether any compound property contributed to either excellent recovery ability or poor recovery ability. the McGowan volume (MV), charge state of the compound, and the logD were considered again. Based on an examination of these properties, the charge state of the compound was also found to be the most important determinant of compound recovery potential. This observation is detailed in Figure 16, where the comparison of the absolute recoveries of each compound and for each SPE material as a function of charge state of the compound at pH 6 is presented. From Figure 16, it is clear that none of the positively charged compounds are recovered from P-CDP with methanol, while most negatively charged and neutral compounds have similar absolute recovery rates for both adsorbents. This result matches the speculation that P-CDP "likes" positively charged compounds, and the hypothesis derived from this result is that the positively charged compounds are attracted too tightly onto P-CDP to be released. The final optimization step is to identify a suitable procedure to release positively charged compounds from P-CDP.

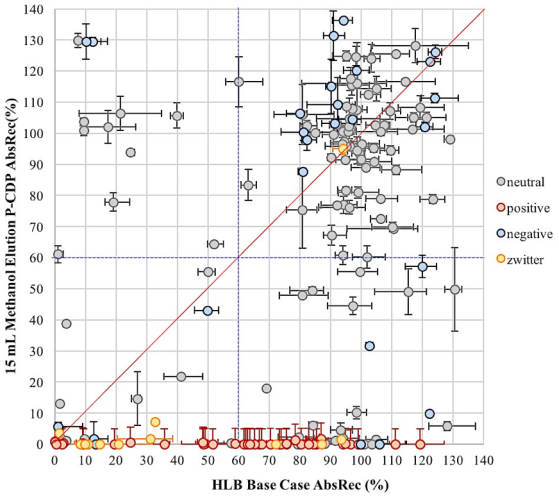


Figure 16. Distribution of absolute recovery rates for 189 target compounds with P-CDP (15 mL methanol elution) and HLB as adsorbents; error bars represent the minimum and maximum of the triplicate measurements; charge states are estimated at pH 6 from Marvin.

Two options were identified for enhancing the release of positively charged compounds from P-CDP. First, I hypothesized that increasing the pH of the eluent solvent would enhance the release of positively charged compounds by changing their charge state from positive to

neutral. The pH of the methanol eluent was increased to a pH of 10 by adding either ammonia or sodium hydroxide. Unfortunately, the pH modified methanol could not pass through the P-CDP material, and the color of the top thin polymer layer changed, apparently due to swelling of the material. As a result, this hypothesis could not be directly tested.

Second, I hypothesized that increasing the ionic strength of the eluent solvent would enhance the release of positively charged compounds by means of ion exchange. The ionic strength of the methanol eluent was increased by dissolving 100 mg of sodium chloride into 15 mL of methanol at ambient temperature (around 25 °C) to yield a 6.67 g L^{-1} solution. The amended eluent was passed through the loaded SPE cartridges under vacuum at 20 inches of mercury. High concentrations of sodium are known to interfere with electrospray ionization mass spectrometry (Sargent et al., 2013), but internal standards were used to correct for changes in ionization efficiency. During instrumental analysis procedure, 9 compounds were missing due to the interference of sodium ions, therefore absolute recovery rates for only 180 compounds were calculated and compared with HLB in Figure 17. These data reveal two important observations. First, the presence of sodium ions enables the release of positively charged compounds from P-CDP resulting in a greatly improved absolute recovery for those compounds. Second, the absolute recovery rates with my optimized SPE procedure compare favorably with the optimized SPE procedure for HLB; among all 180 targeted compounds with robust data, 135 (75%) could be moderately recovered

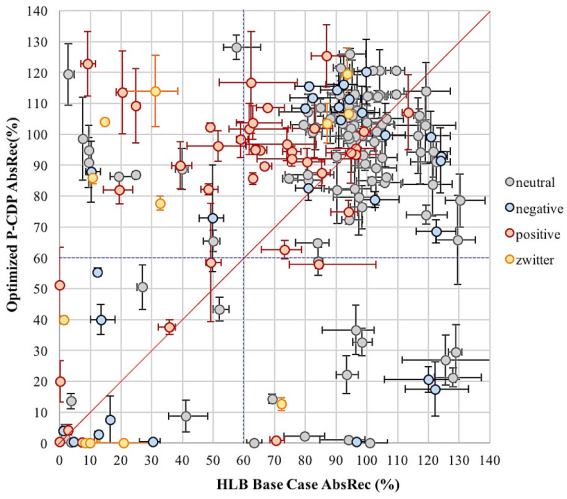


Figure 17. Distribution of absolute recovery rates for 180 target compounds with P-CDP and HLB adsorbents under optimized condition; error bars represent the minimum and maximum of triplicate measurements; charge states are estimated at pH 6 from Marvin.

(AbsRec≥60%) with P-CDP versus 130 (72%) with HLB, and 121 (67%) could be well recovered (AbsRec≥80%) using P-CDP versus 109 (61%) with HLB.

There are 17 compounds in the bottom right section of Figure 17, indicating these compounds could be recovered moderately or well with HLB as adsorbent but had poor recoveries with P-CDP. Among those 17 compounds, metolachlor ESA, hexamethylphosphoramide and sucralose are three compounds that confirmed previously cannot be captured well with P-CDP, so their absolute recoveries were poor as well. The remaining 14 compounds are listed in Table 1.

Table 1. Fourteen Compounds that could be recovered well by HLB but not P-CDP.

Compound Name	Charge State (pH 6)	LogD (pH6)	MV	HLB AbsRec (%)	P-CDP AbsRec (%)	P-CDP AbsCap (%)
Candesartan	-	2.49	3.16	120.0	20.6	100.0
Trinexapac-ethyl	-	-1.67	1.84	122.3	17.5	99.2
Amisulpride	+	-0.13	2.81	70.4	1.0	100.0
Hydrocodone	+	-0.59	2.21	84.3	57.8	100.0
2-ethyl-2-phenyl malonamide monohydrate	n	-2.92	1.65	69.1	14.4	NA
Acetochlor	n	3.50	2.14	129.0	29.5	100.0
Alachlor	n	3.50	2.14	129.0	29.5	100.0
Dehydroacetic Acid	n	0.42	1.19	125.6	26.9	100.0
Molinate	n	2.34	1.55	96.4	36.6	NA
Sulfadimethoxine	n	1.22	2.12	93.3	22.1	98.7
Sulfamethazine	n	0.61	2.00	128.0	21.3	100.0
Sulfamethoxazole	n	0.60	1.72	98.4	32.7	100.0
Sulfathiazole	n	0.93	1.69	94.0	1.1	NA
Ranitidine HCl	z	-0.36	1.77	72.2	12.6	NA

Reasons for the poor recoveries for these compounds vary and are not always clear. Since ion exchange principles were used to help during elution, charge state is not as important as described for capture part. There are no common features among molecular size or logD values, either. However, some special functional groups might play important roles here.

Among those 14 compounds, four are neutral sulfonamides (sulfamethoxine, sulfamethazine, sulfamethoxazole and sulfamethiazole). Neutral sulfonamides have been demonstrated in other studies to be recovered well with regular silica based material and ion exchange materials at neutral pH with pure methanol as an elution solvent (Lindsey et al., 2001), but cannot be recovered well in complex matrices due to matrix effects (Pavlović et al., 2007). While in this study, P-CDP could not recover neutral sulfonamides well. Nevertheless, the mechanisms contributing to the poor recoveries of those 14 compounds with P-CDP remain unknown. Further studies are required to more fully understand the factors that influence capture and release of organic chemicals on P-CDP. The final absolute recovery rates for each of the 180 compounds based on the fully optimized SPE procedure are provided in Table C4 in Appendix C.

2.3.4 Optimized P-CDP Based SPE Procedure

After systematically improving the capture and recovery ability of P-CDP, an optimized SPE procedure was developed with P-CDP as the adsorbent. The optimized steps are determined as: (1) after filtration and before the loading step, the pH of the water samples are adjusted to 3.0±0.1 using 10% formic acid; (2) pack 500 mg P-CDP in each SPE cartridge, then load each 1 L water sample to corresponding cartridges; (3) during the elution step, dissolve 100 mg sodium chloride in 15 mL methanol to yield a 6.67 g L^{-1} methanol-salt mixture, then load the elution mixture through cartridge under vacuum. After P-CDP based SPE procedure, the concentration of target compounds would be enriched 1000 times. Among 189 tested compounds, except for 9 compounds that cannot be detected as a result of interference by sodium ions during instrumental analysis, 67% of the total compounds have high absolute recovery rates (≥80%), which outperformed HLB material.

CHAPTER 3: FUTURE WORK

3.1 Conclusions

During the research, an offline SPE method was developed and optimized with a novel P-CDP material as the adsorbent. This novel material was reported to be a great adsorbent in batch experiments, and its unique charge selectivity property was proved by this research as well as previous studies (Ling et al., 2017). Realizing the fact that P-CDP favors positively charged compounds, I improved the capture rates of target compounds by increasing the mass of adsorbents and lowering the pH of water samples. Many neutral compounds, including ubiquitous water contaminants carbamazepine and DEET, were fully captured with increased mass even at neutral pH. Likewise, some compounds that are neutral or negatively charged at neutral pH become neutral or positively charged compounds at pH 3 and exhibited improved capture. For example, ibuprofen and warfarin exhibited greatly improved capture at pH 3. Recovery rates were also improved using ion exchange principles. With the help of 100 mg sodium chloride, 67% of target compounds can achieve a recovery rate above 80% with one step elution.

After optimization, the P-CDP material could compete with the leading SPE material, HLB, in both capture and recovery steps, and could be used as an alternative and good SPE adsorbent for more than 120 of compounds examined. We estimate that P-CDP is one thousand times cheaper than HLB, but is also broadly effective and can be easily manipulated in SPE workflows. Additionally, P-CDP favors positively charged compounds during capture step, therefore it can also be used for charge selective treatments via simple pH controls, such as charge selective adsorption or MP removal and charge selective SPE.

Above all, several conclusions can be drawn as:

(i) An equivalent mass of HLB outperforms P-CDP as an SPE adsorbent when loaded at pH 6 and eluted with 5 mL of methanol;

(ii) P-CDP material has great ability for capturing and releasing a broad range of MPs, and can perform better than HLB under optimized conditions;

(iii) The optimized condition for P-CDP based SPE was 500 mg P-CDP, loading at pH 3, and elution with 15 mL methanol containing 100 mg sodium chloride;

(iv) The charge state of compounds is the most important factor influencing both capture and release of adsorbates with P-CDP as adsorbent;

(v) Some special properties including compounds that are both highly acidic and hydrophilic and those containing neutral sulfonamide groups limit capture and release on P-CDP;

(vi) P-CDP can be used as a charge selective adsorbent in both MP treatment and SPE procedures.

3.2 Future Work

In the future, the P-CDP based SPE procedure could be improved even further. First, the optimization of the elution step was not perfect. A very high concentration of sodium chloride was used in the elution step (almost half of the solubility of sodium chloride in methanol), and the high concentration of sodium ions leads to the interferences during instrumental analysis. An optimal concentration of sodium chloride should be selected following a systematic series of elution tests. Different concentrations of sodium chloride in methanol should be tested, and the lowest concentration with the highest recovery rates would be the optimal concentration.

Furthermore, calcium chloride might be a preferred alternative salt that would also assist elution. Calcium is a divalent cation and calcium chloride can be dissolved easily in methanol, so the ionic strength of the elution solvent would also be increased with calcium chloride, and we

may need lower concentrations of calcium chloride to elute same moles of MPs. Besides, calcium ions would not interfere with instrumental analysis for there aren't any calcium adducts formed with target compounds, and we could get better and more accurate measurements compared to sodium chloride elution. Similar to the experiments expected for sodium chloride, the concentration of calcium chloride would also need to be optimized if applicable.

In addition to procedure optimizations, the optimized SPE method needs to be applied to real water samples, like tap water and lake water. In this research we already demonstrated the good performance of P-CDP in aqueous solution, and some batch experiments demonstrated that the adsorption ability of P-CDP will not be affected by NOM in real waters (Ling et al., 2017). I therefore expect good recoveries using P-CDP in SPE procedure with real water samples. To analyze MPs in real waters, the concentration of MPs might be a little bit lower, but the matrix is much more complex than the synthetic solution prepared in this research. To minimize the complexity of real waters, I would first select fifty stable MPs with low LODs and different polarizability as "standard MPs", a mixture of those compounds would be prepared. After filtration and adding buffers, I would spike in the mixture of the "standards" at three different concentration levels, such as 10 ng L^{-1}, 50 ng L^{-1} and 250 ng L^{-1}. Internal standards could help diminish the matrix effects and recoveries could be calculated for those fifty MPs. In this way, the performance of P-CDP in real waters could be evaluated. From all capture and recovery data for a broader range of MPs, we would also figure out the possible adsorption and desorption mechanisms of P-CDP materials, and therefore further develop different SPE conditions for different SPE target.

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APPENDICES

Appendix A - Property Information of Compounds and Reagents

Table A1. Physiochemical properties of all 242 compounds.

No.[a]	Compound Name	CAS No.	Supplier[b]	Chemical Formula	pK_a[c]	Log K_{ow}[d]	Charge 3[e]	Charge 6[e]	LogD 3[e]	LogD 6[e]	MV[f]	Class[g]
1	10,11-dihydrocarbamazepine	58955-93-4	Sigma	C15H14N2O3	12.84	-0.21	n	n	0.85	0.85	1.85	Pharm
2	2-aminobenzimidazole	934-32-7	Sigma	C7H7N3	8.11	0.88	+	+	-1.26	-1.23	1.01	Pesticide
3	2-ethyl-2-phenyl malonamide monohydrate	7206-76-0	Fluka	C11H14N2O2	15.73	0.40	n	n	-2.92	-2.92	1.65	Pharm
4	2-mercaptobenzothiazole	149-30-4	Sigma	C7H5NS2	3.63	1.83	n	-	2.88	2.88	1.13	Pesticide
5	2-methyl-4-isothiazolin-3-one (MI)	2682-20-4	Fluka	C4H5NOS	NA	-0.83	n	n	0.23	0.23	0.80	Pesticide
6	2,4-D	94-75-7	Fluka	C8H6Cl2O3	2.81	2.62	-	-	2.10	-0.52	1.38	Pesticide
7	2,6-dichlorobenzamide	2008-58-4	Fluka	C7H5Cl2NO	-1.42	0.90	n	n	1.44	2.31	1.22	Pesticide
8	2,6-dimethoxyphenol	91-10-1	Aldrich	C8H10O3	9.37	1.16	n	n	1.35	1.35	1.17	Lifestyle
9	6-benzylaminopurine	1214-39-7	Sigma	C12H11N5	3.42	1.23	+	n	1.48	1.50	1.67	Pesticide
10	Abacavir	136470-78-5	Fluka	C14H18N6O	-0.27	1.62	+	n	-2.77	-2.07	2.09	Pharm
11	Abscisic Acid	21293-29-8	Sigma	C15H20O4	4.74	2.38	n	-	2.09	0.81	2.13	Pesticide
12	Acebutolol HCl	37517-30-9	Fluka	C18H28N2O4	9.57	1.19	+	+	-0.98	-0.25	2.76	Pharm
13	Acephate	30560-19-1	Sigma	C4H10NO3PS	6.54	-0.90	n	n	0.04	0.03	1.27	Pesticide
14	Acesulfame K	55589-62-3	Sigma	C4H4KNO4S	2.00	-1.33	-	-	-0.21	-1.97	0.98	Lifestyle
15	Acetaminophen	103-90-2	USP	C8H9NO2	9.46	0.27	n	n	1.62	0.97	1.17	Pharm
16	Acetamiprid	135410-20-7	Sigma	C10H11ClN4	-0.27	2.55	+	n	-0.06	1.11	1.67	Pesticide
17	Acetazolamide	1424-27-7	Sigma	C4H5N4NaO3S2	6.55	-0.72	n	n	-0.42	-2.75	1.34	Pharm
18	Acetochlor	34256-82-1	Fluka	C14H20ClNO2	16.60	3.37	n	n	3.50	3.50	2.14	Pesticide
19	Adrenalone HCl	99-45-6	Sigma	C9H11NO3	7.50	0.47	+	+	-2.80	-1.40	1.37	Pharm
20	Adrenosterone	382-45-6	Aldrich	C19H24O3	NA	1.41	n	n	3.01	3.01	2.36	Hormone

21	Alachlor	15972-60-8	Fluka	C14H20ClNO2	16.60	3.37	n	n	3.59	3.59	2.14	Pesticide
22	Albuterol Sulfate	18559-94-9	Fluka	C13H21NO3	9.40	0.64	+	+	-2.36	-2.21	1.98	Pharm
23	Amicinonide	51022-69-6	Sigma	C28H35FO7	13.59	NA	n	n	3.20	3.20	3.62	Pharm
24	Amisulpride	71675-85-9	Sigma	C17H27N3O4S	-0.11	1.11	+	+	-2.52	-0.13	2.81	Pharm
25	Amitriptyline HCl	50-48-6	Fluka	C20H23N	9.76	4.95	+	+	1.31	1.50	2.40	Pharm
26	Amphetamine	300-62-9	Cerilliant	C9H13N	10.01	1.76	+	+	-1.23	-1.19	1.24	Pharm
27	Ampicillin	69-53-4	Sigma	C16H19N3O4S	3.24	1.45	+	z	-1.40	-3.49	2.48	Pharm
28	Arecoline HBr	63-75-2	Sigma	C8H13NO2	8.23	0.78	+	+	-2.84	-1.56	1.26	Natural
29	Atenolol	29122-68-7	USP	C14H22N2O3	9.67	-0.03	+	+	-4.64	-4.50	2.18	Pharm
30	Atenolol Acid	56392-14-4	Aldrich	C14H21NO4	3.54	-2.34	+	z	-1.69	-1.24	2.14	Pharm
31	Atomoxetine HCl	83015-26-3	Sigma	C17H21NO	9.80	4.23	+	+	0.57	0.67	2.19	Pharm
32	Atrazin-2-Hydroxy	2163-68-0	Fluka	C8H15N5O	12.48	-1.74	n	n	-2.84	-2.84	1.56	Pesticide
33	Atrazin-desethyl	6190-65-4	Sigma	C6H10ClN5	3.38	1.78	+	n	-1.57	0.23	1.34	Pesticide
34	Atrazine	1912-24-9	Fluka	C8H14ClN5	3.20	2.82	+	n	-0.96	0.98	1.62	Pesticide
35	Atrazine-desethyl-desisopropyl	3397-62-4	Sigma Fluka	C3H4ClN5	3.58	0.32	+	n	-2.58	-0.88	0.92	Pesticide
36	Atropine	51-55-8	Sigma	C17H23NO3	9.39	1.91	+	+	-1.93	-1.57	2.28	Pharm
37	Azoxystrobin	131860-33-8	Fluka	C22H17N3O5	0.94	1.58	n	n	4.22	4.22	2.92	Pesticide
38	Baclofen	1134-47-0	Cerilliant	C10H12ClNO2	3.89	-1.32	+	z	-1.36	-0.78	1.58	Pharm
39	Bendiocarb	22781-23-3	Sigma	C11H13NO4	14.76	2.55	n	n	2.12	-0.25	1.60	Pesticide
40	Bentazon	25057-89-0	Fluka	C10H12N2O3S	2.03	1.67	-	-	0.06	-0.19	1.67	Pesticide
41	Benzisothiazolin-3-on (BIT)	2634-33-5	Sigma	C7H5NOS	9.50	0.64	n	n	1.92	0.66	1.03	Pesticide
42	Benzotriazole	95-14-7	Sigma	C6H5N3	0.22	1.17	n	n	1.30	1.30	0.86	Industrial
43	Benzotriazole-methyl-1H	136-85-6	Fluka	C7H7N3	0.45	1.71	n	n	1.81	1.81	1.01	Industrial
44	Benzoylecgonine	519-09-5	Cerilliant	C16H19NO4	3.15	-1.32	+	z	-0.88	-0.59	2.16	Drug
45	Bis(2-ehtylhexyl) phthalate	117-81-7	Fluka	C24H38O4	NA	NA	n	n	8.03	8.03	3.40	Industrial
46	Bromacil	314-40-9	Fluka	C9H13BrN2O2	9.95	1.68	n	n	2.41	0.13	1.63	Pesticide
47	Caffeine	58-08-2	USP	C8H10N4O2	-1.16	0.16	n	n	-0.55	-0.55	1.36	Lifestyle

48	Candesartan	139481-59-7	TRC	C24H20N6O3	-1.45	4.79	n	-	5.18	2.49	3.16	Pharm
49	Carbamazepine	298-46-4	Sigma Aldrich	C15H12N2O	15.96	2.25	n	n	2.59	2.81	1.81	Pharm
50	Carbendazim	10605-21-7	Sigma	C9H9N3O2	-1.81	1.55	+	n	2.31	0.13	1.36	Pesticide
51	Carbofuran	1563-66-2	Fluka	C12H15NO3	14.76	2.30	n	n	2.62	0.55	1.69	Pesticide
52	Carisoprodol	78-44-4	Cerilliant	C12H24N2O4	15.06	2.36	n	n	0.55	-0.84	2.15	Pharm
53	Celecoxib	169590-42-5	Fluka	C17H14F3N3O2S	-0.41	3.47	n	n	4.01	4.01	2.47	Pharm
54	Chloridazon	1698-60-8	Fluka	C10H8ClN3O	-1.77	0.76	n	n	1.11	1.11	1.52	Pesticide
55	Cimetidine	51481-61-9	Fluka	C10H16N6S	4.51	0.57	+	+	-2.83	-0.83	1.96	Pharm
56	Ciprofloxacin	85721-33-1	Sigma	C17H18FN3O3	-0.22	0.00	+	z	-1.68	-0.95	2.30	Pharm
57	cis-diltiazem	42399-41-7	Cerilliant	C22H26N2O4S	8.18	2.79	+	+	-0.77	0.57	3.14	Pharm
58	Citalopram HBr	59729-33-8	Cerilliant	C20H21FN2O	9.78	3.74	+	+	0.26	0.44	2.53	Pharm
59	Clarithromycin	81103-11-9	Sigma	C38H69NO13	8.38	5.24	+	+	-1.60	0.89	5.91	Pharm
60	Climbazole	38083-17-9	Sigma	C15H17ClN2O2	6.49	3.76	+	+	3.75	3.98	2.19	Pharm
61	Clofibric Acid	882-09-7	Fluka	C10H11ClO3	3.37	2.84	n	-	2.75	0.32	1.54	Pharm
62	Codeine	76-57-3	Cerilliant	C18H21NO3	9.19	1.28	+	+	-2.16	-1.68	2.21	Pharm
63	Corticosterone	50-22-6	Sigma	C21H30O4	-0.26	1.99	n	n	2.02	2.02	2.74	Pharm
64	Cotinine	486-56-6	Cerilliant	C10H12N2O	-1.83	0.34	+	n	-0.72	0.19	1.39	Drug
65	Coumarin	91-64-5	Sigma	C9H6O2	NA	1.51	n	n	1.78	1.78	1.06	Natural
66	Cyanazine	21725-46-2	Sigma	C9H13ClN6	-0.63	2.51	n	n	-1.27	-0.33	1.77	Pesticide
67	Cyflufenamid	180409-60-3	Sigma	C20H17F5N2O2	15.15	5.60	n	n	NA	NA	2.66	Pesticide
68	DEET	134-62-3	Sigma Aldrich Fluka	C12H17NO	-0.95	2.26	n	n	2.50	2.50	1.68	Pesticide
69	Dehydroacetic Acid	520-45-6	Sigma	C8H8O4	6.49	0.78	n	n	0.44	0.42	1.19	Pesticide
70	Desvenlafaxine	93413-62-8	Fluka	C16H25NO2	8.87	2.72	+	+	-0.91	-0.22	2.23	Pharm
71	Dexamethasone	50-02-2	Sigma	C22H29FO5	12.42	1.72	n	n	1.68	1.68	2.91	Pharm
72	Dextromethorphan HBr	125-71-3	Fluka	C18H25NO	9.85	3.60	+	+	-0.01	0.15	2.24	Pharm
73	Diclofenac Na	15307-86-5	Fluka	C14H11Cl2N1O2	4.00	4.02	n	-	4.22	2.26	2.03	Pharm

74	Diethyl Phthalate	84-66-2	Fluka	C12H14O4	NA	NA	n	n	2.69	2.69	1.71	Industrial
75	Dimethachlor	50563-36-5	Sigma	C13H18ClNO2	16.77	2.33	n	n	2.59	2.59	2.00	Pesticide
76	Dimethoate	60-51-5	Fluka	C5H12NO3PS2	15.93	0.28	n	n	-1.48	-1.48	1.58	Pesticide
77	Diphenhydramine HCl	58-73-1	Fluka	C17H21NO	8.87	3.11	+	+	0.15	0.87	2.19	Pharm
78	Diuron	330-54-1	Fluka	C9H10Cl2N2O1	13.18	2.67	n	n	2.30	2.30	1.60	Pesticide
79	Efavirenz	154598-52-4	Sigma	C14H9ClF3NO2	-1.49	4.15	n	n	4.45	1.89	1.89	Pharm
80	Estrone	53-16-7	Fluka	C18H22O2	10.33	3.43	n	n	4.31	4.31	2.16	Hormone
81	Ethofumesate	26225-79-6	Fluka	C13H18O5S1	NA	1.51	n	n	2.34	2.34	2.05	Pesticide
82	Ethyl butylacetyl amnopropionate	52304-36-6	Aldrich	C11H21NO3	-1.29	1.51	n	n	0.96	0.96	1.85	Pesticide
83	Famciclovir	104227-87-4	Sigma	C14H19N5O4	-1.96	0.64	n	n	-3.46	-1.51	2.34	Pharm
84	Famotidine	76824-35-6	Fluka	C8H15N7O2S3	1.74	-0.65	+	+	-5.07	-2.96	2.26	Pharm
85	Fexofenadine HCl	83799-24-0	Sigma	C32H39NO4	4.04	NA	+	z	2.32	2.94	4.09	Pharm
86	Fluconazole	86386-73-4	Fluka	C13H12F2N6O	1.70	0.25	n	n	0.49	0.56	2.01	Pharm
87	Fluoxetine HCl	54910-89-3	Fluka	C17H18F3NO	9.80	4.65	+	+	0.93	1.04	2.24	Pharm
88	Folic Acid	59-30-3	Sigma	C19H19N7O6	2.09	-2.81	n	-	-1.59	-4.68	3.04	Natural
89	Furosemide	54-31-9	Cerilliant	C12H11ClN2O5S	-1.52	2.32	n	-	1.72	0.00	2.10	Pharm
90	Gabapentin	60142-96-3	Sigma	C9H17NO2	4.63	-1.37	+	z	-2.00	-1.29	1.44	Pharm
91	Gemfibrozil	25812-30-0	Fluka	C15H22O3	4.42	4.77	n	-	4.37	2.80	2.12	Pharm
92	Gibberellic Acid	77-06-5	Sigma	C19H22O6	-0.90	0.45	n	-	0.32	-1.48	2.42	Pesticide
93	Hexamethylphosphoramide	680-31-9	Sigma	C6H18N3OP	-0.12	-0.22	n	n	-1.41	-1.40	1.52	Industrial
94	Hexazinone	51235-04-2	Sigma	C12H20N4O2	-1.24	2.15	n	n	1.37	1.37	1.97	Pesticide
95	Hydrochlorothiazide	58-93-5	Sigma	C7H8ClN3O4S2	9.09	-0.10	n	n	-0.58	-0.58	1.73	Pharm
96	Hydrocodone	125-29-1	Cerilliant	C18H21NO3	8.61	2.16	+	+	-1.54	-0.59	2.21	Pharm
97	Hydrocortisone	50-23-7	Sigma	C21H30O5	12.59	1.62	n	n	1.28	1.28	2.80	Pharm
98	Ibuprofen	15687-27-1	USP	C13H18O2	4.85	3.79	n	-	3.84	2.67	1.78	Pharm
99	Imidacloprid	138261-41-3	Fluka	C9H10ClN5O2	-0.40	-0.41	z	z	-0.95	1.02	1.68	Pesticide
100	Iodocarb	55406-53-6	Fluka	C8H12INO2	14.40	2.45	n	n	3.19	0.68	1.58	Pesticide

101	Iopromide	73334-07-3	Sigma	C18H24I3N3O8	-2.31	NA	n	n	0.48	-2.31	3.82	Pharm
102	Ioxynil	1689-83-4	Fluka	C7H3I2NO	2.85	3.94	n	-	3.38	2.85	1.45	Pesticide
103	Irbesartan	138402-11-6	Sigma	C25H28N6O	5.13	5.31	+	-	4.37	5.13	3.32	Pharm
104	Isophorone Diisocyanate	4098-71-9	Sigma	C12H18O2N2	2.13	4.75	n	n	2.13	2.13	1.84	Industrial
105	Isoproturon	34123-59-6	Fluka	C12H18N2O1	2.57	2.84	n	n	2.57	2.57	1.78	Pesticide
106	Ketamine HCl	6740-88-1	Cerilliant	C13H16ClNO	7.16	3.12	+	+	0.15	2.16	1.83	Pharm
107	Ketoprofen	22071-15-4	Fluka	C16H14O3	3.88	3.00	n	-	3.56	1.51	1.98	Pharm
108	Lamotrigine	84057-84-1	Sigma	C9H7Cl2N5	5.87	0.99	+	n	-0.59	1.10	1.65	Pharm
109	Levetiracetam	102767-28-2	Sigma	C8H14N2O2	-1.56	-0.49	n	n	-2.42	-2.42	1.36	Pharm
110	Lidocaine	137-58-6	Fluka	C14H22N2O	7.75	1.66	+	+	0.51	0.92	2.06	Pharm
111	Linuron	330-55-2	Fluka	C9H10Cl2N2O2	11.94	2.91	n	n	2.30	2.30	1.66	Pesticide
112	Losartan Potassium	114798-26-4	Sigma	C22H23ClN6O	-1.45	4.01	+	-	4.22	4.72	3.12	Pharm
113	Mabuterol HCl	56341-08-3	Sigma	C13H18ClF3N2O	0.90	2.32	+	+	-0.64	-0.48	2.14	Pharm
114	MCPA	94-74-6	Fluka	C9H9ClO3	3.36	2.52	n	-	2.25	-0.17	1.39	Pesticide
115	Mecoprop	93-65-2	Fluka	C10H11ClO3	3.47	2.94	n	-	2.85	0.49	1.54	Pesticide
116	Meprobamate	57-53-4	Cerilliant	C9H18N2O4	15.17	0.98	n	n	-2.79	-2.79	1.73	Pharm
117	Metalaxyl	57837-19-1	Sigma	C15H21NO4	15.80	1.70	n	n	2.12	2.12	2.23	Pesticide
118	Metamitron	41394-05-2	Fluka	C10H10N4O1	2.78	1.44	n	n	0.24	0.44	1.50	Pesticide
119	Metaxalone	1665-48-1	Cerilliant	C12H15NO3	13.14	2.60	n	n	3.09	1.26	1.69	Pharm
120	Metformin HCl	657-24-9	Fluka	C4H11N5	-1.55	-1.40	+	+	-5.75	-5.74	1.09	Pharm
121	Methadone	76-99-3	Cerilliant	C21H27NO	9.12	4.17	+	+	1.51	2.04	2.71	Pharm
122	Methocarbamol	532-03-6	Fluka	C11H15NO5	13.60	-0.26	n	n	-1.41	-1.41	1.77	Pharm
123	Methomyl	16752-77-5	Fluka	C5H10N2O2S	0.69	0.61	n	n	1.39	-0.96	1.21	Pesticide
124	Metolachlor	51218-45-2	Fluka	C15H22ClNO2	16.75	3.24	n	n	3.45	3.45	2.28	Pesticide
125	Metolachlor-ESA	171118-09-5	Sigma	C15H23N1O5S1	-0.68	1.69	-	-	-0.24	-0.26	2.50	Pesticide
126	Metoprolol Tartrate	37350-58-6	Fluka	C15H25NO3	9.67	1.69	+	+	-1.48	-1.34	2.26	Pharm
127	Metribuzin	21087-64-9	Fluka	C8H14N4OS	2.46	1.49	n	n	1.85	1.96	1.62	Pesticide

128	Metsulfuron-methyl	74223-64-6	Sigma	C14H15N5O6S	0.22	2.00	n	-	0.54	-0.53	2.53	Pesticide
129	Molinate	2212-67-1	Fluka	C9H17NOS	NA	2.91	n	n	2.34	2.34	1.55	Pesticide
130	Morphine	57-27-2	Cerilliant	C17H19NO3	9.12	0.72	+	+	-2.30	-1.83	2.06	Pharm
131	N,N-didesmethylvenlafaxine	93413-77-5	TRC	C15H23N1O2	-0.96	2.60	+	+	-1.10	-0.96	2.09	Pharm
132	N4-acetylsulfamethoxazole	21312-10-7	Sigma	C12H13N3O4S	-0.11	1.21	n	-	1.57	-0.11	2.02	Pharm
133	Nadolol	42200-33-9	Fluka	C17H27NO4	-2.26	1.17	+	+	-2.38	-2.26	2.49	Pharm
134	Naproxen	22204-53-1	USP	C14H14O3	1.18	3.10	n	-	2.96	1.18	1.78	Pharm
135	Nicotine	54-11-5	Fluka	C10H14N2	-1.37	1.00	+	+	-2.49	-1.37	1.37	Drug
136	Norfloxacin	70458-96-7	Sigma	C16H18FN3O3	-1.06	-0.31	+	z	-1.79	-1.06	2.27	Pharm
137	Ofloxacin	82419-36-1	Sigma	C18H20FN3O4	5.45	-2.00	+	z	-1.38	0.65	2.50	Pharm
138	Oxazepam	604-75-1	Cerilliant	C15H11ClN2O2	-1.47	3.34	n	n	1.95	0.15	1.99	Pharm
139	Oxcarbazepine	28721-07-5	Fluka	C15H12N2O2	13.18	1.11	n	n	2.29	1.61	1.87	Pharm
140	Oxybenzone	131-57-7	Fluka	C14H12O3	7.07	3.52	n	n	3.62	3.59	1.74	Lifestyle
141	Paraxanthine	611-59-6	Cerilliant	C7H8N4O2	-1.10	-0.39	n	n	-0.17	-2.72	1.22	Lifestyle
142	Penciclovir	39809-25-1	Sigma Aldrich	C10H15N5O3	2.59	-3.71	n	n	-3.81	-3.03	1.80	Pharm
143	Pentoxyfylline	6493-05-6	Sigma	C13H18N4O3	-1.16	0.56	n	n	0.23	0.23	2.08	Pharm
144	Perfluoroctanoic acid (PFOA)	335-67-1	Aldrich	C8HF15O2	-4.20	6.30	-	-	1.58	1.58	1.58	Industrial
145	Phenobarbital	50-06-6	Cerilliant	C12H12N2O3	7.14	1.33	n	n	-0.35	-4.48	1.70	Pharm
146	Phenytoin (Dilantin)	57-41-0	Fluka	C15H12N2O2	8.49	2.16	n	n	2.62	-1.53	1.87	Pharm
147	Pirimicarb	23103-98-2	Fluka	C11H18N4O2	4.99	1.40	+	n	0.13	1.76	1.89	Pesticide
148	Pirimiphos-Ethyl	23505-41-1	Sigma	C12H14N2O2	5.09	4.42	+	n	1.97	3.63	2.55	Pesticide
149	Primidone	125-33-7	Fluka	C13H24N3O3PS	11.50	0.73	n	n	1.66	-0.92	1.68	Pharm
150	Progesterone	57-83-0	Sigma Aldrich	C21H30O2	NA	3.67	n	n	4.15	4.15	2.62	Hormone
151	Prohexadione Calcium	127277-53-6	Sigma	C10H12O5	3.42	1.06	n	-	0.76	-1.23	1.52	Pesticide
152	Prometon	1610-18-0	Sigma Aldrich-Fluka	C10H19N5O	-1.66	3.57	+	n	-1.03	-0.70	1.84	Pesticide

153	Propachlor	1918-16-7	Fluka	C11H14ClNO	16.77	2.42	n	n	2.39	2.39	1.66	Pesticide
154	Propachlor ESA Na	123732-85-4	Sigma Aldrich-Fluka	C11H15N1O4S1	-0.88	0.87	-	-	-1.32	-1.33	1.86	Pesticide
155	Propachlor OXA	70628-36-3	Sigma Aldrich-Fluka	C11H13N1O3	3.03	0.60	n	-	1.51	-1.06	1.61	Pesticide
156	Propazine	139-40-2	Sigma	C9H16ClN5	3.17	3.24	n	n	-0.50	1.52	1.76	Pesticide
157	Propoxur	114-26-1	Sigma	C11H15NO3	14.76	1.90	n	n	2.66	0.62	1.65	Pesticide
158	Propranolol HCl	525-66-6	Fluka	C16H21NO2	9.67	2.60	+	+	-0.66	-0.52	2.15	Pharm
159	Propyzamide	23950-58-5	Fluka	C12H11Cl2NO	-1.52	3.57	n	n	4.00	3.95	1.84	Pesticide
160	Pseudoephedrine	299-42-3	Cerilliant	C10H15NO	9.52	0.68	+	+	-1.92	-1.74	1.44	Pharm
161	Pyrazophos	13457-18-6	Sigma	C14H20N3O5PS	-0.58	3.53	n	n	3.14	3.14	2.61	Pesticide
162	Ranitidine HCl	66357-35-5	USP	C13H22N4O3S	7.12	0.29	z	z	-2.82	-0.81	2.40	Pharm
163	Ritalinic Acid	19395-41-6	Sigma	C13H17NO2	3.73	-1.07	+	z	-0.89	-0.36	1.77	Pharm
164	Serotonin HCl	153-98-0	Sigma	C10H12N2O	9.31	0.79	+	+	-1.85	-1.76	1.39	Natural
165	Siduron	1982-49-6	Fluka	C14H20N2O	13.56	3.86	n	n	2.99	2.99	1.95	Pesticide
166	Simazine	122-34-9	Fluka	C7H12ClN5	3.23	2.40	+	n	-1.37	0.58	1.48	Pesticide
167	Sitagliptin	486460-32-6	Enamine	C16H15F6N5O	0.66	1.39	+	+	-1.78	-1.33	2.44	Pharm
168	Sucralose	56038-13-2	USP	C12H19Cl3O8	11.91	-1.00	n	n	-0.47	-0.47	2.42	Lifestyle
169	Sulfadimethoxine	122-11-2	Fluka	C12H14N4O4S	1.95	1.17	n	n	1.22	1.22	2.12	Pharm
170	Sulfamethazine	57-68-1	Sigma	C12H14N4O2S	-1.97	0.76	n	n	0.61	0.61	2.00	Pharm
171	Sulfamethoxazole	723-46-6	USP	C10H11N3O3S	0.25	0.48	n	n	0.75	0.60	1.72	Pharm
172	Sulfathiazole	72-14-0	Fluka	C9H9N3O2S2	0.35	0.72	n	n	0.93	0.93	1.69	Pharm
173	TDCPP	13674-87-8	Sigma	C9H15Cl6O4P	NA	3.65	n	n	4.28	4.28	2.55	Industrial
174	Temazepam	846-50-4	Cerilliant	C16H13ClN2O2	-1.40	2.15	n	n	2.79	2.79	2.13	Pharm
175	Terbutylazine	5915-41-3	Fluka	C9H16ClN5	3.18	3.27	n	n	-0.42	-0.35	1.76	Pesticide
176	Testosterone	58-22-0	Cerilliant	C19H28O2	-0.88	3.27	n	n	3.37	3.37	2.38	Hormone
177	Theophylline	58-55-9	Fluka	C7H8N4O2	-0.78	-0.39	n	n	-0.90	-0.81	1.22	Pharm
178	Thiabendazole	148-79-8	Fluka	C10H7N3S	-0.22	2.00	+	n	1.38	2.32	1.40	Pharm

179	cis-Tramadol HCl	27203-92-5	Cerilliant	C16H25NO2	9.23	3.01	+	+	-1.05	-0.59	2.23	Pharm
180	Triamterene	396-01-0	Sigma	C12H11N7	1.86	0.80	n	n	-2.22	-1.44	1.83	Pharm
181	Tributyl phosphate (TBP)	126-73-8	Fluka	C12H27O4P	NA	3.82	n	n	4.09	4.09	2.24	Industrial
182	Triclosan	3380-34-5	Aldrich	C12H7Cl3O2	7.68	4.66	n	n	4.98	4.97	1.81	Pesticide
183	Trimethoprim	738-70-5	USP	C14H18N4O3	-0.90	0.73	+	+	-3.92	-2.35	2.18	Pharm
184	Trinexapac-ethyl	95266-40-3	Fluka	C13H16O5	4.56	0.63	n	-	0.75	-1.67	1.84	Pesticide
185	Tris (2-chloro-ethyl) phosphate (TCEP)	115-96-8	Aldrich	C6H12Cl3O4P	NA	1.63	n	n	2.11	2.11	1.76	Industrial
186	Valsartan	137862-53-4	USP	C24H29N5O3	-1.52	3.65	n	-	5.25	3.27	3.41	Pharm
187	Venlafaxine HCl	93413-69-5	USP	C17H27NO2	8.91	3.28	+	+	-0.76	-0.07	2.37	Pharm
188	Verapamil HCl	52-53-9	Fluka	C27H38N2O4	9.68	4.80	+	+	1.54	1.76	3.79	Pharm
189	Warfarin	2610-86-8	Fluka	C19H16O4	5.56	2.23	n	-	2.72	2.17	2.28	Pesticide
190	1-Naphthol	90-15-3	Sigma	C10H8O	9.60	2.69	n	n	2.76	2.76	1.14	Pesticide
191	Bisphenol A	80-05-7	Fluka	C15H16O2	9.78	3.64	n	n	4.32	4.32	1.86	Industrial
192	2-amino-5-chlorothiazole HCl	55506-37-1	Sigma	C3H4Cl2N2S	3.91	NA	+	n	NA	NA	0.82	Pesticide
193	2-aminothiazole	96-50-4	Sigma	C3H4N2S	5.09	0.83	+	n	-0.70	0.48	0.70	Pesticide
194	3-amino-5-methylisoxazole	1072-67-9	Sigma	C4H6N2O	2.44	-0.16	n	n	0.37	0.48	0.74	Pesticide
195	4-aminophenol	123-30-8	Sigma	C6H7NO	5.43	0.24	+	n	-1.40	0.88	0.87	Industrial
196	Acyclovir	59277-89-3	Fluka	C8H11N5O3	2.63	-4.27	n	n	-1.85	-1.85	1.52	Pharm
197	Aldicarb	116-06-3	Fluka	C7H14O2N2S	1.63	1.36	n	n	1.97	-0.16	1.49	Pesticide
198	Allopurinol	315-30-0	Fluka	C5H4N4O	-0.45	-1.14	n	n	0.35	0.34	0.88	Pharm
199	Astemizole	68844-77-9	Sigma	C28H31FN4O	6.24	6.43	+	+	0.23	1.66	3.56	Pharm
200	Atorvastatin Ca	134523-00-5	Fluka	C33H35FN2O5	4.31	NA	n	-	6.09	3.58	4.28	Pharm
201	Benzoic Acid	65-85-0	Fisher	C7H6O2	4.08	1.87	n	-	1.60	-0.29	0.93	Pesticide
202	Benzophenone	119-61-9	Supelco	C13H10O	NA	3.15	n	n	3.43	3.43	1.48	Lifestyle
203	Bifenazate	149877-41-8	Fluka	C17H20N2O3	13.69	4.14	n	n	4.67	2.87	2.36	Pesticide
204	Bupropion HCl	34841-39-9	Cerilliant	C13H18ClNO	8.22	3.85	+	+	0.03	1.09	1.94	Pharm
205	Butalbital	77-26-9	Cerilliant	C11H16N2O3	7.48	1.87	n	n	0.65	-3.85	1.75	Pharm

206	Butocarboxim	34681-10-2	Sigma	C7H14N2O2S	1.33	1.21	n	n	2.04	-0.10	1.49	Pesticide
207	Carbamazepine-10,11 -epoxide	36507-30-9	Sigma	C15H12N2O2	15.96	0.95	n	n	2.03	1.83	1.80	Pharm
208	Carbaryl	63-25-2	Fluka	C12H11NO2	14.77	2.35	n	n	2.96	1.33	1.54	Pesticide
209	Carbazole	86-74-8	Fluka	C12H9N	14.97	3.29	n	n	3.09	3.09	1.32	Industrial
210	Catechol (1,2-dihydroxybenzene)	120-80-9	Sigma	C6H6O2	9.34	1.03	n	n	1.37	1.37	0.83	Natural
211	Chloroxylenol	88-04-0	Fluka	C8H9ClO	9.21	NA	n	n	3.30	3.30	1.18	Pesticide
212	Chlorpheniramine Maleate	132-22-9	Fluka	C16H19ClN2	3.57	3.82	+	+	-0.54	0.40	2.21	Pharm
213	Citric Acid	77-92-9	Sigma	C6H8O7	3.05	-1.67	n	-	-1.60	-6.20	1.24	Pesticide
214	DI-tert-butyl dicarbonate	24424-99-5	Sigma	C10H18O5	NA	1.87	n	n	2.53	2.53	1.73	Pesticide
215	Diazepam	439-14-5	Sigma	C16H13ClN2O	2.92	2.70	n	n	1.09	2.75	2.07	Pharm
216	Diazinon	333-41-5	Fluka	C12H21N2O3PS	4.19	3.86	+	n	3.00	4.19	2.31	Pesticide
217	Dikegulac	52508-35-7	Sigma	C12H18O7	3.05	1.76	n	-	NA	NA	1.84	Pesticide
218	Emtricitabine	143491-57-0	TRC	C8H10FN3O3S	14.29	-2.56	n	n	0.07	0.07	1.55	Pharm
219	Epinephrine	51-43-4	Sigma	C9H13NO3	8.91	-0.69	+	+	-3.28	-3.28	1.42	Pharm
220	Erythromycin	114-07-8	Fluka	C37H67NO13	8.38	NA	+	+	-0.90	0.25	5.77	Pharm
221	17α-Estradiol	57-91-0	Sigma	C18H24O2	-0.88	3.94	n	n	3.71	3.71	2.20	Hormone
222	Estriol	50-27-1	Fluka	C18H24O3	10.33	2.81	n	n	2.67	2.67	2.26	Hormone
223	17α-Ethynyl-estradiol	57-63-6	Fluka	C20H24O2	-1.66	4.12	n	n	3.72	3.72	2.39	Pharm
224	Flucytosine	2022-85-7	Sigma	C4H4FN3O	8.31	-1.42	n	n	-1.29	-0.42	0.81	Pharm
225	Glyphosate	1071-83-6	Fluka	C3H8NO5P	-0.58	-4.47	z	z	-3.71	-6.53	1.09	Pesticide
226	Histamine	51-45-6	Sigma	C5H9N3	7.14	-0.73	+	+	-5.66	-4.90	0.92	Natural
227	Indole	120-72-9	Sigma	C8H7N	16.44	2.05	n	n	2.15	2.15	0.95	Pesticide
228	Lamivudine	134678-17-4	Sigma	C8H11N3O3S	0.21	-2.62	n	n	-0.33	-0.27	1.53	Pharm
229	Malaoxon	1634-78-2	Fluka	C10H19O7PS	NA	0.52	n	n	0.97	0.97	2.21	Pesticide
230	Melamine	108-78-1	Sigma	C3H6N6	1.84	-0.38	+	+	-7.88	-5.95	0.89	Industrial
231	Meptyldinocap	131-72-6	Sigma	C18H24N2O6	NA	5.90	n	n	6.30	6.30	2.79	Pesticide
232	Metaldehyde	108-62-3	Sigma	C8H16O4	NA	0.85	n	n	0.86	0.86	1.36	Pesticide

233	Nitrosobenzene	586-96-9	Fluka	C6H5NO	1.61	1.86	n	n	1.82	1.82	0.83	Natural
234	Nonylphenol	84852-15-3	Fluka	C15H24O	10.31	5.92	n	n	5.33	5.33	2.04	Industrial
235	Paraquat dichloride hydrate	1910-42-5	Sigma	C12H14Cl2N2	-7.00	NA	z	z	-6.70	-6.70	1.54	Pesticide
236	Pentobarbital	76-74-4	Cerilliant	C11H18N2O3	7.48	2.00	n	n	1.86	1.85	1.80	Pharm
237	Perfluorobutanoic acid (PFBA)	375-22-4	Aldrich	C4HF7O2	1.07	2.43	-	-	0.38	-1.20	0.87	Industrial
238	Phthalimide	85-41-6	Sigma	C8H5NO2	8.40	1.30	n	n	0.38	0.38	1.02	Pesticide
239	Propofol	2078-54-8	Cerilliant	C12H18O	10.98	3.57	n	n	4.15	4.15	1.62	Pharm
240	Sertraline HCl	79617-96-2	Cerilliant	C17H17Cl2N	9.56	5.29	+	+	1.91	2.08	2.26	Pharm
241	Sulfanilic Acid	121-57-3	Sigma	C6H7NO3S	-3.39	-2.08	-	-	-1.44	-2.20	1.16	Industrial
242	β-Estradiol	50-28-2	Sigma	C18H24O2	-0.88	3.94	n	n	3.71	3.71	2.20	Hormone

a. Number is used for further reference. Compounds with number from 190 (1-Naphthol) to 242 (β-Estradiol) are compounds that either cannot be detected or cannot be quantified well using the instrumental analysis method adopted in this research;
b. "TRC" stands for Toronto Research Chemicals;
c. All pK_a values are the lowest pK_a obtained from Marvin from ChemAxon;
d. All Log K_{ow} are adopted from Chemspider website (http://www.chemspider.com), which are estimated values reported by the KOWWIN package in the EPIsuite software;
e. All LogD data and charge state of major microspecies are estimated data predicted by Marvin from ChemAxon; 3 and 6 are pH values; "+" represents cations, "-" represents anions, "n" represents neutral species and "z" represents zwitters; "NA" stands for Not Applicable;
f. "MV" stands for McGowan volume, units in $cm^3\ mol^{-1}$; all MV data are obtained from ufz database;
g. "Pharm" stands for pharmaceuticals; "Drug" means illicit drugs.

Table A2. Chemicals and solvents.

Substance	CAS No.	Supplier
Acetone (HPLC Purity)	67-64-1	Sigma-Aldrich
Ammonia, 7N	7664-41-7	Fisher Scientific
Ammonium Acetate, ≥98%	631-61-8	Sigma-Aldrich
Formic Acid, 14N	64-18-6	Acros-Sigma
Methanol (HPLC Purity)	67-56-1	Fisher Scientific
Nitrogen Gas (>99%)	NA	AirGas
Oasis HLB (60μm; 20 cc Vac Cartridge)	NA	Waters
Sodium Chloride	7647-14-5	Fisher Scientific

Table A3. Information on 44 isotope labeled internal standards (ILIS).

No.	Internal Standard	CAS No.	Supplier
1	2-methyl-3-isothiazolinone-d3 HCl	1329509-49-0	TRC
2	Acetaminophen-ring-d4	64315-36-2	Aldrich
3	Allopurinol-d2	916979-34-5	TRC
4	Atenolol-d7	1202864-50-3	Aldrich
5	Atrazine-d5, 99.7%	163165-75-1	Aldrich
6	Azoxystrobin-d4	1346606-39-0	TRC
7	Caffeine-13C3	200-659-6	Aldrich
8	Carbamazepine-13C6	Not available	Aldrich
9	Carbaryl-d7	362049-56-7	TRC
10	Carbofuran-d3	1007459-98-4	Aldrich
11	Celecoxib-d4	544686-20-6	TRC
12	Cimetidine-d3	1185237-29-9	TRC
13	Citalopram-d66	1246819-94-2	TRC
14	Dextromethorphan-d3	524713-56-2	TRC
15	Diclofenac-(acetophenyl ring-13C6) sodium salt hemi(nonahydrate), 99.9%	1261393-73-0	Aldrich
16	Diltiazem-d4 HCl	Not available	TRC
17	Dimethoate-d6	1219794-81-6	TRC
18	rac-Efavirenz-d4	1246812-58-7	TRC
19	Erythromycin-13C,d3	959119-26-7	TRC
20	Estrone-d2	56588-58-0	TRC
21	Fexofenadine-d6	548783-71-7	TRC
22	Fluoxetine-d5	1173020-43-3	Aldrich
23	Gemfibrozil-d6	Not available	TRC
24	Ibuprofen-d3, ≥ 98%	121662-14-4	Aldrich
25	Imidacloprid-d4	1015855-75-0	Aldrich
26	Iodocarb-d9	1246815-08-6	TRC
27	Iopromide-d3	1189947-73-6	TRC
28	Isoproturon-d6	217487-17-7	Aldrich
29	Mecoprop-d3	352431-15-3	TRC
30	Metformin-d6 HCl	1185166-01-1	TRC
31	Metoprolol Acid-d5	Not available	TRC
32	Morphine-d3	118357-24-7	Aldrich
33	Naproxen-(methoxy)-d3	958293-79-3	Fluka
34	Oxybenzone-d3	Not available	TRC
35	Pirimicarb-d6	1015854-66-6	Aldrich
36	Ranitidine-d6	1185238-09-8	TRC

37	Sucralose-d6	Not available	TRC
38	Sulfadimethoxine-d6, 99.4%	73068-02-7	Aldrich
39	Sulfamethoxazole-(phenyl-13C6), 99.5%	1196157-90-0	Aldrich
40	Thiabendazole-d4	1190007-20-5	TRC
41	Triclosan-d3	1020719-98-5	TRC
42	Trimethoprim-d9, 99.9%	1189460-62-5	Aldrich
43	Tris(2-chloroethyl)phosphate-d12	1276500-47-0	TRC
44	Venlafaxine-D6 HCl	1062606-12-5	Aldrich

Appendix B - Analytical Information of Targeted Compounds

Table B1. Analytical information for 189 target compounds.

No.	Compound Name	Exact Mass [M]	Ionization Mode[a]	Offline SPE RT[b]	Offline LOD[c]	Online SPE RT[b]	Online LOD[c]	Fragment[d]		Internal Standard
								Mass	Formula	
1	10,11-dihydrocarbamazepine	238.1101	Positive	7.02	1	12.52	5	194.0967	C14H12N	Carbamazepine
2	2-aminobenzimidazole	133.0635	Positive	2.67	5	8.26	100	92.0498	C6H6N	Iopromid
3	2-ethyl-2-phenyl malonamide monohydrate	206.1055	Positive	3.35	25	9	100	119.0856	C9H11	Iopromid
4	2-mercaptobenzothiazole	166.9858	Positive	6.1	1	11.6	5	135.0138	C7H5NS	Carbofuran
5	2-methyl-4-isothiazolin-3-one (MI)	115.0086	Positive	1.57	1	7.1	500	88.076	C3H6NS	2-methylisothiazolinon-3-one
6	2,4-D	219.9689	Negative	8.1	5	13.74	25	160.9556	C6H3OCl2	Mecoprop
7	2,6-dichlorobenzamide	188.9748	Positive	3.5	5	9.1	100	172.9557	C7H3OCl2	Dimethoate
8	2,6-dimethoxyphenol	154.0630	Positive	4.7	50	10.45	NA	95.0494	C6H7O	Erythromycin
9	6-benzylaminopurine	225.1009	Positive	4.6	1	10.25	10	148.0620	C6H6N5	Dimethoate
10	Abacavir	286.1542	Positive	3.35	5	8.88	5	191.1041	C8H11N6	Sulfamethoxazole
11	Abscisic Acid	264.1356	Positive	6.13	1	11.4	100	187.1120	C13H15O	Carbofuran
12	Acebutolol HCl	336.2044	Positive	4.4	1	9.65	5	319.2014	C18H27O3N2	Atenolol
13	Acephate	183.0114	Positive	2.1	5	7.55	1000	142.9928	C2H8O3PS	Acetaminophen
14	Acesulfame K	200.9493	Negative	1.7	5	7.3	1500	82.0285	C4H4ON	Mecoprop
15	Acetaminophen	151.0628	Positive	2.3	5	7.95	250	110.0602	C6H8ON	Acetaminophen
16	Acetamiprid	222.0667	Positive	4.45	5	10.07	50	144.0212	C4H5N4Cl	Dimethoate
17	Acetazolamide	221.9876	Positive	2.56	5	8.01	NA	181.9690	C2H4O3N3S2	Iopromid

18	Acetochlor	269.1177	Positive	10.3	5	15.9	10	162.1278	C11H16N	Celecoxib
19	Adrenalone HCl	181.0734	Positive	1.1	25	6.4	1000	146.0601	C9H8ON	Metformin
20	Adrenosterone	300.1725	Positive	6.55	1	11.97	10	257.1536	C17H21O2	Carbofuran
21	Alachlor	269.1177	Positive	10.3	5	15.9	10	162.1278	C11H16N	Celecoxib
22	Albuterol	239.1521	Positive	2.18	1	7.68	100	148.0758	C9H10ON	Iopromid
23	Amicinonide	502.2361	Positive	11.9	5	17.32	10	321.1486	C21H21O3	Ibuprofen_Na
24	Amisulpride	369.1717	Positive	3.21	1	8.71	25	242.0483	C10H12O4NS	Metoprolol Acid
25	Amitriptyline HCl	277.1830	Positive	7.75	1	12.97	5	233.1325	C18H17	Fluoxetine
26	Amphetamine	135.1048	Positive	3.3	5	8.84	50	91.0545	C7H7	Venlafaxine
27	Ampicillin	349.1091	Positive	4.17	25	9.69	50	192.0477	C10H10ONS	Pirimicarb
28	Arecoline HBr	155.0941	Positive	1.22	5	6.46	750	81.0340	C5H5O	Metformin
29	Atenolol	266.1625	Positive	2.3	1	7.68	50	190.0863	C11H12O2N	Atenolol
30	Atenolol Acid	267.1471	Positive	3.3	5	8.8	10	191.0705	C11H11O3	Metoprolol Acid
31	Atomexine HCl	255.1618	Positive	7.05	1	12.36	10	224.0840	C15H14ON	Atrazine
32	Atrazin-2-Hydroxy	197.1271	Positive	3.8	1	9.32	5	156.0882	C5H10ON5	Sulfamethoxazole
33	Atrazin-desethyl	187.0619	Positive	4.8	1	10.58	5	146.0229	C3H5N5Cl	Dimethoate
34	Atrazine	215.0932	Positive	7.3	1	12.79	0.5	174.0542	C5H9N5Cl	Atrazine
35	Atrazine-desethyl-desisopropyl	145.0155	Positive	1.7	25	7.7	NA	104.0011	C2H3N3Cl	Metformin
36	Atropine	289.1673	Positive	3.72	1	9.24	5	260.1645	C16H22O2N	Sulfamethoxazole
37	Azoxystrobin	403.1163	Positive	8.7	1	14.17	5	372.0980	C21H14O4N3	Azoxystrobin
38	Baclofen	213.0551	Positive	3.5	5	9.12	50	151.0311	C9H8Cl	Thiabendazole

39	Bendiocarb	223.0839	Positive	6.17	5	11.68	10	167.0703	C9H11O3	Tris (2-chloro-ethyl) phosphate
40	Bentazon	240.0563	Negative	6.6	5	12.12	5	175.0867	C10H11ON2	Triclosan
41	Benzisothiazolin-3-on (BIT)	151.0086	Positive	4.4	5	10.1	10	109.0108	C6H5S	Dimethoate
42	Benzotriazole	119.0478	Positive	3.9	1	9.58	10	92.0497	C6H6N	Sulfamethoxazole
43	Benzotriazole-methyl-1H	133.0635	Positive	5.1	1	10.7	5	106.0652	C7H8N	Fexofenadine
44	Benzoylecgonine	289.1309	Positive	4	1	9.58	0.5	168.1020	C9H14O2N	Imidacloprid
45	Bis(2-ehtylhexyl) phthalate	390.2770	Positive	18.3	1	24.06	NA	313.2050	C24H25	Celecoxib
46	Bromacil	260.0155	Positive	6.1	25	11.66	10	204.9610	C5H6O2N2Br	Erythromycin
47	Caffeine	194.0798	Positive	3.4	25	9.04	100	138.0664	C6H8ON3	Caffeine
48	Candesartan	440.1592	Positive	8.15	1	13.63	5	263.1292	C16H15N4	Fluoxetine
49	Carbamazepine	236.0944	Positive	6.6	1	12.12	5	194.0966	C14H12N	Carbamazepine
50	Carbendazim	191.0690	Positive	3.06	1	8.62	10	160.0507	C8H6ON3	Iopromid
51	Carbofuran	221.1057	Positive	6.05	25	11.61	10	165.0912	C10H13O2	Carbofuran
52	Carisoprodol	260.1736	Positive	7.6	5	13.07	25	158.1176	C8H16O2N	Atrazine
53	Celecoxib	381.0759	Positive	10.85	5	16.36	10	362.0769	C17H14O2M3F2S	Celecoxib
54	Chloridazon	221.0350	Positive	4.5	1	10.23	10	128.9851	C4H2ON2Cl	Imidacloprid
55	Cimetidine	252.1157	Positive	2.3	5	7.83	100	159.0700	C5H11N4S	Cimetidine
56	Ciprofloxacin	331.1327	Positive	3.78	5	9.2	NA	288.1506	C18H19ON3F	Sulfamethoxazole
57	cis-diltiazem	414.1613	Positive	6.4	1	11.69	5	310.1695	C14H19O2N2PS	Diltiazem
58	Citalopram HBr	324.1638	Positive	5.9	1	11.19	5	262.1026	C18H13NF	Citalopram
59	Clarithromycin	747.4764	Positive	8.75	5	13.93	25	590.3900	C30H56O10N	Azoxystrobin

60	Climbazole	292.0973	Positive	7	1	12.39	5	197.0730	C11H14OCl	Atrazine
61	Clofibric Acid	214.0391	Negative	8.9	5	14.4	10	126.9944	C6H4OCl	Mecoprop
62	Codeine	299.1521	Positive	2.52	1	8	100	215.1068	C14H15O2	Iopromid
63	Corticosterone	346.2139	Positive	8.2	5	13.43	5	329.2113	C21H29O3	Azoxystrobin
64	Cotinine	176.0950	Positive	1.2	1	6.5	750	146.0602	C9H8ON	Metformin
65	Coumarin	146.0363	Positive	4.92	25	10.65	5	91.0545	C7H7	Sulfadimethoxine
66	Cyanazine	240.0885	Positive	5.67	25	11.1	25	214.0855	C8H13N5Cl	Venlafaxine
67	Cyflufenamid	412.1205	Positive	12.2	5	17.72	10	241.0396	C16H5ON2	Ibuprofen_Na
68	DEET	191.1305	Positive	7.5	1	12.9	0.5	119.0492	C8H7O	Fexofenadine
69	Dehydroacetic Acid	168.0417	Positive	5.03	1	10.8	50	106.9436	C6H3O2	Venlafaxine
70	Desvenlafaxine	263.1880	Positive	4.24	1	9.7	10	201.1278	C14H17O	Sulfamethoxazole
71	Dexamethasone	392.1999	Positive	8	5	13.42	5	237.1278	C17H17O	Carbofuran
72	Dextromethorphan HBr	271.1936	Positive	5.8	1	11.13	5	215.1432	C15H19O	Dextromethorphan
73	Diclofenac	295.0161	Positive	11.5	25	16.99	10	215.0498	C13H10NCl	Diclofenac
74	Diethyl Phthalate	222.0887	Positive	7.72	1	13.2	25	149.0234	C8H5O3	Isoproturon
75	Dimethachlor	255.1021	Positive	7.92	1	13.41	5	224.0838	C12H15ONCl	Isoproturon
76	Dimethoate	229.0002	Positive	4.5	1	10.19	10	142.9928	C2H8O3PS	Dimethoate
77	Diphenhydramine HCl	255.1623	Positive	5.95	1	11.26	5	167.0857	C13H11	Citalopram
78	Diuron	232.0165	Positive	7.9	5	13.44	10	159.9717	C6H4NCl2	Isoproturon
79	Efavirenz	315.0274	Positive	11.5	25	16.99	10	244.0137	C11H6NClF3	Efavirenz
80	Estrone	270.1620	Positive	5.8	25	14.57	100	157.0648	C11H9O	Estrone

81	Ethofumesate	286.0869	Positive	8.9	5	14.33	10	161.0598	C10H9O2	Azoxystrobin
82	Ethyl butylacetyl amnopropionate	215.1521	Positive	6.6	5	12	NA	128.1069	C7H14ON	Atrazine
83	Famciclovir	321.1432	Positive	3.6	5	8.97	10	202.1088	C10H12N5	Thiabendazole
84	Famotidine	337.0449	Positive	2.3	25	7.77	100	189.0264	C5H9N4S2	Acetaminophen
85	Fexofenadine HCl	501.2879	Positive	7.35	1	12.62	5	484.2849	C32H38O3N	Fexofenadine
86	Fluconazole	306.1035	Positive	4.5	1	10.07	5	220.0681	C11H8N3F2	Dimethoate
87	Fluoxetine HCl	309.1335	Positive	8.35	5	13.54	5	265.1587	C16H19OF2	Fluoxetine
88	Folic Acid	441.1391	Positive	3.3	25	8.8	100	295.0939	C14H11O2N6	Metoprolol Acid
89	Furosemide	330.0072	Negative	5.7	25	11.2	25	204.9838	C6H6O2N2ClS	Sucralose
90	Gabapentin	171.1254	Positive	3.23	1	8.76	25	137.0963	C9H13O	Metoprolol Acid
91	Gemfibrozil	250.1563	Positive	13.5	5	18.9	25	83.0859	C6H11	Gemfibrozil
92	Gibberellic Acid	346.1411	Negative	4.55	25	10.4	100	221.1333	C17H17	Sucralose
93	Hexamethyl-phosphoramide	179.1182	Positive	4.67	1	10.18	5	135.0683	C4H12ON2P	Dimethoate
94	Hexazinone	252.1581	Positive	6.1	5	11.59	5	171.0877	C6H11O2N4	Carbofuran
95	Hydrochlorothiazide	296.9634	Positive	2.33	50	7.9	NA	232.9782	C7H6O3N2ClS	Atenolol
96	Hydrocodone	299.1521	Positive	2.84	5	8.36	50	199.0754	C13H11O2	Ranitidine
97	Hydrocortisone	362.2093	Positive	7	5	12.38	10	327.1948	C21H27O3	Carbaryl
98	Ibuprofen	206.1301	Positive	11.9	25	17.4	10	181.9883	C11H4O2N	Ibuprofen_Na
99	Imidacloprid	255.0523	Positive	4	5	9.69	10	175.0980	C9H11N4	Imidacloprid
100	Iodocarb	280.9907	Positive	7.4	1	12.85	500	164.9199	C3H2I	Iodocarb
101	Iopromide	790.8692	Positive	2.45	50	7.97	NA	572.9014	C15H15O6N2I2	Iopromid

102	Ioxynil	370.8299	Negative	8.3	1	13.91	5	230.9186	C6H2ONI	Mecoprop
103	Irbesartan	428.2319	Positive	7.9	1	13.41	5	386.2226	C25H28ON3	Isoproturon
104	Isophorone Diisocyanate	222.1368	Positive	7.02	5	12.5	100	204.9605	C10O2NK	Erythromycin
105	Isoproturon	206.1414	Positive	7.7	1	13.13	5	134.0965	C9H12N	Isoproturon
106	Ketamine HCl	237.0915	Positive	3.9	1	9.47	5	179.0623	C11H12Cl	Sulfamethoxazole
107	Ketoprofen	254.0937	Positive	8.45	1	13.91	10	209.0962	C15H13O	Carbofuran
108	Lamotrigine	255.0073	Positive	4.66	1	10.19	5	210.9825	C9H5N2Cl2	Dimethoate
109	Levetiracetam	170.1050	Positive	2.75	1	8.33	NA	126.0914	C7H12ON	Iopromid
110	Lidocaine	234.1732	Positive	3.7	1	9.29	10	163.0282	C11H3N2	Iopromid
111	Linuron	248.0114	Positive	8.9	5	14.43	5	159.9717	C6H4NCl2	Isoproturon
112	Losartan Potassium	422.1616	Positive	7.9	1	13.35	5	235.0978	C14H11N4	Isoproturon
113	Mabuterol HCl	310.1054	Positive	4.7	1	10.1	5	237.0403	C9H9N2ClF3	Dimethoate
114	MCPA	200.0235	Negative	8.5	5	14.02	10	141.0099	C7H6OCl	Mecoprop
115	Mecoprop	214.0391	Negative	9.7	5	15.22	10	141.0101	C7H6OCl	Mecoprop
116	Meprobamate	218.1267	Positive	5.4	5	10.89	25	203.1429	C9H19O3N2	Erythromycin
117	Metalaxyl	279.1465	Positive	7.6	1	13	5	160.1122	C11H14N	Isoproturon
118	Metamitron	202.0860	Positive	4.3	5	10.01	10	175.0985	C9H11N4	Imidacloprid
119	Metaxalone	221.1057	Positive	7.05	1	12.57	5	133.1013	C10H13	Atrazine
120	Metformin	129.1014	Positive	1.1	25	6.23	NA	71.0609	C3H7N2	Metformin
121	Methadone	309.2093	Positive	7.45	1	12.69	5	265.1587	C19H21O	Fluoxetine
122	Methocarbamol	241.0950	Positive	4.7	5	10.23	10	163.0755	C10H11O2	Erythromycin

123	Methomyl	162.0463	Positive	3.15	5	8.73	250	102.9699	C2HO2NS	Thiabendazole
124	Metolachlor	283.1334	Positive	10.5	1	16	1	252.1151	C14H19ONCl	Azoxystrobin
125	Metolachlor-ESA	329.1292	Positive	6.64	1	12.3	10	298.1107	C14H20O4NS	Carbamazepine
126	Metoprolol	267.1829	Positive	4.5	1	9.75	5	159.0806	C11H11O	Metoprolol Acid
127	Metribuzin	214.0883	Positive	6	1	11.62	5	187.1011	C7H15N4S	Carbamazepine
128	Metsulfuron-methyl	381.0738	Positive	6.1	25	11.59	NA	167.0565	C6H7O2N4	Carbofuran
129	Molinate	187.1031	Positive	9.55	5	14.98	5	126.0914	C7H12ON	Oxybenzone
130	Morphine	285.1359	Positive	1.56	5	7.06	250	201.0911	C13H13O2	Morphine
131	N,N-didesmethylvenlafaxine	249.1724	Positive	5.52	1	10.87	5	147.0805	C10H11O	Venlafaxine
132	N4-acetylsulfamethoxazole	295.0622	Positive	4.8	1	10.19	5	198.0221	C8H8O3NS	Sulfamethoxazole
133	Nadolol	309.1935	Positive	3.55	1	9	5	254.1388	C13H20O4N	Iopromid
134	Naproxen	230.0937	Positive	9	1	14.44	10	185.0963	C13H13O	Naproxen
135	Nicotine	162.1157	Positive	1.11	5	6.23	NA	102.9704	C6H3N2	Metformin
136	Norfloxacin	319.1327	Positive	3.7	5	9.2	NA	276.1507	C15H19ON3F	Thiabendazole
137	Ofloxacin	361.1433	Positive	3.53	5	9.02	NA	318.1613	C17H21O2N3F	Thiabendazole
138	Oxazepam	286.0504	Positive	7.8	5	13.3	50	241.0528	C14H10N2Cl	Isoproturon
139	Oxcarbazepine	252.0899	Positive	5.7	1	11.18	5	208.0749	C14H10ON	Carbamazepine
140	Oxybenzone	228.0786	Positive	10.95	1	16.33	5	151.0391	C8H7O3	Oxybenzone
141	Paraxanthine	180.0647	Positive	2.8	5	8.4	50	124.0507	C5H6ON3	Acetaminophen
142	Penciclovir	253.1170	Positive	1.32	25	6.78	2000	152.0568	C5H6ON5	Allopurinol
143	Pentoxyfylline	278.1379	Positive	4.7	1	10.12	5	181.0722	C7H9O2N4	Carbofuran

144	Perfluoroctanoic acid (PFOA)	413.9743	Negative	11.2	1	17	5	218.9857	C4F9	Triclosan
145	Phenobarbital	232.0848	Negative	5.25	5	10.82	100	160.0843	C6H12O3N2	Sucralose
146	Phenytoin (Dilantin)	252.0899	Positive	6.5	5	11.95	10	182.0966	C13H12N	Carbofuran
147	Pirimicarb	238.1430	Positive	4.1	1	9.69	1	182.1289	C9H16ON3	Pirimicarb
148	Pirimiphos-Ethyl	333.1271	Positive	12.9	1	18.54	5	198.1062	C9H16N3S	Efavirenz
149	Primidone	218.1050	Positive	4.6	5	10.3	10	162.0915	C10H12ON	Erythromycin
150	Progesterone	314.2246	Positive	11.6	5	16.92	10	297.2211	C21H29O3	Efavirenz
151	Prohexadione Ca	462.0833	Negative	5.45	5	11.07	10	111.0438	C6H7O2	Sucralose
152	Prometon	225.1584	Positive	5.8	1	11.2	0.1	142.0725	C4H8ON5	Carbaryl
153	Propachlor	211.0758	Positive	7.5	1	13	0.5	170.0368	C8H9ONCl	Fexofenadine
154	Propachlor ESA	257.0716	Negative	4.7	5	10.43	25	162.0220	C5H8O3NS	Mecoprop
155	Propachlor OXA	207.0890	Positive	4.8	5	10.54	10	120.0444	C7H6ON	Carbofuran
156	Propazine	229.1089	Positive	8.64	1	14.18	0.5	146.0229	C3H5N5Cl	Azoxystrobin
157	Propoxur	209.1047	Positive	6	25	11.55	5	111.0441	C6H7O2	Carbaryl
158	Propranolol HCl	259.1572	Positive	6.16	1	11.15	5	183.0806	C13H11O	Erythromycin
159	Propyzamide	255.0218	Positive	9.6	1	15.08	5	172.9557	C7H3OCl2	Isoproturon
160	Pseudoephedrine	165.2345	Positive	2.8	1	8.35	50	133.0887	C9H11N	Iopromid
161	Pyrazophos	373.0856	Positive	12.1	1	17.61	10	222.0875	C10H12O3N3	Ibuprofen_Na
162	Ranitidine HCl	314.1407	Positive	2.2	5	7.74	250	176.0490	C5H10O2N3S	Ranitidine
163	Ritalinic Acid	219.1254	Positive	4.05	1	9.6	5	174.1278	C12H16N	Imidacloprid
164	Serotonin HCl	176.0944	Positive	1.75	5	7.16	750	146.0602	C9H8ON	Morphine

165	Siduron	232.1576	Positive	8.9	5	14.39	5	137.0711	C7H9ON2	Celecoxib
166	Simazine	201.0776	Positive	6	1	11.56	5	132.0324	C4H7N3Cl	Atrazine
167	Sitagliptin	407.1181	Positive	4.55	5	9.98	5	235.0802	C8H10ON4F3	Erythromycin
168	Sucralose	396.0146	Negative	3.9	5	9.5	100	278.1482	C11H18O8	Sucralose
169	Sulfadimethoxine	310.0730	Positive	4.9	1	10.41	5	237.0401	C12H5O2N4	Sulfadimethoxine
170	Sulfamethazine	278.0832	Positive	3.27	5	8.91	10	204.0440	C12H4N4	Caffeine
171	Sulfamethoxazole	253.0516	Positive	3.9	1	9.56	10	156.0114	C6H6O2NS	Sulfamethoxazole
172	Sulfathiazole	255.0131	Positive	2.6	25	8.16	250	156.0114	C6H6O2NS	Sulfadimethoxine
173	TDCPP	427.8834	Positive	11.9	1	17.34	100	98.9843	CH4O3Cl	Tris (2-chloro-ethyl) phosphate
174	Temazepam	300.0660	Positive	8.1	1	13.59	25	255.0684	C15H12N2Cl	Isoproturon
175	Terbutylazine	229.1089	Positive	9	1	14.46	0.5	174.0543	C5H9N5Cl	Celecoxib
176	Testosterone	288.2089	Positive	9.6	1	14.95	10	253.1953	C19H25	Isoproturon
177	Theophylline	180.0647	Positive	2.92	5	8.4	50	124.0507	C5H6ON3	Imidacloprid
178	Thiabendazole	201.0355	Positive	3.45	1	9.11	5	175.0326	C9H7N2S	Thiabendazole
179	Tramadol	263.1885	Positive	4.2	1	9.7	10	201.1278	C14H17O	Sulfamethoxazole
180	Triamterene	253.1076	Positive	4	1	9.49	5	237.0884	C9H8ON5Cl	Imidacloprid
181	Tributyl phosphate (TBP)	266.1647	Positive	13.1	1	18.5	10	155.0468	C4H12O4P	Gemfibrozil
182	Triclosan	287.9506	Negative	13.5	50	18.96	50	165.8927	C5HCl3	Triclosan
183	Trimethoprim	290.1373	Positive	3.4	1	8.83	5	245.1035	C12H13O2N4	Trimethoprim
184	Trinexapac-ethyl	252.0992	Positive	7.9	1	13.33	5	183.0290	C8H7O5	Isoproturon
185	Tris (2-chloro-ethyl) phosphate (TCEP)	283.9539	Positive	6.3	5	11.8	5	160.9766	C2H7O4ClP	Tris (2-chloro-ethyl) phosphate

186	Valsartan	435.2270	Positive	9.7	1	15.19	10	235.0985	C14H11N4	Isoproturon
187	Venlafaxine HCl	277.2036	Positive	5.5	1	10.76	10	215.1431	15H19O	Venlafaxine
188	Verapamil HCl	454.2832	Positive	6.4	1	11.67	50	303.2066	C18H27O2N2	Citalopram
189	Warfarin	308.1043	Positive	9.5	1	14.86	5	251.0705	C16H11O3	Fexofenadine

a. The major ionization mode of compounds after electrospray ionization (ESI);
b. "RT" stands for retention time, unit in minutes;
c. Units in ng L^{-1}; "NA" stands for Not Available; reported LODs are direct inject concentration;
d. "Fragment" means most intense fragment used for LOD determination.

Appendix C - Experimental Data for Targeted Compounds

Table C1. Base case absolute recovery rates obtained using HLB and P-CDP.

No.[a]	180 mg HLB AbsRec (%)[b]	Measured HLB Min AbsRec (%)	Measured HLB Max AbsRec (%)	Reported HLB AbsRec (%)[c]	180mg P-CDP AbsRec (%)[b]	Measured P-CDP Min AbsRec (%)	Measured P-CDP Max AbsRec (%)
1	117.0	115.1	118.1	109	53.4	52.7	53.9
2	58.8	57.4	61.3	58	0.1	0.0	0.2
3	69.1	68.8	69.4		5.1	4.8	5.3
4	13.4	10.2	18.1		90.9	82.5	98.7
5	1.8	1.6	2.0	25	1.3	0.8	1.6
6	81.1	76.5	89.2	90	1.0	0.8	1.2
7	94.3	91.7	98.5	93	24.4	23.0	25.7
8	111.4	106.6	119.7		122.5	116.1	130.0
9	104.8	101.5	108.7		95.2	85.4	100.9
10	79.2	75.2	85.7		14.3	12.4	17.7
11	90.2	84.8	95.0		1.0	0.7	1.4
12	80.4	74.1	86.3		0.1	0.0	0.1
13	3.7	2.9	4.1		0.4	0.2	0.5
14	1.1	1.0	1.1		0.0	0.0	0.0
15	24.7	23.8	26.0		32.1	30.9	33.1
16	98.4	95.1	101.9	97	81.7	78.9	85.8
17	39.8	37.7	41.9	24	36.7	34.8	39.4
18	107.5	104.9	109.4	89	13.9	9.0	19.9
19	0.1	0.0	0.2		0.0	0.0	0.0
20	94.0	91.8	97.7		83.6	77.3	87.2
21	107.5	104.9	109.4	89	13.9	9.0	19.9
22	24.7	24.0	26.1	14	0.2	0.1	0.2
23	60.1	55.7	67.8		98.1	86.8	111.7
24	70.4	68.4	73.1	85	0.0	0.0	0.0

25	19.4	14.3	23.7	83	0.1	0.0	0.1
26	75.6	72.6	78.5	26	0.0	0.0	0.0
27	31.2	20.4	38.5		2.0	0.0	3.2
28	2.8	2.5	3.2		0.0	0.0	0.0
29	49.0	48.1	49.7	35	0.0	0.0	0.0
30	14.6	14.2	15.1	4	1.7	1.2	2.5
31	9.1	6.9	11.7	75	0.1	0.0	0.1
32	74.5	72.5	77.5	93	7.6	5.4	10.9
33	106.4	98.4	111.8	93	44.5	43.6	46.2
34	96.4	94.1	98.2	98	84.8	80.9	88.3
35	1.6	1.5	1.7	93	3.5	2.4	5.0
36	66.7	65.4	69.1		0.0	0.0	0.0
37	96.9	89.3	102.6	91	90.2	89.8	90.7
38	10.7	10.4	11.1		2.8	2.3	3.7
39	102.3	99.8	106.3		61.1	58.4	63.8
40	126.7	125.2	127.5	96	0.1	0.1	0.1
41	96.4	95.6	97.2	87	72.5	66.0	76.3
42	80.8	75.6	85.5	88	34.0	32.9	35.7
43	7.5	7.2	7.7	50	13.2	11.1	15.2
44	93.5	91.8	94.9	93	19.7	19.1	20.2
45	0.9	0.0	2.8		0.5	0.0	1.4
46	106.3	101.6	111.9	91	85.8	70.6	96.7
47	99.3	97.0	101.1		26.2	25.4	26.9
48	101.4	87.1	110.2	96	2.4	1.6	3.0
49	95.8	94.8	97.2	97	72.6	70.1	76.3
50	88.1	85.9	89.6	99	66.0	63.7	70.0
51	94.0	91.5	95.6	91	45.2	45.0	45.4
52	82.3	80.0	85.5		67.5	65.4	69.7
53	98.5	80.6	108.3		92.8	89.2	95.7

54	94.5	91.0	99.5	95	76.6	72.0	82.3
55	48.4	46.1	51.5		0.1	0.1	0.2
56	8.2	5.1	12.0	77	0.0	0.0	0.0
57	94.0	88.3	97.1	85	0.1	0.0	0.2
58	51.5	41.4	60.7	86	0.0	0.0	0.1
59	62.3	52.0	77.3	84	0.7	0.0	1.8
60	86.8	81.8	93.9	95	128.0	123.7	132.8
61	79.9	75.6	82.9	98	0.6	0.4	0.8
62	61.7	55.1	74.3	87	0.0	0.0	0.0
63	99.9	96.0	105.7		65.0	57.2	79.8
64	41.1	35.5	48.2		15.4	14.0	16.8
65	80.7	73.3	89.3		54.9	49.5	60.3
66	111.3	103.1	115.8		126.0	125.4	127.2
67	21.4	7.9	34.9		125.2	120.7	129.8
68	9.5	9.1	9.8	100	11.1	8.6	14.0
69	117.7	103.6	134.9		73.5	65.3	81.1
70	63.7	61.7	65.3	79	0.0	0.0	0.0
71	91.0	87.2	95.2	92	67.1	65.6	68.2
72	96.5	86.7	102.6	79	0.0	0.0	0.0
73	97.0	94.1	102.0	93	19.8	14.7	23.9
74	121.3	111.2	127.7		127.2	122.5	130.8
75	104.1	101.4	107.6	95	65.1	56.0	70.3
76	97.1	95.4	100.3	93	63.3	61.0	65.3
77	119.3	111.4	127.1	88	0.0	0.0	0.0
78	96.5	93.0	98.8	97	99.7	94.9	105.3
79	92.0	86.9	95.6		98.2	95.3	104.0
80	90.3	87.6	95.1		45.5	43.4	49.3
81	96.0	86.1	101.3	90	71.3	65.0	81.5
82	95.2	88.2	102.4		69.7	66.9	75.0

83	105.7	100.6	111.6		75.9	68.9	87.0
84	73.3	65.5	78.8		0.0	0.0	0.0
85	87.1	85.7	87.9	90	1.0	0.7	1.5
86	101.4	96.6	106.2	93	20.8	19.8	21.5
87	85.3	80.1	88.1	71	0.1	0.0	0.3
88	16.3	15.4	17.2		0.0	0.0	0.0
89	96.6	91.0	101.0	87	33.2	24.9	43.6
90	1.3	1.2	1.4	1	1.6	1.3	1.8
91	90.8	88.0	93.6		57.2	51.6	63.4
92	12.7	11.5	13.8		0.1	0.1	0.2
93	79.7	72.9	86.3		1.0	1.0	1.1
94	95.1	93.2	97.2	90	73.0	69.3	77.8
95	95.1	90.6	103.8	97	79.2	70.9	83.5
96	84.3	74.7	102.8		0.0	0.0	0.0
97	104.2	101.0	110.0		53.0	48.4	57.9
98	94.2	91.0	98.0	102	13.1	9.0	16.3
99	93.9	90.8	96.7	98	73.9	71.2	75.4
100	80.8	71.5	91.0	94	89.1	80.6	93.9
101	101.0	94.4	106.7	88	0.0	0.0	0.0
102	98.4	88.3	104.1	98	28.1	27.5	29.0
103	99.4	95.3	103.2	93	124.3	120.0	128.9
104	123.4	119.1	127.2	97	68.6	62.9	73.0
105	92.0	89.6	93.4	91	97.6	95.6	100.2
106	62.8	62.5	63.4	101	0.1	0.1	0.1
107	124.2	121.9	126.2	96	21.7	15.2	25.8
108	103.5	101.9	106.5	92	2.3	1.7	3.1
109	9.6	9.0	10.0	5	0.7	0.7	0.8
110	82.9	75.8	88.8	93	0.3	0.3	0.3
111	98.3	94.7	102.7	98	114.6	101.4	127.2

112	123.9	122.0	125.0	75	82.4	70.3	91.8
113	62.8	57.4	72.4		0.1	0.0	0.2
114	82.3	75.0	92.2	97	1.3	0.9	1.6
115	91.3	90.7	92.0		0.7	0.4	0.9
116	99.6	92.3	105.3		57.9	51.1	68.5
117	100.1	96.4	105.8	92	49.1	44.0	52.3
118	97.3	89.1	103.4	93	63.5	60.4	68.2
119	98.7	95.5	100.9		96.5	91.0	104.9
120	0.0	0.0	0.1		0.0	0.0	0.0
121	2.4	0.4	3.6	88	0.0	0.0	0.0
122	98.9	92.5	105.8	89	112.9	99.7	126.3
123	83.9	76.8	87.6	66	32.4	29.6	37.6
124	106.2	103.0	108.3	94	69.3	64.5	76.5
125	96.5	92.8	99.4	99	0.0	0.0	0.0
126	67.6	63.9	73.1	90	0.0	0.0	0.0
127	119.2	112.1	127.0	90	91.2	86.0	94.1
128	106.0	101.8	112.4	91	0.0	0.0	0.0
129	115.4	104.4	121.4		40.6	34.5	48.5
130	65.2	62.6	67.4	77	0.0	0.0	0.0
131	73.9	60.5	83.4	27	0.0	0.0	0.0
132	80.9	76.7	85.2	97	10.6	8.1	13.3
133	94.7	86.8	99.4		0.0	0.0	0.0
134	102.6	98.2	110.4	91	36.5	29.0	44.7
135	9.4	6.3	13.4		0.0	0.0	0.0
136	9.9	6.4	13.1	78	0.0	0.0	0.0
137	20.7	12.4	31.2		0.0	0.0	0.0
138	96.0	93.8	97.1	92	70.4	69.1	71.2
139	128.9	127.0	129.9	79	83.2	79.8	87.3
140	110.5	95.4	118.4	84	54.2	49.6	62.7

141	52.0	49.9	55.1		18.1	16.6	18.9
142	3.6	3.3	3.9		6.1	5.5	6.5
143	90.1	89.3	90.6		55.9	54.1	59.0
144	10.4	8.7	13.4		0.6	0.3	0.9
145	101.9	97.0	107.8		30.4	27.4	36.0
146	84.9	83.2	86.4		62.1	56.5	65.0
147	94.8	91.7	99.5	95	87.4	86.0	89.9
148	19.1	16.3	24.4		48.3	44.0	53.0
149	110.2	103.5	117.0	96	32.6	25.2	37.5
150	130.5	127.3	132.9		111.4	102.7	119.5
151	49.7	45.4	53.2		0.3	0.2	0.3
152	91.5	89.1	94.4	90	68.6	66.8	70.1
153	9.4	9.2	9.6	97	11.6	9.4	14.4
154	30.3	26.0	32.7	31	0.0	0.0	0.0
155	4.4	4.3	4.6	4	0.0	0.0	0.0
156	94.9	92.3	96.9	90	58.2	47.4	66.0
157	109.5	106.0	112.3		56.3	51.2	62.4
158	48.3	46.6	51.6	97	0.1	0.0	0.1
159	105.0	96.9	109.8		99.6	98.3	100.7
160	78.4	75.7	82.3		0.1	0.0	0.1
161	17.3	9.7	26.5		76.8	70.3	81.3
162	72.2	71.5	73.3	55	0.0	0.0	0.0
163	32.6	32.3	33.0	17	2.6	2.4	2.8
164	35.7	32.0	37.6		2.3	0.0	6.8
165	116.6	108.4	127.1		14.6	10.5	20.3
166	96.1	85.3	106.0	93	95.0	89.9	98.1
167	111.1	109.1	114.3	45	0.0	0.0	0.0
168	84.1	82.9	85.6	75	0.8	0.6	1.1
169	93.3	90.0	97.2	99	70.1	65.7	77.6

170	128.0	122.0	137.3	94	79.2	77.4	81.3
171	98.4	95.3	101.6	97	34.6	29.0	39.9
172	94.0	84.7	99.3	101	36.4	29.8	42.3
173	104.5	101.5	109.1		122.7	119.4	124.8
174	109.4	106.9	112.9		86.8	81.4	91.8
175	114.3	104.3	124.2	100	14.0	9.8	19.9
176	103.2	101.0	106.0		117.9	112.6	122.9
177	50.0	46.8	52.2		14.3	12.9	16.4
178	94.2	89.9	96.6		27.4	23.9	33.5
179	63.7	61.7	65.3	100	0.0	0.0	0.0
180	57.5	53.3	65.5		0.0	0.0	0.0
181	26.9	25.1	28.0		18.3	16.5	20.0
182	63.2	60.8	65.8	89	72.5	71.5	73.8
183	75.6	64.2	97.3	99	0.6	0.0	1.6
184	122.3	112.4	133.1	98	16.2	14.1	19.0
185	93.8	90.0	96.9		61.2	58.6	65.3
186	125.8	119.4	132.2	91	1.5	0.5	2.0
187	98.9	96.4	101.1	92	0.0	0.0	0.0
188	0.4	0.0	1.1	87	0.4	0.2	0.8
189	12.3	11.5	13.0		12.0	10.5	13.1

a. No. refers each targeted compound in Table B;
b. all SD value in this table were calculated from three replicates; value in red means SD is greater than 10%;
c. all data reported are obtained from the previous study with 200 mg HLB as adsorbent (Vogler, 2013); value in blue means the difference between reported data and measure data is above 20

Table C2. Base case absolute capture rates obtained using HLB and P-CDP.

Compound Name	HLB[a] AbsCap (%)	HLB[b] R/C Ratio	P-CDP[a] AbsCap (%)	P-CDP[b] R/C Ratio
10,11-dihydrocarbamazepine	93.4 ± 9.8	1.25	65.7 ± 10.7	0.81
2-aminobenzimidazole	95 ± 7.9	0.62	99.7 ± 0.6	0.00
2-mercaptobenzothiazole	100 ± 0	0.13	98.2 ± 2.8	0.93
2,4-D	96.4 ± 5	0.84	18.5 ± 8.3	0.05
6-benzylaminopurine	100 ± 0	1.05	99.4 ± 0.6	0.96
Abacavir	94.9 ± 7.5	0.83	99.7 ± 0.3	0.14
Abscisic Acid	85.3 ± 8.5	1.06	9.4 ± 7.1	0.11
Acebutolol HCl	100 ± 0	0.80	100 ± 0	0.00
Acetamiprid	99.8 ± 0.6	0.99	87.9 ± 7.6	0.93
Acetochlor	100 ± 0	1.29	90.6 ± 5.3	0.15
Adrenosterone	97 ± 5.1	0.97	94.6 ± 3.9	0.88
Alachlor	100 ± 0	1.29	90.6 ± 5.3	0.15
Albuterol	19.6 ± 6.4	1.26	100 ± 0	0.00
Amicinonide	96.3 ± 9.2	0.62	99.8 ± 0.5	0.98
Amisulpride	100 ± 0	0.70	100 ± 0	0.00
Amitriptyline HCl	100 ± 0	0.19	100 ± 0	0.00
Amphetamine	89.8 ± 8.9	0.84	100 ± 0	0.00
Ampicillin	41.1 ± 13.3	0.76	11.3 ± 8.4	0.18
Atenolol	80 ± 14.5	0.61	100 ± 0	0.00
Atenolol Acid	23.9 ± 7.3	0.61	85.3 ± 7	0.02
Atomexine HCl	100 ± 0	0.09	100 ± 0	0.00
Atrazin-2-Hydroxy	95.5 ± 7.5	0.78	99.8 ± 0.3	0.08
Atrazin-desethyl	95.2 ± 9.6	1.12	48.6 ± 6.1	0.92
Atrazine	98 ± 3.4	0.98	78.8 ± 6.2	1.08
Atropine	100 ± 0	0.67	100 ± 0	0.00
Azoxystrobin	95.2 ± 6.6	1.02	99.4 ± 0.5	0.91
Baclofen	11.6 ± 5.5	0.93	14.6 ± 6.5	0.19
Bendiocarb	100 ± 0	1.02	67.1 ± 6.3	0.91
Bentazon	88.5 ± 6.4	1.36	33.6 ± 13.5	0.00
Benzisothiazolin-3-on (BIT)	94.4 ± 7.4	1.02	77.3 ± 8	0.94
Benzotriazole	83.3 ± 14.5	0.97	66.5 ± 17	0.51
Benzotriazole-methyl-1H	95.3 ± 6.4	0.08	92.9 ± 4.5	0.14
Benzoylecgonine	84.1 ± 11.8	1.11	24.4 ± 4	0.81
Bromacil	92.2 ± 5.1	1.32	63 ± 6.5	2.00

Caffeine	95 ± 6.1	1.05	51.8 ± 14.8	0.51
Candesartan	100 ± 0	1.20	3.5 ± 2.8	0.68
Carbamazepine	90.4 ± 10.6	1.06	73 ± 8.2	1.00
Carbendazim	82.2 ± 6.4	1.07	98.7 ± 0.6	0.67
Carbofuran	100 ± 0	0.94	52.2 ± 8.1	0.87
Carisoprodol	89.9 ± 5.9	0.91	63 ± 8.2	1.07
Celecoxib	100 ± 0	0.99	8.1 ± 3.2	11.45
Chloridazon	100 ± 0	0.94	90.6 ± 6.6	0.84
Cimetidine	100 ± 0	0.48	100 ± 0	0.00
cis-diltiazem	100 ± 0	0.94	100 ± 0	0.00
Citalopram HBr	100 ± 0	0.52	100 ± 0	0.00
Clarithromycin	100 ± 0	0.62	99.6 ± 1.2	0.01
Climbazole	98.1 ± 3.4	0.89	99.9 ± 0.2	1.28
Clofibric Acid	94.9 ± 6.1	0.84	4.5 ± 3.5	0.14
Codeine	100 ± 0	0.62	100 ± 0	0.00
Corticosterone	99.7 ± 0.6	1.00	92.8 ± 4.6	0.70
Coumarin	96.7 ± 3.7	0.84	93.1 ± 4.4	0.59
Cyanazine	100 ± 0	1.23	87.5 ± 9.9	1.44
Cyflufenamid	100 ± 0	0.21	99.8 ± 0.3	1.22
DEET	96.1 ± 5.5	0.10	62.5 ± 11.8	0.18
Dehydroacetic Acid	96.8 ± 6.2	1.30	13.3 ± 8.9	5.54
Desvenlafaxine	100 ± 0	0.64	100 ± 0	0.00
Dexamethasone	100 ± 0	0.91	84.9 ± 8.3	0.79
Dextromethorphan HBr	100 ± 0	0.96	100 ± 0	0.00
Diclofenac	100 ± 0	0.97	7.5 ± 3.3	2.63
Diethyl Phthalate	79 ± 10.5	1.54	79.5 ± 10.9	1.60
Dimethachlor	100 ± 0	1.04	67.4 ± 7.2	0.97
Dimethoate	98.4 ± 4	0.99	64.7 ± 10.7	0.98
Diphenhydramine HCl	100 ± 0	0.97	100 ± 0	0.00
Diuron	97.4 ± 4.7	0.99	99.9 ± 0.1	1.00
Efavirenz	98.9 ± 2.6	0.93	99.6 ± 0.4	0.99
Estrone	100 ± 0	0.90	100 ± 0	0.46
Ethofumesate	98.9 ± 2.7	0.97	99.8 ± 0.5	0.71
Famciclovir	86.6 ± 13.8	1.22	96.5 ± 2.4	0.79
Famotidine	100 ± 0	0.73	100 ± 0	0.00
Fexofenadine HCl	100 ± 0	0.87	100 ± 0	0.01

Fluconazole	93.3 ± 6.4	1.09	16.1 ± 7.6	1.29
Fluoxetine HCl	100 ± 0	0.85	100 ± 0	0.00
Folic Acid	18.4 ± 8.1	0.89	4.8 ± 3.2	0.00
Furosemide	96 ± 9.7	0.96	4.1 ± 4.9	8.07
Gabapentin	13.8 ± 2.7	0.10	1.8 ± 2.1	0.88
Gemfibrozil	98.6 ± 1.8	0.92	60.3 ± 9.2	0.95
Gibberellic Acid	100 ± 0	0.13	5.4 ± 6.1	0.03
Hexamethylphosphoramide	58.7 ± 8.4	1.36	6 ± 5.8	0.17
Hexazinone	90.5 ± 6.4	1.05	78.6 ± 9.6	0.93
Hydrocodone	100 ± 0	0.84	100 ± 0	0.00
Hydrocortisone	99.7 ± 0.5	1.04	75.7 ± 7.1	0.70
Ibuprofen	94.3 ± 7.9	1.00	23.3 ± 7.2	0.56
Imidacloprid	90.5 ± 3.3	1.04	86.1 ± 7.5	0.86
Ioxynil	97.2 ± 6	1.01	12.5 ± 8.9	2.24
Irbesartan	93.4 ± 6.1	1.07	68 ± 11.2	1.83
Isophorone Diisocyanate	92.6 ± 4.3	1.27	60.6 ± 6.2	1.90
Isoproturon	91.1 ± 6.6	1.01	98.3 ± 1.1	0.99
Ketamine HCl	99.5 ± 1.1	0.63	100 ± 0	0.00
Ketoprofen	100 ± 0	1.24	3.1 ± 5.1	7.00
Lamotrigine	100 ± 0	1.03	100 ± 0	0.02
Lidocaine	100 ± 0	0.83	100 ± 0	0.00
Linuron	94.1 ± 6.2	1.04	99.9 ± 0.1	1.15
Losartan Potassium	99.3 ± 1.7	1.25	26.8 ± 7.3	3.07
Mabuterol HCl	100 ± 0	0.63	100 ± 0	0.00
MCPA	98.2 ± 3.5	0.84	25.7 ± 10.4	0.05
Mecoprop	91.6 ± 9.9	1.00	5.3 ± 6.3	0.13
Meprobamate	100 ± 0	1.30	29.7 ± 9.3	1.50
Metalaxyl	91.2 ± 5.9	1.10	58 ± 12.7	0.85
Metamitron	92.8 ± 7.7	1.05	95.1 ± 4	0.67
Metaxalone	90.2 ± 5.3	1.09	96.9 ± 2.3	1.00
Methadone	100 ± 0	0.20	100 ± 0	0.00
Methocarbamol	100 ± 0	1.19	74.6 ± 8.4	1.74
Metolachlor	100 ± 0	1.06	87.2 ± 6.4	0.79
Metolachlor-ESA	89.3 ± 8.9	1.08	15.6 ± 6.4	0.00
Metoprolol	100 ± 0	0.68	100 ± 0	0.00
Metribuzin	100 ± 0	1.19	75.4 ± 8.7	1.21

Molinate	100 ± 0	0.96	91.5 ± 5.9	0.44
N,N-didesmethylvenlafaxine	100 ± 0	0.74	100 ± 0	0.00
N4-acetylsulfamethoxazole	100 ± 0	0.81	29.7 ± 9.6	0.36
Nadolol	100 ± 0	0.95	100 ± 0	0.00
Naproxen	99.8 ± 0.4	1.03	50.3 ± 6.3	0.73
Oxazepam	81.8 ± 13.5	1.17	74.9 ± 8.9	0.94
Oxcarbazepine	96.5 ± 3.6	0.86	64.5 ± 11	1.29
Oxybenzone	95.7 ± 5	0.84	99.8 ± 0.8	0.54
Paraxanthine	39.2 ± 8.6	1.33	13.4 ± 7.3	1.20
Pentoxyfylline	84.1 ± 7	1.07	86.7 ± 8.4	0.64
Perfluoroctanoic acid (PFOA)	91.9 ± 8.2	0.11	0 ± 0	0.00
Phenobarbital	86.2 ± 8.2	1.18	43.4 ± 9.9	0.70
Phenytoin (Dilantin)	91.2 ± 1.5	0.93	74.8 ± 5.2	0.83
Pirimicarb	99.1 ± 1.7	0.96	96.6 ± 3	0.90
Pirimiphos-Ethyl	100 ± 0	0.19	100 ± 0	0.48
Primidone	100 ± 0	1.03	22 ± 10.3	2.05
Progesterone	97.5 ± 6.4	1.34	99.9 ± 0.1	1.12
Prohexadione Ca	39.1 ± 8.9	1.27	0.8 ± 0.2	0.35
Prometon	94.1 ± 6.7	0.97	96.4 ± 2.1	0.71
Propachlor	100 ± 0	0.09	66.4 ± 7.8	0.17
Propachlor ESA	80.7 ± 11.3	0.38	7.5 ± 5.9	0.00
Propachlor OXA	83.7 ± 2.8	0.05	5.3 ± 3.4	0.00
Propazine	98.9 ± 1.9	0.96	98.5 ± 4.2	0.59
Propoxur	100 ± 0	1.09	65.2 ± 11.3	0.86
Propranolol HCl	100 ± 0	0.49	100 ± 0	0.00
Propyzamide	100 ± 0	1.05	95.7 ± 2.8	1.04
Pseudoephedrine	58.9 ± 10.6	0.67	100 ± 0	0.00
Pyrazophos	98.3 ± 3	0.28	100 ± 0	0.77
Ritalinic Acid	27.9 ± 4.3	1.17	0.7 ± 1.1	3.94
Siduron	89.2 ± 9.5	1.31	97.5 ± 1.6	0.15
Simazine	99.9 ± 0.2	0.96	75.2 ± 7.2	1.26
Sitagliptin	100 ± 0	1.13	100 ± 0	0.00
Sucralose	84.1 ± 9.3	1.00	1.1 ± 2.5	0.76
Sulfadimethoxine	98.9 ± 2.6	0.94	70.7 ± 8.7	0.99
Sulfamethazine	100 ± 0	1.28	34.5 ± 9.7	2.29
Sulfamethoxazole	100 ± 0	0.98	25 ± 9.4	1.38

TDCPP	89.6 ± 8.3	1.17	98.6 ± 2.5	1.24
Temazepam	99.5 ± 1.1	1.10	84.9 ± 8.4	1.02
Terbutylazine	100 ± 0	1.19	98.5 ± 4.2	0.14
Testosterone	88.4 ± 12.4	1.17	98.1 ± 1.5	1.20
Theophylline	35.7 ± 10.6	1.40	13.4 ± 7.3	1.07
Thiabendazole	96.7 ± 6.5	0.97	100 ± 0	0.27
Tramadol	100 ± 0	0.64	100 ± 0	0.00
Triamterene	100 ± 0	0.57	100 ± 0	0.00
Tributyl phosphate (TBP)	84.8 ± 8.9	0.32	94.1 ± 5.2	0.19
Triclosan	83.3 ± 4.8	0.76	98.3 ± 3.2	0.74
Trimethoprim	99.8 ± 0.4	0.76	99.9 ± 0.3	0.01
Trinexapac-ethyl	98.3 ± 4.1	1.24	17.8 ± 6	0.91
Tris (2-chloro-ethyl) phosphate (TCEP)	95.4 ± 6.6	0.98	68.2 ± 7.1	0.90
Valsartan	100 ± 0	1.23	0.3 ± 0.6	4.99
Venlafaxine HCl	100 ± 0	0.99	100 ± 0	0.00
Verapamil HCl	100 ± 0	0.00	100 ± 0	0.00
Warfarin	97.7 ± 5.6	0.13	43 ± 8.7	0.28

a. all SD data were standard deviations calculated from nine data points from three replicates;
b. R/C ratios were calculated using Equation (3);

Table C3. Improved absolute capture rates obtained using P-CDP.

Compound Name	pH 6 / 500 mg [b]	pH 3 / 500 mg [b]
10,11-dihydrocarbamazepine	100 ± 0	100 ± 0
2-aminobenzimidazole	100 ± 0	100 ± 0.1
2-mercaptobenzothiazole	100 ± 0	79.8 ± 12.4
2,4-D	15.5 ± 9.6	100 ± 0
6-benzylaminopurine	100 ± 0	100 ± 0
Abacavir	100 ± 0	100 ± 0
Abscisic Acid	11.9 ± 8	100 ± 0
Acebutolol HCl	100 ± 0	100 ± 0
Acetamiprid	100 ± 0	99.9 ± 0.2
Acetochlor	100 ± 0	100 ± 0
Adrenosterone	100 ± 0	100 ± 0
Alachlor	100 ± 0	100 ± 0
Albuterol Sulfate	100 ± 0	100 ± 0
Amicinonide	100 ± 0	100 ± 0
Amisulpride	100 ± 0	100 ± 0
Amitriptyline HCl	100 ± 0	100 ± 0
Amphetamine	100 ± 0	100 ± 0
Ampicillin	35.2 ± 12.2	94.2 ± 6
Atenolol	100 ± 0	100 ± 0
Atenolol Acid	100 ± 0	100 ± 0
Atomexine HCl	100 ± 0	100 ± 0
Atrazin-2-Hydroxy	100 ± 0	100 ± 0
Atrazin-desethyl	99.1 ± 2.2	98.9 ± 2.3
Atrazine	100 ± 0	100 ± 0.1
Atropine	99.9 ± 0	99.9 ± 0.2
Azoxystrobin	82.3 ± 6.6	100 ± 0
Baclofen	100 ± 0	100 ± 0
Bendiocarb	100 ± 0	100 ± 0
Bentazon	72.6 ± 8.6	100 ± 0
Benzisothiazolin-3-on (BIT)	100 ± 0	95.2 ± 5.1
Benzotriazole	99.5 ± 1.2	100 ± 0
Benzotriazole-methyl-1H	99.8 ± 0.3	100 ± 0
Benzoylecgonine	100 ± 0	100 ± 0
Bromacil	99.5 ± 1.2	100 ± 0
Caffeine	65.8 ± 16.2	95.4 ± 11.5
Candesartan	15 ± 6.7	100 ± 0
Carbamazepine	99.1 ± 0.1	99.4 ± 0.9

Carbendazim	100 ± 0	100 ± 0
Carbofuran	100 ± 0	94 ± 6.9
Carisoprodol	100 ± 0	100 ± 0
Celecoxib	19.9 ± 8.3	99.8 ± 0.6
Chloridazon	100 ± 0	100 ± 0
Cimetidine	100 ± 0	100 ± 0
cis-diltiazem	100 ± 0	100 ± 0
cis-Tramadol HCl	100 ± 0	100 ± 0
Citalopram HBr	100 ± 0	100 ± 0
Clarithromycin	100 ± 0	100 ± 0
Climbazole	99.9 ± 0	100 ± 0
Clofibric Acid	12.4 ± 6.8	100 ± 0
Codeine	100 ± 0	100 ± 0
Corticosterone	100 ± 0	100 ± 0
Coumarin	98.6 ± 1.3	99.8 ± 0.3
Cyanazine	100 ± 0	100 ± 0
Cyflufenamid	100 ± 0	100 ± 0
DEET	86.2 ± 8.9	99.9 ± 0.1
Dehydroacetic Acid	58.7 ± 13.1	100 ± 0
Desvenlafaxine	100 ± 0	100 ± 0
Dexamethasone	99.9 ± 0.2	100 ± 0
Dextromethorphan HBr	100 ± 0	100 ± 0
Diclofenac Na	97.6 ± 4.2	100 ± 0
Diethyl Phthalate	85.6 ± 7.8	77.8 ± 13.2
Dimethachlor	100 ± 0	100 ± 0
Dimethoate	100 ± 0	100 ± 0
Diphenhydramine HCl	100 ± 0	99.8 ± 0.3
Diuron	100 ± 0	100 ± 0
Efavirenz	100 ± 0	100 ± 0
Estrone	100 ± 0	100 ± 0
Ethofumesate	84.6 ± 6	100 ± 0
Famciclovir	100 ± 0	100 ± 0
Famotidine	100 ± 0	100 ± 0
Fexofenadine HCl	100 ± 0	100 ± 0
Fluconazole	100 ± 0	90.7 ± 12.9
Fluoxetine HCl	100 ± 0	100 ± 0
Folic Acid	1.7 ± 2.8	100 ± 0
Furosemide	82.9 ± 8.7	100 ± 0
Gabapentin	31.8 ± 16.2	53.3 ± 15.7

Gemfibrozil	94.3 ± 8.3	100 ± 0
Gibberellic Acid	8.6 ± 7.4	82.7 ± 7.5
Hexamethylphosphoramide	22.6 ± 7.4	8.5 ± 7.3
Hexazinone	100 ± 0	100 ± 0
Hydrocodone	100 ± 0	100 ± 0
Hydrocortisone	100 ± 0	100 ± 0
Ibuprofen	92.3 ± 8.9	100 ± 0
Imidacloprid	100 ± 0	100 ± 0
Ioxynil	62.1 ± 8.1	100 ± 0
Irbesartan	100 ± 0	100 ± 0
Isophorone Diisocyanate	99.5 ± 0.4	86.1 ± 11.9
Isoproturon	100 ± 0	100 ± 0
Ketamine HCl	100 ± 0	100 ± 0
Ketoprofen	65.4 ± 10	100 ± 0
Lamotrigine	100 ± 0	100 ± 0
Lidocaine	100 ± 0	100 ± 0
Linuron	100 ± 0	99.6 ± 0.9
Losartan Potassium	99.9 ± 0.3	100 ± 0
Mabuterol HCl	100 ± 0	100 ± 0
MCPA	12.4 ± 1.4	100 ± 0
Mecoprop	12 ± 0.7	100 ± 0
Meprobamate	100 ± 0	77.6 ± 8.3
Metalaxyl	100 ± 0	100 ± 0
Metamitron	99.2 ± 0.6	100 ± 0
Metaxalone	100 ± 0	100 ± 0
Methadone	100 ± 0	100 ± 0
Methocarbamol	100 ± 0	100 ± 0
Metolachlor	99.8 ± 0.2	100 ± 0
Metolachlor-ESA	17.1 ± 5.4	7.1 ± 9.5
Metoprolol Tartrate	100 ± 0	100 ± 0
Metribuzin	100 ± 0	100 ± 0
Molinate	100 ± 0	100 ± 0
N,N-didesmethylvenlafaxine	100 ± 0	100 ± 0
N4-acetylsulfamethoxazole	96.5 ± 6.3	99.7 ± 0.9
Nadolol	100 ± 0	100 ± 0
Naproxen	99.3 ± 0.5	100 ± 0
Oxazepam	99.7 ± 0.1	100 ± 0
Oxcarbazepine	100 ± 0	100 ± 0
Oxybenzone	58.8 ± 5.2	100 ± 0

Paraxanthine	97.2 ± 3.1	73.5 ± 7.6
Pentoxyfylline	100 ± 0	100 ± 0
Perfluorooctanoic acid (PFOA)	14.9 ± 8	96.5 ± 4.9
Phenobarbital	100 ± 0	100 ± 0
Phenytoin (Dilantin)	100 ± 0	100 ± 0
Pirimicarb	100 ± 0	100 ± 0
Pirimiphos-Ethyl	100 ± 0	100 ± 0
Primidone	97.9 ± 1.6	89.1 ± 10.2
Progesterone	99.9 ± 0.1	100 ± 0
Prohexadione Ca	12.4 ± 3.9	100 ± 0
Prometon	99.4 ± 0.2	100 ± 0
Propachlor	99.8 ± 0.2	100 ± 0
Propachlor ESA Na	9.5 ± 5.4	4.5 ± 4.1
Propachlor OXA	12.3 ± 5.8	3.6 ± 4.8
Propazine	100 ± 0	100 ± 0
Propoxur	99.4 ± 0.7	100 ± 0
Propranolol HCl	99.3 ± 0.6	99.8 ± 0.4
Propyzamide	100 ± 0	100 ± 0
Pseudoephedrine	100 ± 0	95.8 ± 6.9
Pyrazophos	100 ± 0	100 ± 0
Ritalinic Acid	41.8 ± 15.2	76.8 ± 12.5
Siduron	100 ± 0	100 ± 0
Simazine	98.9 ± 0.2	99.9 ± 0.2
Sitagliptin	100 ± 0	99.8 ± 0.3
Sucralose	53.4 ± 15.3	11.4 ± 6.8
Sulfadimethoxine	99.9 ± 0.1	98.7 ± 2.4
Sulfamethazine	100 ± 0	100 ± 0
Sulfamethoxazole	99.7 ± 0.3	100 ± 0
TDCPP	76 ± 2.9	98.5 ± 3.5
Temazepam	99.5 ± 0.4	100 ± 0
Terbutylazine	0 ± 0	100 ± 0
Testosterone	99.8 ± 0.2	100 ± 0
Theophylline	94 ± 5.2	73.6 ± 13.8
Thiabendazole	100 ± 0	100 ± 0
Triamterene	70 ± 9.4	100 ± 0
Tributyl phosphate (TBP)	90.4 ± 8.8	100 ± 0.2
Triclosan	100 ± 0	100 ± 0
Trimethoprim	95 ± 5.9	99.8 ± 0.3
Trinexapac-ethyl	82.2 ± 15.1	99.2 ± 1.5

Tris (2-chloro-ethyl) phosphate (TCEP)	93.3 ± 9.2	100 ± 0
Valsartan	0 ± 0	100 ± 0
Venlafaxine HCl	100 ± 0	100 ± 0
Verapamil HCl	100 ± 0	100 ± 0
Warfarin	100 ± 0	100 ± 0

a. Charge state of each compound at reported pH, estimated using Marvin Desktop;
b. Standard deviations were calculated from 6 data points (duplicates; sample collected during loading, at 1 hr, 3 hr and 5 hr).

Table C4. Improved absolute recovery rates obtained using P-CDP.

No. [a]	10 mL MeOH [b]	15 mL MeOH [b]	15 mL MeOH + NaCl [c]	R/C Ratio [d]
1	102.4 ± 1.3	105.1 ± 2.9	106 ± 3	1.06
2	0 ± 0	0.1 ± 0.1	98.3 ± 8.2	0.98
3	15.6 ± 2.5	17.9 ± 0.8	14.4 ± 2.1	NA
4	0 ± 0	25.1 ± 5.2	40 ± 6.8	0.50
5	2.1 ± 0.1	2.1 ± 0.1	1.7 ± 0.1	NA
6	98.7 ± 4.5	106 ± 7.6	115.5 ± 1.7	1.16
7	74.5 ± 3	77 ± 2	72.3 ± 0.3	NA
8	12.1 ± 10.6	88.3 ± 2.8	78.6 ± 12.2	NA
9	0 ± 0	1.5 ± 1.1	103.3 ± 3.1	1.03
10	0 ± 0	0.1 ± 0.1	103 ± 0.9	1.03
11	101.4 ± 3	106.6 ± 2.2	114.3 ± 0.1	1.14
12	0 ± 0	0.1 ± 0.1	91 ± 6.1	0.91
13	1 ± 0.3	1.2 ± 0.1	0.2 ± 0.3	NA
14	3.6 ± 0.3	3.7 ± 0.1	4 ± 0.3	NA
15	90.9 ± 1.8	93.8 ± 0.9	86.8 ± 1.3	NA
16	52.4 ± 2.1	107.5 ± 2.9	99.5 ± 0.6	1.00
17	56.8 ± 2.1	105.7 ± 6.2	88.8 ± 9.3	NA
18	113.2 ± 10	102.6 ± 12.5	29.5 ± 6.6	0.30
19	0 ± 0	0.9 ± 0.1	20.1 ± 9.4	NA
20	19.3 ± 1.7	100.6 ± 2.6	109.1 ± 4.5	1.09
21	113.2 ± 10	102.6 ± 12.5	29.5 ± 6.6	0.30
22	0.5 ± 0	0.5 ± 0.2	109.2 ± 8.5	1.09
23	64.6 ± 4.9	116.5 ± 6.1	NA	NA
24	0 ± 0	0 ± 0.1	1 ± 0.7	0.01
25	0 ± 0	0 ± 0	82 ± 6.5	0.82
26	0 ± 0	0 ± 0	94.4 ± 2.4	0.94
27	1.1 ± 0.1	1.7 ± 0.2	114 ± 14.7	1.21
28	0.3 ± 0.1	0.4 ± 0.1	4.3 ± 2.3	NA
29	0 ± 0	0.2 ± 0.1	102.4 ± 1.9	1.02
30	0 ± 0	0.1 ± 0	104.1 ± 0.4	1.04
31	0 ± 0	0.3 ± 0.4	122.8 ± 7.9	1.23
32	0.1 ± 0	0.1 ± 0.1	85.6 ± 0.1	0.86
33	94.3 ± 4.7	100.6 ± 0.4	105 ± 2.9	1.06
34	95.5 ± 1.3	101.1 ± 1.1	94.7 ± 2.8	0.95
35	10.5 ± 1.7	13.1 ± 0.9	4.6 ± 2	NA
36	0 ± 0	0.1 ± 0.1	89.7 ± 1.4	0.90
37	78.8 ± 3.8	115.5 ± 9.9	107.5 ± 16.7	1.08

38	0 ± 0	0 ± 0	85.9 ± 2.7	0.86
39	108.9 ± 3	112.5 ± 0.2	97.5 ± 4.1	0.97
40	83.1 ± 15.2	82.6 ± 1.7	99.1 ± 13	0.99
41	67.7 ± 1.3	95.7 ± 3.8	98.1 ± 0.9	1.03
42	67.7 ± 1.6	75.4 ± 6.7	85.1 ± 3.6	0.85
43	110.4 ± 10.6	129.9 ± 1.4	98.6 ± 19.1	0.99
44	0 ± 0	1.5 ± 2.1	119.5 ± 11.8	1.20
45	68.5 ± 0.3	61.1 ± 6.5	119.4 ± 11.4	NA
46	61.7 ± 12.2	78.9 ± 0.3	94.4 ± 13.7	0.94
47	18.6 ± 0.9	93.5 ± 1.6	90.4 ± 3	0.95
48	5.6 ± 1.5	6.8 ± 0.8	20.6 ± 5.9	0.21
49	95.7 ± 1.7	100.6 ± 1.5	102.8 ± 0.8	1.03
50	0 ± 0	0.2 ± 0.2	105.1 ± 11.6	1.05
51	60.3 ± 6.9	60.8 ± 4.8	99.9 ± 0.8	1.06
52	97 ± 1.8	102.4 ± 3	100.8 ± 2.7	1.01
53	106.7 ± 3.1	116 ± 8.9	NA	NA
54	34.7 ± 1.2	97.4 ± 1.9	125.9 ± 2.7	1.26
55	0 ± 0	0 ± 0	82.1 ± 2.6	0.82
56	0 ± 0	0 ± 0	0 ± 0	NA
57	0 ± 0	0 ± 0	74.8 ± 5.4	0.75
58	0 ± 0	0 ± 0	96.2 ± 6.9	0.96
59	0 ± 0	0 ± 0	116.8 ± 11.7	1.17
60	0 ± 0	1.7 ± 0.1	125.3 ± 14.2	1.25
61	104.5 ± 1.4	108 ± 4.9	108.4 ± 1.8	1.08
62	0.1 ± 0.1	0 ± 0	101.7 ± 5.8	1.02
63	66.3 ± 6.5	91.6 ± 8.2	103.9 ± 8.5	1.04
64	7.1 ± 1.4	21.7 ± 2.3	8.8 ± 7.3	NA
65	23.5 ± 1.3	47.8 ± 3.2	86.8 ± 5.6	0.87
66	122.9 ± 12.3	125.6 ± 6.6	91 ± 9.3	0.91
67	39.5 ± 9.8	106.4 ± 14	NA	NA
68	78.9 ± 4.3	101 ± 1	94.9 ± 9.8	0.95
69	10.5 ± 7.1	128.2 ± 15.8	26.9 ± 11.5	0.27
70	0 ± 0	0.1 ± 0.1	95 ± 2.3	0.95
71	95.3 ± 1.5	99.6 ± 4	112.8 ± 8.7	1.13
72	0.1 ± 0.1	0 ± 0	95.4 ± 4.8	0.95
73	64.4 ± 2.8	69.4 ± 2.5	NA	NA
74	68.5 ± 0.5	105.1 ± 1.9	83.8 ± 29.2	1.08
75	89.7 ± 3.2	95.3 ± 1.8	112.7 ± 1.6	1.13
76	100.8 ± 3.5	107.9 ± 3.5	106.1 ± 1	1.06

77	0.1 ± 0.1	0 ± 0	93.5 ± 1.4	0.94
78	2.5 ± 0.3	117.5 ± 5	93.8 ± 5.6	0.94
79	70.5 ± 12.6	76.9 ± 0.2	NA	NA
80	63.9 ± 1.4	67.2 ± 3.1	81.9 ± 7.6	0.82
81	76.9 ± 5.8	76.2 ± 7.3	82.3 ± 12.5	0.82
82	87.4 ± 2.2	95.9 ± 0.2	106.6 ± 3.6	NA
83	0 ± 0	0.1 ± 0.1	84.3 ± 1.5	0.84
84	0 ± 0	0 ± 0	62.6 ± 4.3	0.63
85	0 ± 0	0 ± 0	103.5 ± 9.1	1.04
86	83 ± 1.5	89 ± 1.2	84.9 ± 1.8	0.94
87	0 ± 0	0 ± 0	87.5 ± 5.8	0.87
88	0 ± 0	0 ± 0	7.7 ± 5.4	0.08
89	72.2 ± 11.1	99.3 ± 6.2	116.1 ± 13.1	1.16
90	1.8 ± 0.1	3.7 ± 0.3	39.9 ± 1.9	0.75
91	124.2 ± 11.2	125.1 ± 3.7	108.8 ± 11.9	1.09
92	1.1 ± 0	0.9 ± 0.2	2.9 ± 0.3	0.03
93	1.8 ± 0	2.2 ± 0.1	2.2 ± 0.1	0.26
94	32 ± 4.2	108.7 ± 1.6	106 ± 0	1.06
95	48.3 ± 7.2	124.8 ± 4.1	111.4 ± 9.5	NA
96	0 ± 0	0 ± 0	57.8 ± 1.9	0.58
97	77.2 ± 2	91 ± 2	120.5 ± 9.7	1.21
98	100.4 ± 19.8	108.3 ± 5.4	111.4 ± 3.1	1.11
99	0.1 ± 0.1	95 ± 0	106.6 ± 0.3	1.07
100	115.7 ± 15.1	106 ± 10.1	107.2 ± 8.3	NA
101	3 ± 0.4	0 ± 0	0 ± 0	NA
102	117.3 ± 4.8	113.4 ± 6.4	107.1 ± 12	1.07
103	0 ± 0	120 ± 0	120.2 ± 14.8	1.20
104	62.9 ± 26.5	78.8 ± 3.2	94.2 ± 14.6	1.09
105	90.1 ± 5.6	102.8 ± 1.3	103.5 ± 0.5	1.04
106	0 ± 0	0 ± 0	85.7 ± 2.6	0.86
107	116.4 ± 3.5	124.5 ± 2.6	92.9 ± 2.1	0.93
108	0 ± 0	0 ± 0	112.2 ± 2.6	1.12
109	1.8 ± 0.2	1.6 ± 0.1	0 ± 0	NA
110	0 ± 0	0 ± 0	101.9 ± 6.7	1.02
111	10.9 ± 0.6	124.6 ± 2.6	76.4 ± 9.9	0.77
112	124.7 ± 3.2	121.7 ± 3.2	91.5 ± 30.5	0.92
113	0 ± 0	0 ± 0.1	103.7 ± 7.6	1.04
114	96.2 ± 0.9	107.6 ± 9.8	111.7 ± 1.6	1.12
115	101.4 ± 2.6	106.1 ± 4	104.7 ± 1.7	1.05

116	41.4 ± 17.1	55.5 ± 0.2	65.8 ± 10.3	0.85
117	90.4 ± 4.3	96.6 ± 0.7	112.3 ± 4.2	1.12
118	0.2 ± 0.1	44.5 ± 2.3	79.6 ± 7.5	0.80
119	18.9 ± 0.2	94.4 ± 6.5	93.2 ± 1.4	0.93
120	0.4 ± 0.2	0.7 ± 0	0.5 ± 0.7	NA
121	0 ± 0	0 ± 0	113.6 ± 18.9	1.14
122	55.4 ± 22.6	81 ± 2	73.9 ± 4.4	0.74
123	44 ± 3.4	49.5 ± 5.1	64.9 ± 1.4	NA
124	60.4 ± 1.1	72.5 ± 4.1	86.1 ± 1	0.86
125	0 ± 0	0 ± 0	0.4 ± 0.6	0.06
126	0 ± 0	0 ± 0	108.6 ± 1	1.09
127	97.7 ± 4.5	108.3 ± 6.1	113.9 ± 13.1	1.14
128	0 ± 0	126.3 ± 4.9	99.8 ± 14.5	NA
129	29.5 ± 0.6	49.1 ± 0.5	36.6 ± 11.4	0.37
130	0 ± 0	0 ± 0	94.8 ± 0.5	NA
131	0 ± 0	0 ± 0	96.8 ± 7.5	0.97
132	43.7 ± 2.9	55.9 ± 0.7	82.5 ± 5.6	0.83
133	0 ± 0	0.1 ± 0.2	93.9 ± 14	0.94
134	10.8 ± 4.8	108 ± 6.7	78.9 ± 3.7	0.79
135	0 ± 0	0 ± 0	0.4 ± 0.5	NA
136	0 ± 0	0 ± 0	0 ± 0	NA
137	0 ± 0	0 ± 0	0 ± 0	NA
138	86.1 ± 5.3	102.2 ± 3.6	113 ± 4.2	1.13
139	87.1 ± 2.5	98.1 ± 0	102.2 ± 10.1	1.02
140	0 ± 0	69.3 ± 0.6	NA	NA
141	34.1 ± 0.8	64.4 ± 0.1	43.3 ± 5.4	0.59
142	11.8 ± 0.4	38.8 ± 0.4	13.6 ± 3.4	NA
143	0 ± 0	92.3 ± 1.8	92.8 ± 2.7	0.93
144	99.5 ± 19.3	100.2 ± 0.4	87.9 ± 12.9	0.91
145	67.2 ± 7	60.2 ± 2	120.6 ± 0.4	1.21
146	100.1 ± 3.8	100.1 ± 1	108.6 ± 4	1.09
147	0.7 ± 0.3	91.4 ± 3.3	102 ± 1	1.02
148	56.5 ± 0.6	77.9 ± 7.7	86.4 ± 0	0.86
149	50.1 ± 20.5	69.9 ± 1.4	89.1 ± 15.3	1.00
150	13.2 ± 3.1	49.8 ± 4.8	NA	NA
151	28.9 ± 14.4	66.1 ± 2.2	72.8 ± 12.2	0.73
152	0 ± 0	1.1 ± 0.6	121.5 ± 6.1	1.22
153	80.5 ± 4.2	103.7 ± 3.6	90.8 ± 7.7	0.91
154	0.3 ± 0	0.5 ± 0.1	0.4 ± 0.1	0.09

155	0.2 ± 0.3	0.9 ± 0.2	0.4 ± 0.2	0.12
156	79.9 ± 0.2	81.7 ± 8.5	97 ± 13.6	0.97
157	78.1 ± 0.5	94.5 ± 2.9	120.5 ± 1	1.21
158	0 ± 0	0.5 ± 0.7	58.5 ± 27.1	0.59
159	96.9 ± 4.5	114.4 ± 5.3	92.5 ± 6.7	0.92
160	1.8 ± 0.2	1.4 ± 0	89.9 ± 8.8	0.94
161	13.3 ± 0.2	102.1 ± 12.9	NA	NA
162	0 ± 0	0 ± 0	12.6 ± 2.8	NA
163	3.5 ± 0.2	7.2 ± 0.3	77.7 ± 3.2	1.01
164	0 ± 0	0 ± 0	37.6 ± 3.4	NA
165	120.9 ± 6.1	101.4 ± 12.8	99.4 ± 16.1	0.99
166	106.4 ± 0.4	104.7 ± 9.6	99.3 ± 2	0.99
167	0 ± 0	0 ± 0	107 ± 17	1.07
168	5.8 ± 1.8	6.2 ± 0.6	58.9 ± 6.5	5.18
169	4 ± 2.7	4.6 ± 1.2	22.1 ± 8.6	0.22
170	11.6 ± 7	5.8 ± 2.1	21.3 ± 4.4	0.21
171	19.9 ± 7	10.2 ± 1.1	32.7 ± 6.2	0.33
172	0.1 ± 0.1	1.9 ± 0.1	1.1 ± 1.5	NA
173	74.5 ± 7.9	102.7 ± 0.3	NA	NA
174	47.9 ± 3.1	107.2 ± 3.4	112.9 ± 1.5	1.13
175	113.2 ± 9	116.7 ± 15.1	102.8 ± 16.6	1.03
176	113.3 ± 2.3	124 ± 5.9	100.8 ± 3.9	1.01
177	29.2 ± 0.3	55.4 ± 2.1	65.4 ± 4.9	0.89
178	0 ± 0	0.2 ± 0	98.5 ± 2.2	0.98
179	0 ± 0	0.1 ± 0.1	95 ± 2.3	0.95
180	0 ± 0	0.4 ± 0.6	128.2 ± 5.7	1.28
181	6.4 ± 0.4	14.6 ± 2.9	50.5 ± 12.4	0.51
182	79.7 ± 4.8	83.4 ± 2.3	0 ± 0	0.00
183	0 ± 0	0.1 ± 0.1	92 ± 3.2	0.92
184	8.3 ± 6.7	119.3 ± 0.4	17.5 ± 12.4	0.18
185	84.9 ± 5.5	96.6 ± 1.8	99.6 ± 2.6	1.00
186	107.6 ± 3.6	107.5 ± 2.5	68.6 ± 5.2	0.69
187	0 ± 0	0 ± 0	100.9 ± 2.1	1.01
188	0 ± 0	0 ± 0	51.2 ± 7.2	0.51
189	6.8 ± 0.4	7 ± 0.1	55.4 ± 1.8	0.55

a. No. refers to targeted compounds in Table B;
b. Standard deviations were calculated from 3 replicates;
c. NA means not available, 9 compounds cannot be detected or detected well using current instrumental methods;
d. R/C ratio are the relative recovery rates calculated for compounds under optimized P-CDP SPE procedure (optimized capture and recovery condition).