Investigation of Polyethlyene Passive Samplers' Efficacy in Deducing Sediment Pore Water Concentrations of PCBs

by

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Abstract

Polychlorinated biphenyl compounds (PCBs) were manufactured between 1929 and 1977 as heat exchange fluids, flame retardants, and pesticide extenders, among other uses. About 450 million pounds of PCBs are estimated to have entered the environment since manfacture. Assessing the hazard posed by these PCBs is difficult due to PCBs' strong affinity for organic carbon and black carbon, which complicates measurement of pore water concentrations. PE passive samplers are an inexpensive, fast alternative to liquid-liquid extraction of pore waters and sediment extraction with equilibrium partitioning. To demonstrate the potential of PE passive samplers to measure sediment pore water concentrations, we (a) compared observed PRC behavior over 476 days to the model of Fernandez et al. (2009), (b) investigated key data metrics including method detection limit, precision, and comparison to contract lab analysis, (c) assessed PE passive sampler results compared to directly measured pore water concentrations and sediment extraction with equilibrium partitioning, and (d) explored the capabilities of contour mapping software to infer PCB concentrations in the sediment of Lake Cochituate (Natick, MA) from a limited data set. PRC behavior of PCBs 101 and 52 was underpredicted by the model, but estimation of black carbon effects corrected this issue. Method precision was around 20% without PRC correction, but increased with PRCs due to the instability of this correction as PRC load approaches 1. Longer incubation times, thinner passive samplers, or novel materials are suggested in order to encourage PRC loss. PE passive samplers matched directly measured pore water results within a factor of 2, while sediment extraction results were over 10 times too high, suggesting the advantages of PE passive sampling over sediment extraction. Contour mapping software provided "hot spot" results much like traditional mapping, but with tweaks to hot spot size and shape due to incorporation of information from the entire data set.

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Chapter 1

Introduction

Over 1.25 billion pounds of polychlorinated biphenyls (PCBs) were manufactured in the United States between 1929 and 1977 as heat exchange fluids, plasticizers, pesticide extenders, and flame retardants, among other uses [16]. About 450 million pounds are estimated to have entered the environment since manufacture. Today, PCBs are present in about one third of hazardous waste sites listed on EPA's National Priorities List. Chronic PCB exposure is associated with liver damage and acne-like symptoms in adults and impaired cognition in children exposed in utero.

After release into the environment, PCBs strongly absorb into natural organic matter and adsorb to black carbon present in sediment, limiting their transport and remaining shielded from decay [2] [3]. As PCB-contaminated sediment sites such as the Hudson River PCBs Superfund Site move through the cleanup process, sediment sampling is necessary to determine the extent and severity of contamination [1]. As part of EPA's 2002 Record of Decision, which ordered remedial dredging of highly contaminated Hudson River sediments, 5,658 sediment cores were obtained in a triangular grid pattern. The cores produced 38,641 sediment samples, of which 29,442 were extracted with solvent. PCBs were identified in the concentrated extracts via gas chromatography–mass spectrometry (GCMS). However, it is not clear whether this expensive and time-consuming effort will successfully enable cleanup of this river ecosystem. GE reports that Phase 1 sampling and project design cost $64 million [13]. Although this number pales in comparison to the $227 million cost of sediment

dredging, transport, and disposal, a cheaper and faster sampling method such as PE passive samplers would have allowed project designers more information when creating the dredging program.

Humans are primarily exposed to PCBs through consumption of contaminated fish, meat, and poultry [16]. Unlike chemicals with exposure pathways that include drinking water, no national standards exist for PCB contamination levels in sediments. Because of PCBs' interaction with organic matter and black carbon, the specific sediment characteristics must be taken into account when determining the hazards that PCBs pose to a contaminated site. A PCB release in a sandy site that is low in organic matter, organic carbon, and black carbon may result in high levels of PCB in benthic organisms and the water column, while the same contaminant concentrations in a muddy, organic-rich site may result in little PCB contamination in benthic organisms. The PCB sorbs to the muddy sites high concentration of organic matter, organic carbon, and black carbon, resulting in less PCB available to enter the water column and contaminate benthic organisms. A useful measurement method for sediment PCBs must recognize such HOC behavior and sediment characteristics. Measurement methods should deduce the amount of truly dissolved HOC in the sites pore water, allowing comparison across sites and against EPA water quality standards.

Direct measurement of HOC contamination in pore water samples can be time consuming and expensive. Large volumes of water are required to produce a measurable amount of HOC, and colloids and particulate matter must be removed from the water through centrifugation and alum precipitation [7] [22]. Liquid-liquid extraction of such water volumes can use large amounts of solvent relative to other measurement methods. Since investigations of a contaminated sediment site can involve large areas and thousands of measurements [1], a faster and less expensive method is desired.

The truly dissolved concentration of PCBs can also be estimated through sediment extraction and equilibrium partitioning modeling [12]. Sediment extraction measures all of the PCB present in the sediment. This measurement must be corrected for the presence of organic matter to determine the fraction that was truly dissolved

at equilibrium. Sediment extraction without equilibrium partitioning was used at the Hudson River site [1]. Consideration of the impact of organic matter on PCB mobility would have allowed dredging to target those sites posing the greatest risk to river health.

Measurement of HOC contamination in mussels is one way to account for site-specific characteristics and magnify the HOC signal [11]. Mussels metabolize PAHs very slowly, resulting in PAH accumulation. However, mussels have been shown to accumulate HOCs that have sorbed to colloidal particles and particulate matter, as well as HOCs that are truly dissolved in the water column. A mussel measurement would have to be corrected for site-specific colloid and particulate presence in order to reflect the amount of truly dissolved HOC. Mussel lipid composition can vary with life stage, species, and organism health, making prediction of the lipid-water partitioning coefficient difficult [24].

We believe that polyethylene passive samplers offer an inexpensive and expedient alternative. Passive samplers measure only the truly dissolved HOCs, and display the signal magnification properties of mussels. The first passive samplers sought to mimic living samplers with polyethylene tubes containing triolein or hexane [24]. These semipermeable membrane devices (SPMDs) allowed the HOC to diffuse through polyethylene into a triolein core. HOC partitioning and uptake into SPMDs has been well characterized [23] [29] [9]. However, SPMDs are prone to tearing and can disrupt sediment beds during deployment. Solid-phase microextraction (SPME) fibers avoid the messy qualities of SPMDs by coating silica fibers with an organic polymer [8] [27] Although simpler, SPMEs can break in the field and the thin coating absorbs only small amounts of HOC, resulting in a higher detection limit than that of SPMDs.

Seeking a simple, durable, high-capacity passive sampler, researchers began using only the outer polyethylene membrane of SPMDs [4] [34]. Polyethylene strips can be inserted directly into sediment samples and incubated in the lab, or attached to a rigid metal frame or rod for field use [15] [28]. HOCs in the sediment porewater equilibrate with the polyethylene, which can then be removed and analyzed. Since deployment

times are typically too short to reach near-equilibrium levels, performance reference compounds (PRCs) are used [10]. These compounds are often chosen to mimic the target compound as closely as possible, although modeling can be used to infer the behavior of similar compounds from a set of PRCs [14]. As the target compound diffuses into the PE, the PRC diffuses out into the sediment. The PRC movement can be described by a one-dimensional diffusion model. The PRC approach to equilibrium is measured, and the equilibrium behavior of the target compound is assumed to be the same. HOCs with slow rates of diffusion in the polyethylene may not move significantly during the sampling period. Field deployment of polyethylene passive samplers and subsequent calculation of porewater concentrations have occurred in Boston Harbor and San Francisco Bay [33] [28] [15] . Fernandez et al (2009) incubated PRC-containing polyethylene samplers in Boston Harbor sediment for one week to determine PAH concentrations. Oen et al (2011) [28] used PRC-containing PE in a San Francisco mudflat to find PCB concentrations.

In order to demonstrate the potential of PE passive samplers to accurately and inexpensively measure sediment PCB pore water concentrations, we sought to identify difficulties with the method and attempt to resolve them, show how data from passive samplers may be used to design site remediation plans or estimate contamination risk, and encourage industry knowledge of PE passive samplers. We assessed PRC movement in Chapter 3 in order to obtain accurate target compound equilibrium values. The observed PRC movement was compared to the PRC model presented by Fernandez (2009) [14] with measured PRC behavior over 476 days and an appropriate incubation period was determined based on observed PRC behavior. To advance the use of PE passive samplers by industry, we determined the method precision in Chapter 4 as recommended by EPA's "proof of concept" preliminary validation guidelines [5] for inclusion in SW-846, the official EPA compendium of approved analysis and sampling methods for evaluating solid waste. A method detection limit (MDL) was calculated. The accuracy of PE passive samplers was tested in Chapter 5 by comparing pore water data obtained through liquid-liquid extraction to both PE passive sampler data and accelerated solvent extraction, the method used at the

Hudson River site. A technique to infer sediment concentration patterns from data measurements is examined in Chapter 6, which presents sediment mapping efforts using Surfer®9 (Golden Software, Golden, CO), a contour mapping tool.

Chapter 2

A Method to Deduce PCB Pore Water Concentration Using Polyethylene Passive Samplers

Here we present a method to deduce the porewater concentrations of PCBs using polyethylene passive samplers. In order to examine the reproducibility of this method, we homogenized sediment samples and incubated passive samplers in the lab. The sediment was tumbled for at least two weeks to ensure even distribution. Polyethylene strips were cleaned and incubated with PRCs for at least six months. After incubation, the passive samplers were removed from the sediment and rinsed. The PCBs were extracted with dichloromethane and identified through gas chromatography-mass spectrometry (GCMS). We used this method for the experiments discussed in subsequent chapters.

2.1 Materials and Methods

2.1.1 Materials

Solvents

All solvents used were Baker UltraResi-Analyzed (Phillipsburg, NJ USA). Unless otherwise specified, the solvent used is dichloromethane (DCM). Clean laboratory water was purified using an Aries Vaponics (Rockland, MA) ion-exchanged and activated carbon system. The system was run until the water showed 18 milliΩ-cm resistance. In addition to removing metals, particles, and ions, this water purification system contains a charcoal filter to remove organic compounds and a UV source to break up any remaining organic compounds.

Standards

Aroclor 1260 standards and the PCB compounds in hexane were purchased from Ultra Scientific (Kingstown, RI) and used to create recovery, PRC and injection standards. A 50 μL glass micropipette was used to transfer compounds into DCM to create dilute standard solutions.

Glassware

Sediment and standards were stored in either amber glassware or clear glassware covered with aluminum foil. All glassware was washed with soap and water and baked at 450°C for at least 8 hours prior to use. To avoid contamination from and losses to plastic caps, we lined all caps with baked or solvent-rinsed tinfoil by placing a square of tinfoil over the jar, screwing and unscrewing the cap, and cutting the foil along the top thread with a razor blade.

Tumblers

Spiked sediment was tumbled for at least two weeks to evenly distribute the introduced Aroclor 1260 mixture. We constructed our own tumblers, which consist of a peristaltic

pump that moves a shaft attached to a sample basket. The pumps are operated at a gentle rate–one revolution every 7-10 seconds. We sealed each jar with PTFE tape, wrapped lab tape around the outer cap-jar junction, and placed each jar in a plastic bag before starting the tumbler.

Agilent Supplies

Agilent amber glass, 2-mL vials with 250 μL, clear glass inserts were used for sample injection and storage. Screw caps with PTFE/silicone septa were used for injection, and solid PTFE-lined screw caps were used for storage. Agilent supplies were not baked prior to use, but are certified clean.

2.1.2 Polyethylene Preparation and Addition of PRCs

Low-density polyethylene sheets are commonly available at hardware stores. We used Trimware brand 1 mil plastic dropcloth, corresponding to a PE thickness of 25 μm. The polyethylene sheets were cut to 5 cm wide bands with a razor blade and ruler on a laminated cutting mat. The resulting bands were cleaned by two 24 hour soakings in dichloromethane, followed by two 24 hour soakings in methanol, and finally two 24 hour soakings in water. Two batches of polyethylene strips with PRCs were used. The first batch was incubated for over six months with ^{13}C PCBs 52, 101, 153, and 180 in water. We began using a second batch of polyethylene strips because PRCs 52, 101, 153, and 180 interfered with the analysis at Pace Analytical (Chapter 4). The second batch of polyethylene bands was placed in a 90% methanol and 10% water mixture containing PRCs (PCBs 47, 111, 153, and 178) and incubated for at least 5 days.

2.1.3 Sediment Acquisition and Transport

Sediment sample grabs were taken from Lake Cochituate in Natick, MA by Steve Reichenbacher of ICF International Consultants on November 19, 2009 and December 10, 2010. The samples were poured into a metal bowl and homogenized on the

sampling boat. The homogenized sediment was poured into gallon glass jars and transported to MIT in a cooler. The jars were at room temperature in the lab until used, from 17 days to 160 days. Sampling site coordinates are located in Table 2.1. A map of sampling sites is located in Figure 2.1.

2.1.4 Sediment Homogenization

In order to eliminate natural sediment variations, we thoroughly homogenized each sediment sample before use. The sediment jars were opened inside a lab hood. Clams, snail shells, red worms, vegetation and woody materials that accumulated at the mouth of the jar were picked out with solvent-rinsed metal tweezers and placed on a paper towel. Standing water was decanted into 250 mL Erlenmeyer flasks using a 50 mL volumetric glass pipette.

The sediment was stirred with a solvent-rinsed metal spoon to incorporate residual standing water. Once this water was mixed in, the jar was stirred for four one-minute intervals, rotating the jar 90° before each interval. Vegetation that accumulated on the spoon or that was brought to the surface during mixing was removed with metal tweezers and placed on a paper towel.

After homogenization, small subsamples of the sediment were ladled into three aluminum boats to allow water content determination. The remaining sediment was stirred for 2 minutes. Glass jars were filled with sediment in preparation for passive sampler incubation. One scoop of sediment was placed in each jar, the sediment was stirred for 2 minutes, and then a second round of scoops was placed in the jars. This procedure was repeated until all sediment was distributed.

2.1.5 Determination of Percent Water Content

The aluminum boats were tared, filled with sediment, weighed, dried overnight in a 60°C oven, allowed to cool, and re-weighed to determine the percent water content.

Percent water content was determined:

$$\%\ water\ content = \frac{(M_{wet\ sed\ in\ boat} - M_{dry\ sed\ in\ boat})}{M_{wet\ sed\ in\ boat}} * 100 \qquad (2.1)$$

where $M_{wet\ sed\ in\ boat}$ is the mass of the wet sediment in the boat in g and $M_{dry\ sed\ in\ boat}$ is the mass of the dried sediment in the boat in g. The percent water contents from each individual boat were averaged for use in further calculations. The average standard deviation between individual percent water contents was 0.75%. Percent water contents ranged from 33% to 84%.

2.1.6 Sediment Spiking and Tumbling

The filled jars were tared, then weighed after filling. Using the percent water content data, the amount of dry sediment solids in each jar was estimated:

$$M_{dry\ sed\ in\ jar} = \left(1 - \frac{avg.\ \%\ water}{100}\right) * M_{wet\ sed\ in\ jar} \qquad (2.2)$$

where both masses are in g. The volume of Aroclor 1260 solution needed was calculated by multiplying the dry mass by the desired spiking level and solution strength:

$$V_{solution} = M_{dry\ sed\ in\ jar} * \frac{C_{sed}}{C_{solution}} \qquad (2.3)$$

where $V_{solution}$ is the needed volume of the Aroclor 1260 solution in mL, C_{sed} is the desired sediment concentration in μg Aroclor 1260/g dry sediment, and $C_{solution}$ is the concentration of the Aroclor 1260 solution in μg/mL. The Aroclor 1260 solution was introduced to each jar with a solvent-rinsed glass syringe. The sediment was stirred for 1 minute after Aroclor 1260 introduction. The spiked sediments were tumbled for 2 weeks to distribute the Aroclor 1260 spike evenly.

2.1.7 Sediment Preparation and PE insertion

After removal from the tumbler, the jars were stirred to reincorporate a thin film of standing water. The PE strips were carefully handled and cut to minimize contamination from lab air and surfaces. A polyethylene band was removed from the storage jar with solvent-rinsed metal forceps and cut with solvent-rinsed scissors or a solvent-rinsed razor blade. The resulting strips were placed on a solvent-rinsed aluminum foil sheet. "Zero day" strips were inserted into 7-mL vials and immediately covered with DCM. Remaining strips were carefully inserted into sediment in each of the jars with solvent-rinsed metal tweezers to avoid wrinkling or folding, which would decrease strip surface area and reduce uptake from the sediment. The jars were capped and allowed to sit undisturbed at room temperature on a laboratory bench until PE sampler removal.

2.1.8 Lab Processing Procedure

After each incubation period, which we determined through a PE passive sampler time course and modeling (Chapter 3), the jars were opened and some of the strips were removed with solvent-rinsed metal tweezers. Each strip was rinsed with clean water, wiped with a Kimwipe, and then rinsed again. This procedure was repeated until no visible sediment specks remained on the strip. Two strips from each spike level (eight strips total) were sent to Pace Analytical Services (Minneapolis, MN) for analysis. Each remaining strip was placed in an amber glass vial with foil-lined cap. The vials were filled with 7-10 mL of DCM (enough to cover the strip) and incubated for at least 24 hours. Recovery standards (PCBs 19, 77, 105, 167, 170, and 194) were added at this point.

After a 24-hour incubation, the extract was carefully poured into a 30 to 45 mL amber glass vial, allowing the polyethylene strip to remain in the 7-mL incubation vial. The strip was rinsed with 2-3 mL of DCM three times. The resulting strip extract was concentrated to approximately 300 μL under a stream of ultra pure grade nitrogen gas. The stream was adjusted so that the surface of the extract rippled, but

did not break. This avoided spattering of the extract to the vial sides. The extracts were gently heated during evaporation by a hot plate at its lowest setting. At least twice during evaporation, the vials were removed from the nitrogen stream, capped, and rolled gently between two hands to warm the extract and wash residue from the vial sides into the remaining liquid. Condensation was wiped away from the outside of the vials with a Kimwipe or paper towel.

The concentrated extract was transferred to a 2-mL Agilent vial with a 100 μL glass micropipette. After transfer, the large concentration vial was rinsed three times with 50 μL of DCM. Rinses were also transferred to the Agilent vial using the 100 μL pipette. The complete transferred extract (typically measuring 0.5 mL) was concentrated again to 50-100 μL under a gentle stream of nitrogen gas and transferred to a 250 μL Agilent glass insert. If the extract level inside the glass insert reached above the 1.5 mL marking on the outer Agilent vial, the extract was concentrated again so that the level was at or below 1.5 mL to avoid spillage when changing vial caps. Injection standards (PCBs 39, 55, 104, 150, and 188) were added to the finished extract.

2.1.9 Mass of PE Strips

After extraction, polyethylene strips were allowed to sit in their 7-10 mL extraction vials with loosened caps inside a hood for at least 24 hours. The dried strips were massed using a A&D GH-202 scale with readability to 0.00001 g.

2.1.10 GCMS Analysis

Gas chromatography-mass spectrometry (GCMS, JEOL GCmate, JEOL Ltd, Tokyo, Japan) was used to analyze all extracts. Splitless 1 μL injections were made using a Hewlett-Packard 6890 Series auto-injector onto a 30m DB5-MS column with 0.250 mm ID and 25 μm film thickness. The injection port was held at 280°C. The column temperature was held at 75°C for 2 minutes, then raised at 15°C per minute. When the column temperature reached 150°C, the temperature was raised at 2.5°C per

minute until a final temperature of 290°C was reached. This temperature was held for one minute. Each run lasted 64 minutes. Selected ion monitoring (SIM) mode was used with three groupings. Five standard vials, containing DCM, recovery standards, injection standards, PRC standards, and an EPA PCB calibration mixture, were run after every 5-8 samples to check instrument stability and determine response factors. The instrument was calibrated with perfluorokerosene (PFK) every day, before each run, and between each sample. PFK calibration curves were stored every day. PCB calibration curves were run using 25 ng/mL, 50 ng/mL, 100 ng/mL, 200 ng/mL, and 400 ng/mL standards.

2.1.11 Data Analysis

GCMS data files were analyzed using TSS 2000 software v. 2.02 (Shrader Analytical Consulting, Detroit, MI). Peak retention times were identified by comparing the peaks produced by an Aroclor 1260 standard to the Aroclor 1260 signature characterized by Schulz, Patrick and Dulnker [31], using quantification and confirmation ions. Peak retention times varied by about 0.03 minutes between runs. Quantification ion mass chromatogram peaks were manually integrated by looking at the peak and determining the peak front and back, then integrating between the front and back points. The "sub intensities below baseline" and "two point single scan" options were used to allow a line to be drawn from the background level of the peak beginning to the background level of the peak end during integration. In this way, only the actual peak was integrated. The integration value, number of scans integrated, and background levels were manually typed into Excel. An Excel macro was developed to handle data placement and calculations (see Appendix A).

2.1.12 Calculations

A set of calculations was performed in order to find the PCB concentration in the PE passive sampler and deduce the concentration of PCB in pore water. We first calculated the sample volume using the known mass of injection standards added and the

response factors for those standards. Vials of injection standards, recovery standards, PRC standards, and target compound standards were run every 5-8 samples, and the peak areas from each of these runs was averaged for use in calculations. The sample volume was calculated by

$$V_{sample} = \frac{A_{inj\ std} * M_{inj\ added} * 1000}{C_{inj\ std} * A_{sample}} \tag{2.4}$$

where V_{sample} is the sample volume in μL, $A_{inj\ std}$ is the average peak area of the congener in the injection standard (area units/μL), $\frac{A_{inj\ std}}{C_{inj\ std}}$ is the response factor of the recovery standard, $M_{inj\ added}$ is the amount of injection compounds added in ng, 1000 μL/mL is a conversion factor, $C_{inj\ std}$ is the concentration of the injection standard in ng/mL, and A_{sample} is the peak area of the injection congener in the 1 μL of sample injected. Sample volumes were calculated for five injection congeners and averaged for use in further calcualtions. The sample volumes calculated from each congener varied by about 20%.

The fraction of recovery standards left in the analyzed sample was found:

$$rec\ left = \frac{0.001 * A_{sample} * V_{sample}}{A_{rec\ std}/C_{rec\ std} * M_{rec\ added}} \tag{2.5}$$

where A_{sample} is the peak area of the recovery congener in the sample (area units/μL injected), V_{sample} is the average sample volume in μL, 0.001 mL/μL is a conversion factor, $A_{rec\ std}$ is the average peak area of the congener in the recovery standard (area/ng), $C_{rec\ std}$ is the concentration of the recovery standard used in the surrogate standard addition in ng/mL, $\frac{A_{rec\ std}}{C_{rec\ std}}$ is the recovery standard response factor, and $M_{rec\ added}$ is the amount of recovery compounds added to the sample in ng. The amount of each PRC congener left in the PE strip per gram of polyethylene was finally found using:

$$C_{PRC,\ PE} = \frac{ng\ PRC}{g\ PE} = \frac{0.001 * A_{sample} * V_{sample}}{A_{PRC\ std}/C_{PRC\ std} * M_{PE}} \tag{2.6}$$

where A_{sample} is the peak area of the PRC congener in the sample (area units),

$A_{PRC\ std}$ is the average peak area of the congener in the PRC standard (area/ng), $C_{PRC\ std}$ is the PRC standard concentration in ng/mL, $\frac{A_{PRC\ std}}{C_{PRC\ std}}$ is the PRC standard response factor, and M_{PE} is the polyethylene strip mass in grams.

The amount of target congener present in the PE strip per gram of polyethylene was found:

$$C_{target,\ PE} = \frac{ng\ Target}{g\ PE} = \frac{0.001 * A_{sample} * V_{sample}}{A_{target\ std}/C_{target\ std} * M_{PE}} \tag{2.7}$$

where A_{sample} is the peak area of the target congener in the sample (area units), $A_{target\ std}$ is the average peak area of the target congener in the target standard (area units/ng), $C_{target\ std}$ is the concentration of the target compound standard in ng/mL, and $\frac{A_{target\ std}}{C_{target\ std}}$ is the target standard response factor.

Since one cannot assume target compounds in the sediment reached equilibrium with the inserted PE strips, the concentration of target compound present in the PE strip must be corrected using PRC data to reflect the strip's concentration at equilibrium. To assess PRC migration, we compared the amount of each PRC congener present in the incubated strips to the amount of each PRC congener extracted from non-incubated zero day strips.

$$fraction\ PRC\ remaining = \frac{\left(\frac{ng\ PRC}{g\ PE}\right)_{after\ incubation}}{\left(\frac{ng\ PRC}{g\ PE}\right)_{0\ days}} \tag{2.8}$$

The two heaviest PRCs (congeners 151 and 180) migrated very slowly, and were often lost from the strips at fractions comparable to or less than experimental error (15 to 20%). We used the mass transfer model developed by Fernandez et al. [14] to use the measured losses of the lightest PRCs and extrapolate that migration behavior to the heaviest PRCs, so that a realistic fraction of PRC remaining could be obtained for all congeners. A Matlab code was written to automate this procedure (see Appendix A). We can correct the concentration of target compound present per gram of polyethylene by using the PRC values in the passive sampler:

$$\left(\frac{ng\ target}{g\ PE}\right)_{corrected} = \frac{ng\ target/g\ PE}{(1 - fraction\ PRC\ remaining)} \tag{2.9}$$

The corrected $\frac{ng\ target}{g\ PE}$ values were converted to porewater concentrations $\frac{ng\ target\ compound}{L\ porewater}$ with each congener's polyethylene-water partition coefficient, K_{PEW}:

$$\frac{ng\ Target}{L\ porewater} = \frac{920}{K_{PEW}} * \left(\frac{ng\ target}{g\ PE}\right)_{corrected} \tag{2.10}$$

where K_{PEW} is the polyethylene-water partition constant in $\frac{L}{\text{kg polyethylene}}$ and 920±60 g/L is the density of polyethylene. An Excel macro developed to organize data and automate the calculations described here can be found in Appendix A, and a Matlab code to extrapolate PRC behavior from losses of at least two PRCs (e.g., congeners 52 and 101) is located in Appendix B.

Site Number	Easting	Northing
1	211583.255298	892858.28675
2	211535.5887	892875.3443
3	211543.9431	892956.6862
4	211481.5973	893002.3521
5	211511.7634	893082.1235
6	211468.6599	893145.9458
7	211644.1341	893100.1368
8	211743.326323	893155.59761
9	211644.0637	893214.3594
10	211607.495681	893284.932759
11	211468.562	893159.4387
12	211784.6151	893298.8312
13	211743.3263	893155.5976
14	211736.9189	893057.3819
15	211665.8253	892849.8244
16	211626.9239	892945.1302
17	211497.1906	893063.3183
18	211497.1906	893054.1743
19	211506.3346	893063.3183
20	211505.995	893053.8881

Table 2.1: Sediment sampling UTM coordinates for Lake Cochituate, MA

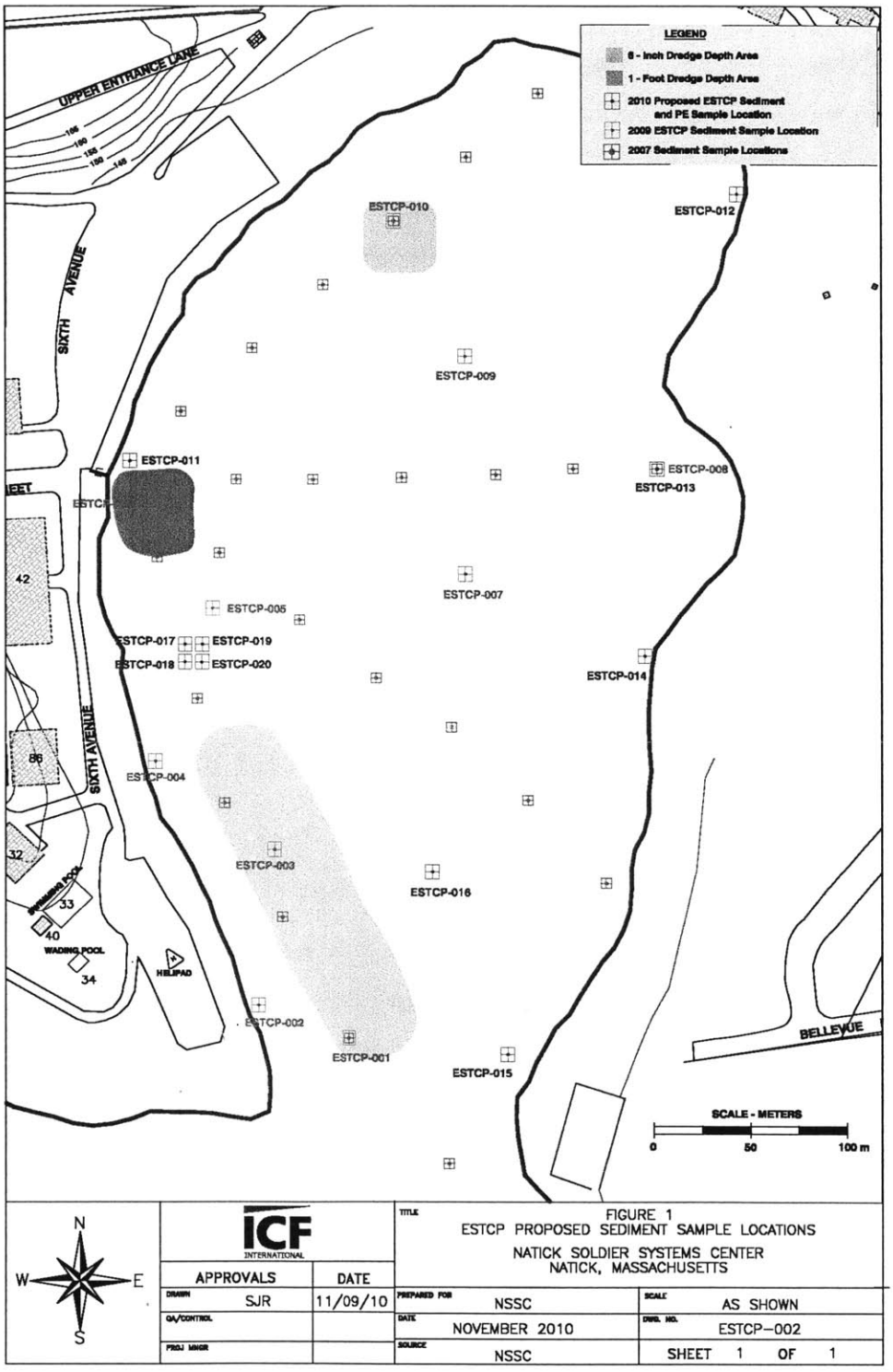


Figure 2-1: Map of sampling sites in Lake Cochituate (Natick, MA) provided by ICF International

Chapter 3

Observation of PRC losses from polyethylene passive samplers and comparison to model

3.1 Introduction

When a polyethylene (PE) passive sampler is placed in contaminated sediment, PCBs begin to diffuse into the sampler. After enough time has passed, the passive sampler equilibrates with the sediment, and porewater concentrations of PCBs can be deduced by extracting the passive sampler and using K_{PEW} to convert PE concentration to porewater concentration. In most situations, however, waiting for equilibrium to be reached is impractical. Consequently, we used performance reference compounds (PRCs) to determine a passive sampler's distance from equilibrium and correct our measurements after a short incubation. We determined a time to incubate the passive samplers so that the method is useful for real world applications but long enough to detect PRC losses beyond measurement error.

To address this issue, we incubated PE passive samplers in two jars of homogenized lake sediment. Strips were removed after 0, 3, 10, 29, 77, and 476 days. The strips were processed according to the method described in Chapter 2. The PRC behavior

over time was compared to expected PRC behavior based on the model by Fernandez et al. (2009)[14] in order to assess the model's predictions in light of observed PRC movement, and an appropriate incubation period was identified.

3.2 Theory

PRCs were introduced by Huckins et al. (1993) [23] to investigate biofouling effects in semipermeable membrane devices (SPMDs). Booij (2003) [10] discussed a one-dimensional diffusion model for polyethylene passive samplers based on SPMD models. Fernandez et al. (2009) [14] noted mass transfer limitations within the sediment bed and compared model results to measurements made using liquid-liquid porewater extractions. We used the mass transfer model introduced by Fernandez et al. (2009) to estimate the behavior of heavier, less mobile PRCs based on data from PCBs 52 and 101. The model predicts PRC behavior based on material properties of the PRC, including K_d, the solid-water distribution ratio (g dry sediment/cm^3 water), using nontraditional units of cm^3 water/cm^3 sediment:

$$K_{d,\,model} = K_d * \rho_s * (1 - \phi) \tag{3.1}$$

where $K_{d,\,model}$ is the sorption coefficient expressed in nontraditional units by the model $\frac{cm^3 H_2O}{cm^3 wet sediment}$,$K_d$ is the traditional sediment distribution coefficient in (cm^3 H_2O/g dry sediment), ρ_s is the sediment density in g/cm^3, and ϕ is the sediment porosity. We iterated over K_d values until the modeled PRC behavior matched observed PRC behavior. Once K_d values had been found for at least two PRC congeners, the K_ds were fit to a line against those PRCs' K_{ow} values. This line was used to obtain estimates of K_d for other congeners where PRC behavior was not known. Then the model was run using these K_ds to estimate the amount of each heavier congener left in the passive sampler. Finally those loss estimates were used to extrapolate observed accumulations of target PCBs in the PE over the finite incubation times up to levels expected at equilibrium. A Matlab code was developed to facilitate this correction

process (Appendix B).

In this work, we compared observed PRC losses during the PE timecourse with model predictions to see if the model adequately described PRC behavior over time.

3.3 Materials and Methods

Sediments from sites 1 and 8 (Figure 2-1) were homogenized and ladled into two 500 mL amber glass jars. PE strips were cut using solvent-rinsed scissors and forceps. The strips were inserted into the sediment in clockwise order. PE strips were removed from the Site 1 jar immediately after insertion and after 3, 10, 29, 77, and 476 days. PE strips were removed from the Site 8 jar immediately and after 5, 8, 27, 75, and 474 days. The strips were extracted and analyzed as described in Chapter 2. The concentrations of PRCs in the PE (ng PRC congner/g PE) were calculated and normalized to the concentrations at time zero (ng PRC congener/g PE) measured in the 0 day strips, which had been briefly inserted into the mud and removed.

3.3.1 Organic and Black Carbon Measurement

Dried sediment samples were ground inside a lab hood in a solvent-rinsed marble mortar and pestle. The samples were sieved (450 μm aperture) and a 10 mg subsample was thinly spread in a crucible and held for 24 hours under air in a Barnstead Thermolyne 47900 muffle furnace at 375°C. The furnace was programmed to slowly increase oven temperature and avoid overshooting. This removed labile organic matter, leaving a black carbon fraction. An Elementar Vario ECIII analyzer was used to measure carbon weight percent. Three to five 10 mg samples were removed from the uncombusted and combusted samples, depending on sediment homogeneity. The samples were transferred to silver capsules and acidified with 100 μL sulfurous acid to remove carbonates. The samples were dried and the capsules were sealed. The measured carbon weight percent in the uncombusted samples was assumed to measure both OC and BC, while the measured carbon weight percent in the combusted sample was operationally defined to measure only BC. CHN response factors were

determined using acetanilide standards (Elemental Microanalysis, Manchester, MA), monitored after every six samples. Acetanilide standard f_{oc} values varied by ± 0.5 ($\pm 1\ \sigma$) from the established value of 71.09 during the run.

3.3.2 Calculations

In addition to the basic calculations described in Chapter 2, modeling the projected PRC load required the sediment porosity (ϕ), fraction of organic carbon present in the sample f_{OC}, PE thickness, octanol-water partition coefficient (K_{ow}), diffusion coefficient of each PCB in PE (D_{pe}), PCB molecular weights, and days of incubation. The sediment porosity was calculated from the percent water content and the solid-water phase ratio by

$$rsw = \frac{1 - \%\ water\ content}{\%\ \text{water content}} \tag{3.2}$$

$$\phi = \frac{\rho_s}{\rho_s + rsw} \tag{3.3}$$

where ρ_s is the solid density assumed here to be 2.5 kg/L and rsw is the ratio of mass of solids to liters of water in the sediment [32].

3.4 Results and Discussion

3.4.1 Sediment Properties

The sediment porosity was found to be 0.88 for site 1 and 0.90 for site 8. The fraction of organic carbon was 0.137 for Site 1 and 0.142 for Site 8, and the fraction of black carbon was 0.0213 for Site 1 and 0.0118 for Site 8.

3.4.2 PRC Losses

As expected, PRC concentrations in the PE declined with increasing time (Figure 3-1). Also, losses of PRCs followed the order: PCB 52 > PCB 101 > PCB 153 > PCB 180, as expected from their relative diffusivities. However, the two sediments

showed quite different behaviors. While about 90 % of the smallest congener, PCB 52, and about 70 % of PCB 101 were lost from both sediments, congener PCB 153 loss to site 1 sediment was about 40 % but lost only 20% into site 8 sediment. This was even more dramatic for the largest congener, PCB 180, which lost to 30% to sediment 1 but only about 5 % to sediment 8. Clearly, some sediment properties play a role in controlling the mass transfers of PCBs to and from PE strips.

3.4.3 Comparison of PRC Losses to Model Predictions

In order to evaluate the behavior of the PCBs we used as PRCs, we used the mass transfer model (described in Ch. 2) with the sediment and chemical properties to calculate expected PRC losses over time to sediments 1 and 8 (lines in Figure 3-1). To provide a quantitative measure of model-data fit, the model-to-measure ratio (modeled result/data) was calculated for each point in time. If the model-to-measure ratio was above 1, more PCB left the PE passive sampler than predicted by the model; if the model to measure ratio was below 1, less PCB left the PE passive sampler than predicted by the model. The model fit the data for congeners 153 and 180 reasonably well, with Site 1 model-to-measure ratios between 0.84–1.07 through Day 77 and rising to 1.5 for Day 476. Site 8 data for PCB 153 and 180 also matched the model closely, with model to measure ratios between 0.84 and 1.25 throughout the 474 day timecourse. Congeners 101 and 52, however, showed much more movement than predicted by the model. Model-to-measure ratios for Site 1 ranged from 1.13–1.58 for the first 77 days and jumped to 3.5 (101) and 6.5 (52) at 476 days, indicating a serious underprediction of PRC movement. Site 8 data was slightly closer to the model, ranging from 0.84–2.05 for the first 77 days and rising to 4.11 and 2.48 at 474 days. The model underpredicted PRC movement at long times for all congeners, but the discrepancy was especially egregrious for the two lightest congeners, 52 and 101. The data followed the general shape of the model, but the observations approached a lower amount of PRCs left in the passive sampler than the model anticipated.

In order to understand what parameters might make the model better fit the observed data, we systematically changed the polyethylene diffusion coefficient D_{pe},

octanol-water partition coefficient K_{ow}, sediment partition constant K_d, and sediment porosity ϕ one at a time and examined the resulting model to measure ratios.

Multiplying the polyethylene diffusion coefficient, D_{pe}, by 100 resulted in no significant change in the model-to-measure ratios (Figure 3-2). This indicates that diffusion through the PE passive sampler is not a limiting factor. The time scale for diffusion from the center of the passive sampler to the edge bordering the sediment ranges from 3–62 days using the unmodified D_{pe} and 0.03–0.63 days after multiplying D_{pe} by 100, with the lightest congeners requiring the shortest diffusion times. The lightest congeners should not be affected by the D_{pe} change since their time scale for diffusion is shorter than all but the first (3 or 5 day) measurement. Yet even the heaviest, slowest congeners showed little changes in model-to-measure ratios, suggesting that diffusion within the PE is not influential in increasing PRC movement beyond model predictions.

Lowering the K_{ow} of each congener by one log unit decreased model to measure ratios to 0.82-2.75 for all congeners during the full time course (476 days) at Site 1 and 0.85-1.76 for the same conditions at Site 8 (Figure 3-3). Although K_{ow} is well characterized compared to other model inputs, it is used to predict K_{PEW}, the polyethylene-water partition coefficient, and K_d, the sediment partition coefficient. The large change produced by altering these paramters suggests that exchange from the sampler into the sediment bed occured to a greater extent in the observed data than predicted by the model. This agrees with the previous observation that diffusion within the passive sampler is not limiting.

Decreasing site porosity ϕ by 10%, the method precision of our percent water content measurement, produced a modest decrease in model-to-measure ratios, but not enough to explain the difference between data and model. Site 1 ratios decreased to 0.83–3.7 from 0.84–4.1, and Site 1 ratios decreased to 0.84–5.98 from 0.84–6.55. Decreasing site porosity would increase the amount of solids in the sediment sample, thereby increasing the amount of organic matter sorbing the PCBs and maintaining low chemical activities in the bed immediately adjacent to the PE. So PRC loss would be increased due to the enhanced PE-organic matter concentration gradient.

Multiplying the sediment-water distribution coefficient (K_d) by 50 lowered the model-to-measure ratios to 0.81–1.77 for Site 1 and 0.69–1.2 for Site 8 (Figure 3-4). The model curves began at 1 and attained a lower long-time value of PRC left in the passive sampler relative to curves with unmodified K_d, so that model to measure ratios decreased dramatically for long time values while the short-time values remained relatively unchanged. K_d is calculated from the sediment porosity, fraction of organic carbon, and the octanol-water partition constant, but the contribution of black carbon was omitted in the model due to its dependency on the PCB porewater concentration:

$$K_{d,\ with\ BC} = f_{oc} * K_{oc} + f_{bc} * K_{bc} * C_w^{(0.7-1)} \tag{3.4}$$

where f_{oc} and f_{bc} are the fraction of organic carbon and black carbon in the sediment (g carbon/g dry sediment), K_{bc} is the black carbon-water partition coefficient determined by Lohmann et al. [26] (μg PCB/g BC)/(μg PCB/mL water)$^{(0.7)}$, K_{oc} is the organic carbon-water partition coefficient determined by Hansen [20] (μg PCB/g OC)/(μg PCB/mL water), C_w is the PCB concentration in the pore water, and 0.7 is the assumed Freundlich exponent. Lohmann et al. determined black carbon-water partition coefficients for four PAHs and four PCBs, including PCB 52, by tumbling contaminated sediments with water and PE passive samplers for up to 6 months. Using their value of 5.9 for logK_{bc} and our measured f_{oc}, f_{bc}, and pore water concentrations for sites 1 and 8, we calculated K_d with and without the BC contribution and took the ratio of the two:

$$\frac{K_{d,\ with\ BC}}{K_{d,\ no\ BC}} = \frac{f_{oc} * K_{oc} + f_{bc} * K_{bc} * C_w^{0.7-1}}{f_{oc} * K_{oc}} \tag{3.5}$$

where C_{iw} is the pore water concentration determined through liquid-liquid extraction (Chapter 4). The K_d with the contribution of black carbon included was 65 times greater than the K_d without black carbon at Site 1 and 30 times greater at Site 8. This suggests that black carbon could have increased our observed K_d by about 50 times at sites 1 and 8, and that black carbon effects could account for our observed model underprediction.

3.4.4 Use of PRC Losses for Small Congeners to Estimate Losses for Larger PCBs

We wanted to incubate our passive samplers until PCB 52 and 101 losses were greater than method precision, around 20%. At both sites, PCB 52 lost 20% of its original load after 10 days. The measured PCB 153 loss approached 20% of the original load at 10 days for both sites, but did not increase above 20% until the final 476 day time point. Based on the diffusion model, we believed that the PRC concentration must always decrease with time and that the hovering of PCB 153 around 20% loss did not reflect real behavior. When determining method precision (Chapter 4), we incubated our PE passive samplers for 39 days based on the PE timecourse results, and found that the average amount of PCB 153 loss after 39 days was 41% of its original load for Site 1 and 44% for Site 8, suggesting that incubation times around 1 month were an appropriate choice for Sites 1 and 8.

3.5 Recommendations

PRCs are a useful way to detect a passive sampler's approach to equilibrium, so that long incubations are unnecessary. A PRC loss model can be used to aid experiment design as well as inform our understanding of passive sampler behavior.

To test the model given by Fernandez et. al. (2009) [14] and determine an appropriate incubation time for the passive samplers in future experiments (Chapter 4), we conducted a time course of PE samplers in homogenized sediment from two different sites. A 39 day incubation period was chosen based on observed PRC losses. At long times, the model's predictions showed much less PRC loss than observed for PCBs 52 and 101.

We investigated possible causes of this underprediction of PRC movement by altering model inputs and examining the changes in model to measure ratios. Diffusion within the PE did not significantly affect model results, suggesting that PRC movement from the sampler into the sediment is underpredicted. This may be due to the

effects of black carbon, which were not included in the model due to the complex nature of this correction. Investigation of black carbons effect on K_d for PCB 52 by calculating the K_d at sites 1 and 8 with black carbon effects included suggests that black carbon could reasonably have accounted for the underprediction of PRC loss.

Site 1 days	3	10	29	77	476
data (52)	0.67	0.67	0.57	0.55	0.10
data (101)	0.69	0.85	0.84	0.82	0.23
data (153)	0.92	0.98	0.98	0.91	0.61
data(180)	1.19	1.13	0.99	1.00	0.67
no change (52)	1.41	1.41	1.58	1.15	6.55
no change (101)	1.42	1.15	1.14	1.13	3.51
no change (153)	1.07	1.01	1.01	1.06	1.50
no change(180)	0.84	0.88	1.00	0.98	1.42
Kd*50 (52)	1.09	1.02	0.92	0.69	1.77
Kd*50(101)	1.26	0.99	0.87	0.74	1.51
Kd*50(153)	1.02	0.94	0.89	0.86	0.95
Kd*50(180)	0.81	0.85	0.94	0.88	1.09
Dpe*100 (52)	1.41	1.41	1.58	1.51	6.54
Dpe*100(101)	1.42	1.15	1.14	1.13	3.51
Dpe*100(153)	1.07	1.01	1.01	1.06	1.50
Dpe*100(180)	0.84	0.88	1.00	0.98	1.42
Kow-1 (52)	1.22	1.18	1.15	0.94	2.75
Kow-1(101)	1.33	1.05	0.98	0.89	2.09
Kow-1(153)	1.04	0.97	0.94	0.95	1.15
Kow-1(180)	0.82	0.86	0.97	0.92	1.23
phi*0.9 (52)	1.39	1.39	1.53	1.45	5.98
phi*0.9 (101)	1.41	1.14	1.13	1.11	3.35
phi*0.9 (153)	1.07	1.01	1.00	1.05	1.47
phi*0.9 (180)	0.84	0.88	1.00	0.98	1.40

Table 3.1: Site 1 Model to Measure Ratios

Site 8 days	5	8	27	75	474
data (52)	0.97	0.60	0.59	0.41	0.16
data (101)	0.98	0.83	0.82	0.85	0.33
data (153)	0.67	0.90	1.04	1.15	0.78
data(180)	1.07	0.80	0.82	1.00	0.93
no change (52)	0.98	1.56	1.53	2.05	4.11
no change (101)	0.99	1.17	1.17	1.09	2.48
no change (153)	0.93	1.10	0.94	0.84	1.17
no change(180)	0.93	1.25	1.20	0.98	1.02
Kd*50 (52)	0.77	1.15	0.91	0.95	1.09
Kd*50(101)	0.89	1.01	0.90	0.73	1.14
Kd*50(153)	0.88	1.03	0.84	0.69	1.09
Kd*50(180)	0.91	1.20	1.13	0.89	0.75
Dpe*100 (52)	0.98	1.56	1.13	2.04	4.10
Dpe*100(101)	0.99	1.17	1.17	1.09	2.48
Dpe*100(153)	0.93	1.10	0.94	0.84	1.17
Dpe*100(180)	0.93	1.25	1.20	0.98	1.03
Kow-1 (52)	0.85	1.31	1.13	1.29	1.76
Kow-1(101)	0.93	1.08	1.01	0.86	1.50
Kow-1(153)	0.90	1.06	0.88	0.75	0.91
Kow-1(180)	0.92	1.22	1.16	0.93	0.89
phi*0.9 (52)	0.97	1.54	1.49	1.95	3.70
phi*0.9 (101)	0.99	1.16	1.15	1.07	2.36
phi*0.9 (153)	0.93	1.10	0.94	0.83	1.14
phi*0.9 (180)	0.93	1.24	1.20	0.98	1.01

Table 3.2: Site 8 Model to Measure Ratios

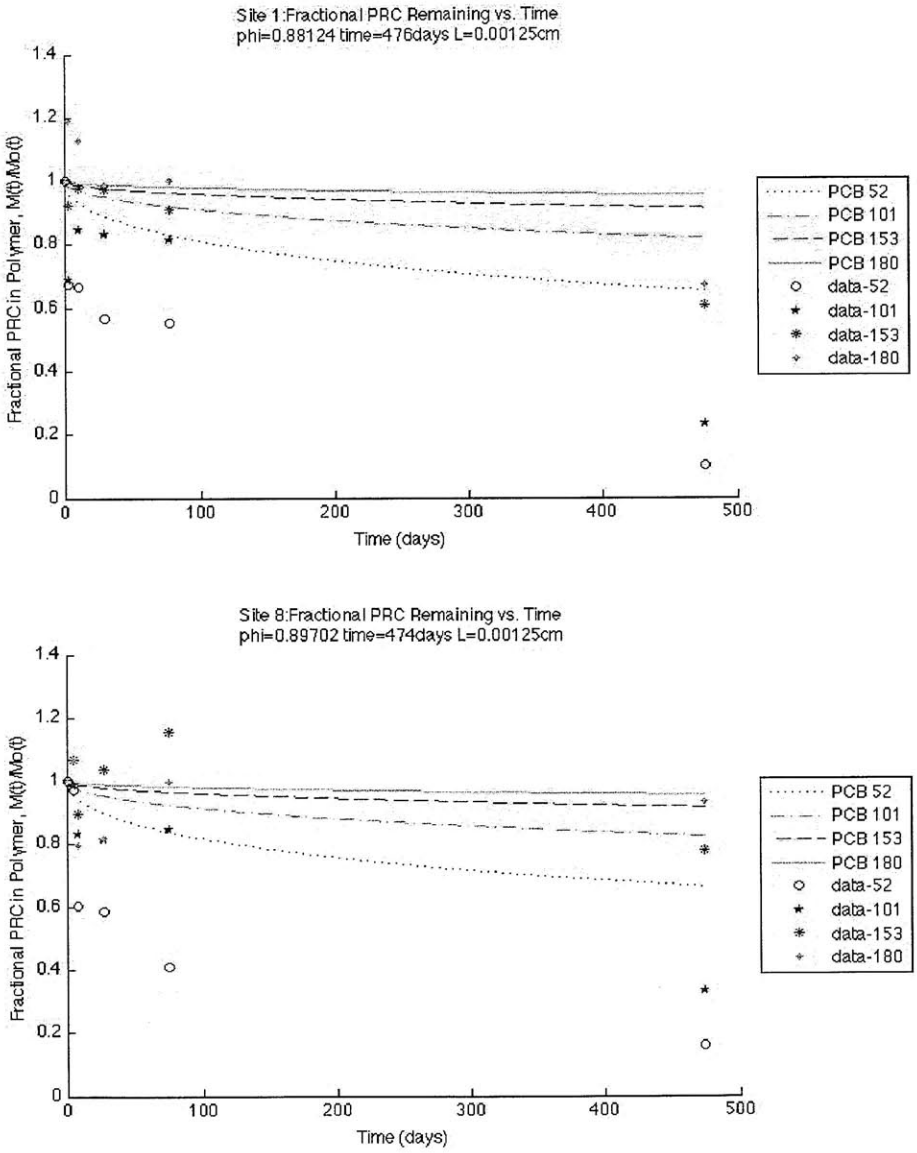


Figure 3-1: Modeled PRC behavior and measured data for PCB 52, 101, 153, and 180 at Sites 1 (a) and 8 (b)

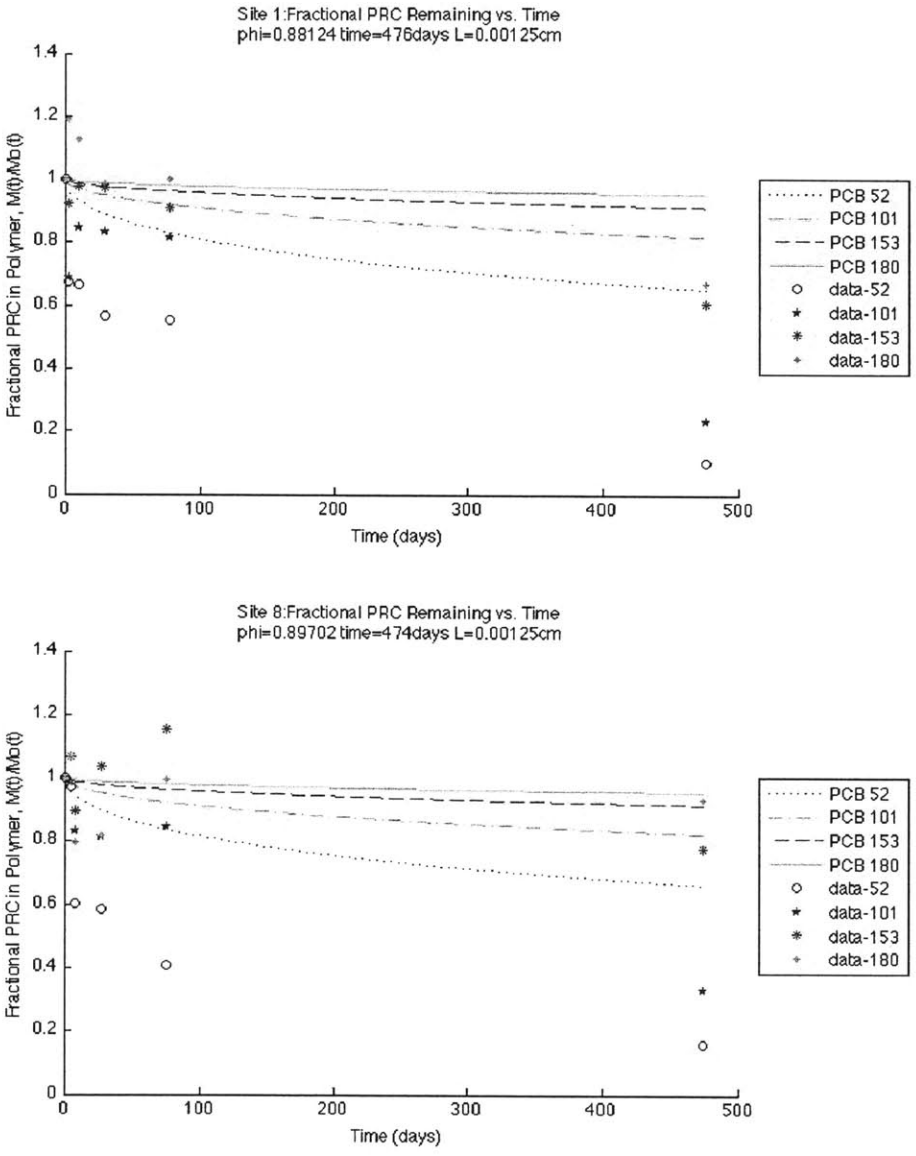


Figure 3-2: Modeled PRC behavior (D_{pe} multiplied by 100) and measured data for PCB 52, 101, 153, and 180 at Sites 1 (a) and 8 (b)

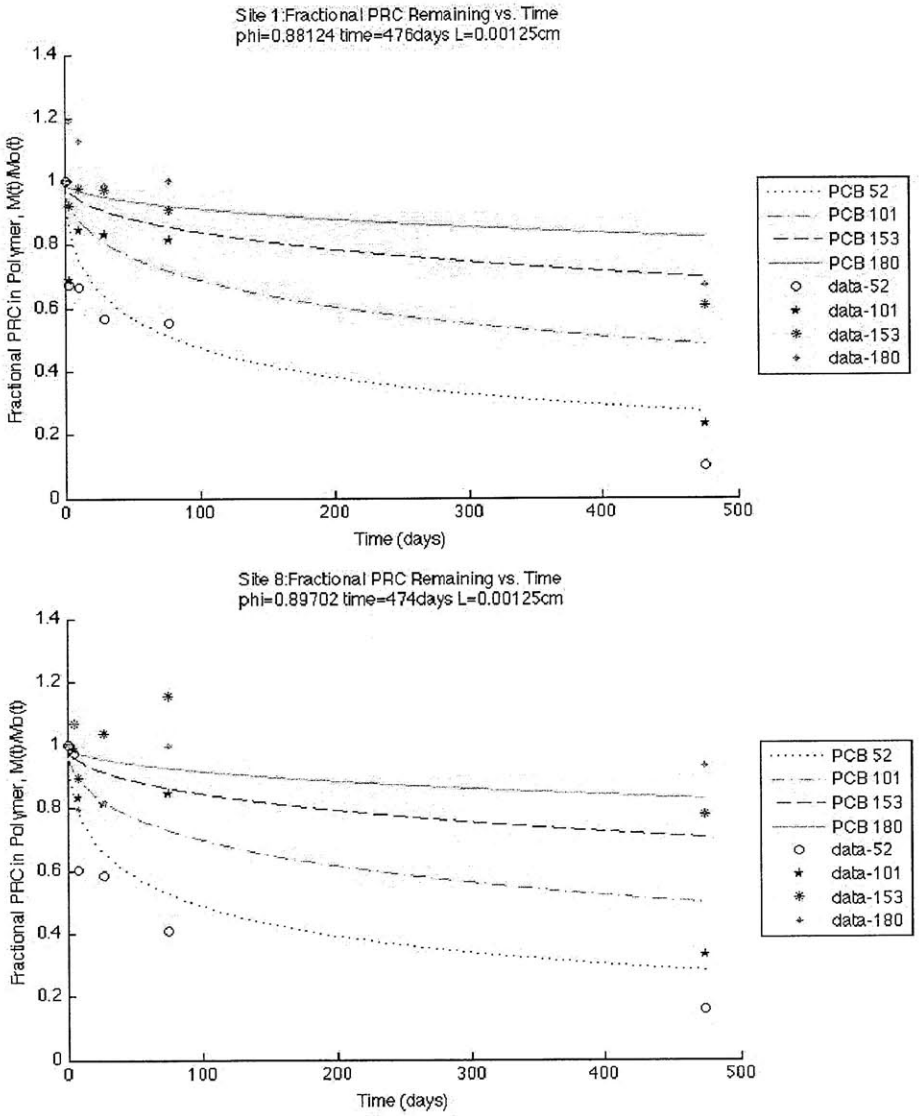


Figure 3-3: Modeled PRC behavior (K_{ow} decreased by 1 log unit) and measured data for PCB 52, 101, 153, and 180 at Sites 1 (a) and 8 (b)

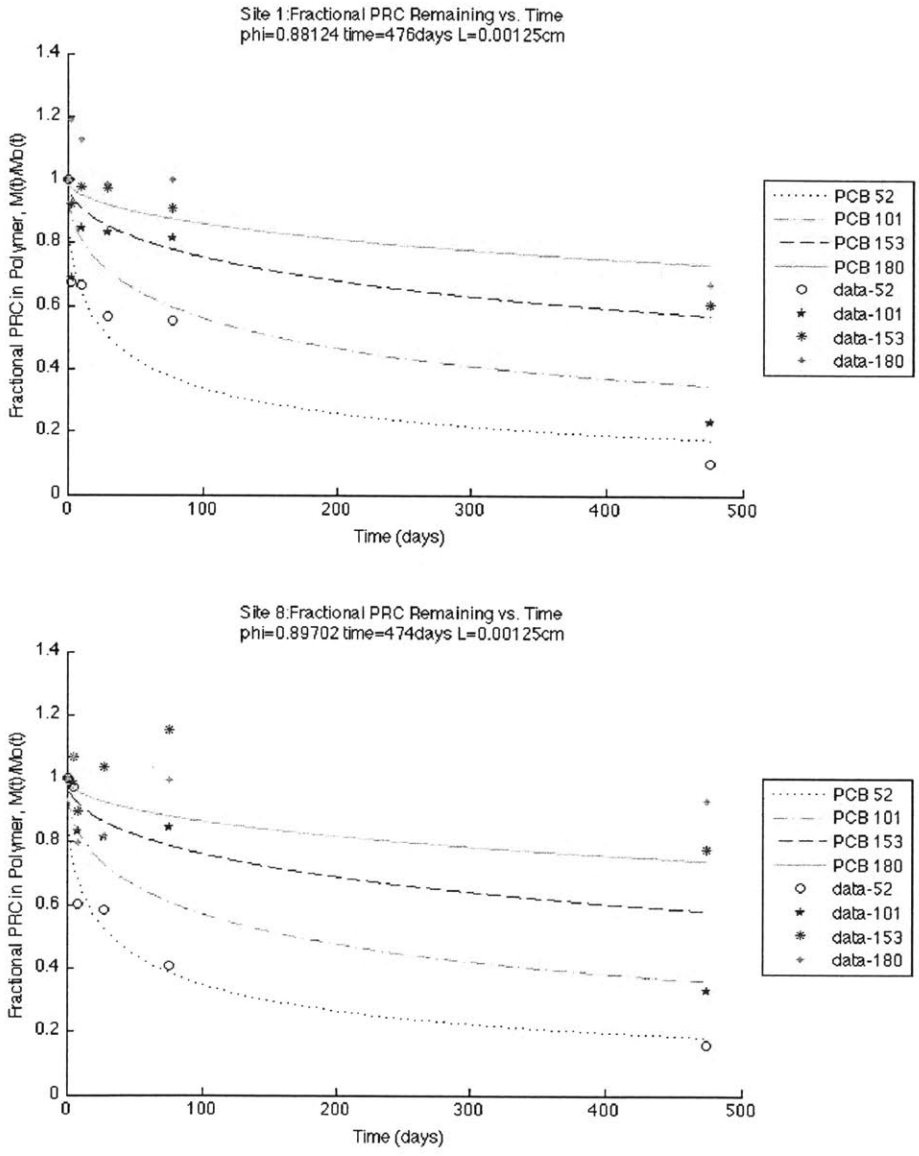


Figure 3-4: Modeled PRC behavior (K_d multiplied by 50) and measured data for PCB 52, 101, 153, and 180 at Sites 1 (a) and 8 (b)

Chapter 4

QA/QC investigation of polyethylene passive samplers

4.1 Introduction

Given the promising results of previous PE passive sampler deployments [15] [14] [33] [28] and the desire for a fast, low-cost sampling method for sediment PCB contamination, we wanted to characterize relevant data quality metrics and to encourage industry use of PE passive samplers. Using EPA's guidelines for method development and validation [5], we sought to quantify the method's precision, accuracy, and minimum detection limit.

Hence, passive samplers were incubated in blank and field sediments and analyzed using GCMS to obtain data needed to determine the precision and method detection limit (MDL) of the PE passive sampler method. The method accuracy was examined by incubating PE passive samplers with known sediment concentrations of PCBs. Some PE passive samplers were sent to Pace Laboratories (Minneapolis, MN) for analysis in order to demonstrate that our analytical methods were consistent with those of a contract laboratory. By involving ICF International in sediment sample collection and Pace Laboratories in sample analyses, we sought to begin involving industry representatives in PE passive sampler use.

4.2 Theory

4.2.1 Precision

Precision (repeatability) was calculated from the standard deviation and mean of a set of replicate samplers incubated under the same conditions:

$$precision = \frac{standard\ deviation}{mean} * 100 \tag{4.1}$$

The EPA guidelines for method development and validation suggest that at least seven replicates should be used when determining method precision [5]. Hence, we calculated the method precision using sets of at least eight replicates placed in two different PCB-contaminated sediments which were also spiked at four levels (none, 0.1 ppm, 1.0 ppm, and 10 ppm of Aroclor 1260).

4.2.2 Method Detection Limit

The method detection limit (MDL) was identified by Kaiser (1965) as the the minimum concentration of a substance that can be measured with 99% confidence that the analytic concentration is greater than zero [17]. MDL estimation techniques comprise two categories: those techniques based on a single concentration response and those based on the response to multiple concentrations in the expected MDL range. MDL estimation techniques based on multiple concentrations are preferable because the method variance may be proportional to concentration.

Therefore, we used the Hubaux and Vos (1970) method, a graphical method based on multiple concentrations [17]. PE passive samplers were incubated in purchased sediment containing no PCBs (RT Corp, Laramie, WY). Samples of this sediment were spiked with PCBs at three levels (0.3, 3, and 30 ppm Aroclor 1260; 30 ppm corresponds to 0.2 ppm PCB 52, 2 ppm PCB 101, 3 ppm PCB 153, and 2 ppm PCB 180) within the expected MDL range. PE strips were also incubated in this material. After incubation for 31 days, the amount of target compounds present in the PE passive samplers was measured using the extraction and GCMS analyses described

in Chapter 2.

The measured PE passive sampler responses (ng each individual congener/gPE) were plotted against the known sediment PCB spike (ng/g dry sediment) and fitted to a line. 99% confidence intervals were constructed using the slope and intercepts of the best fit line. The critical level is defined as the value (ng/gPE) of the upper prediction limit at zero sediment concentration (Figures 4-4, 4-5, 4-6, 4-7). If a PE passive sampler is found to contain PCBs above this level, we can be 99% confident that the corresponding sediment concentration is not zero; if the PE passive sampler is found to have a concentration below the critical level, we cannot say with 99% confidence that the corresponding sediment concentration "detectable". The MDL, or minimum sediment concentration which, when measured, will produce a PE passive sampler concentration greater than the critical level with 99% confidence is the x-coordinate of the intersection between y (ng/g PE)= L_c (the confidence level) and the lower prediction limit.

4.2.3 Accuracy

A method may be precise without being accurate. Without knowledge of the relationship between measured PE passive sampler concentrations and the true concentration of PCBs in the sediment, we may precisely measure concentrations that are meaningless for real world applications. In order to determine the accuracy of our method, we incubated PE passive samplers with sediment at four known PCB concentrations. The concentrations of target PCBs in the PE passive sampler after incubation were measured and plotted against the known sediment concentration. The concentration of PCBs in the passive sampler should go up linearly with sediment concentration. If target PCBs in the passive sampler corresponded to the known sediment concentration in a 1:1 manner, the PE passive sampler would be accurate; if they do not correspond, the relationship may be used to infer sediment concentration from PE passive sampler data.

4.3 Materials and Methods

4.3.1 Determination of Method Precision

Sediment from Lake Cochituate sites 1 and 8 was collected by ICF International as described in Chapter 2. The sediment was brought back to MIT and homogenized according to the method in Chapter 2. The sediment was ladled into four quart jars. Three quart jars were spiked with Aroclor 1260 at levels of 0.082 μg/g dry weight, 0.86 μg/g dry weight, and 8.6 μg/g dry weight (Site 1) and 0.11 μg/g dry weight, 1.19 μg/g dry weight, and 11.9 μg/g dry weight (Site 8). The fourth jar for both sites was left with no introduced Aroclor 1260 except for a preexisting background signal, which was measured via pore water extraction and accelerated solvent extraction with GCMS analysis. Since Aroclor 1260 is a mixture of many PCB congeners, we chose four congeners of varying chlorination (PCBs 52, 101, 153, and 180) to quantitate and discuss. PCBs 52, 101, 153, and 180 comprise 0.56%, 5.02%, 10.8%, and 7.12% of Aroclor 1260, respectively [31]. The sediment spike levels for these congeners are given in Tables 4-1 and 4-2. After tumbling for 14 days, the contents of each quart jar were divided between four 120 mL glass jars, stirring 30 seconds between each scoop. Three PE strips of about 2 cm by 5.5 cm, 25 μm thick, and weighing about 15 mg were placed into each sediment jar, resulting in twelve PE strips sampling each concentration of spiked sediment. These strips were incubated for 39 days. Two strips from each sediment jar were removed from the sediment, rinsed with deionized water, and placed in a dry 7-ml vial. The vial threads were covered with PTFE tape and the closed vial cap was secured with laboratory tape. The vials were wrapped in bubble wrap and sent via FedEx to Pace Laboratories (Minneapolis, MN) for analysis.

Six strips that were never inserted into the sediments were also placed directly into dichloromethane (DCM). Four "zero day" strips were dipped into the sediment at each site and immediately removed and rinsed. These zero day strips were compared to the strips with no sediment contact to determine if the brief sediment contact had any effect on target compound load.

During analysis, some PE passive sampler extracts were spilled or dried during

concentration, and data could not be recovered. However, at least eight out of ten replicates were obtained for each sediment site and spiking level.

4.3.2 Determination of Method Detection Limit

The sediment from Sites 1 and 8 contained a background level of PCBs, which was measured via porewater extraction and accelerated solvent extraction with GCMS analysis. We also wanted to determine the method detection limit using sediment that did not contain PCBs other than those introduced by our spike. Dried clean sediment was purchased from RT Corporation (Laramie, WY) and rehydrated before spiking and tumbling. The dry sediment was placed in a clean glass jar and weighed. Water was added until the water level reached the top of the sediment. The sediment was stirred to distribute the water evenly throughout the sediment. The sediment-water mixture was left to equilibrate overnight. After equilibration, the sediment was distributed between four smaller glass jars and spiked at 0, 0.3, 3.3, and 30 μg Aroclor 1260/g dry sediment using the procedure described in Chapter 2. The jars were tumbled for 15 days. Four PE samplers measuring about 2 cm by 4 cm, 25 μm thick, and weighing around 10 mg were inserted into each jar using DCM-rinsed steel forceps as described in Chapter 2. The samplers were incubated for 31 days. Three PE samplers that were never inserted into the sediments were also collected and inserted directly into DCM at the beginning of these incubations.

After incubation, the passive samplers were removed from the sediment, extracted, and analyzed as described in Chapter 2. Briefly, the strips were rinsed with water and extracted with DCM. Recovery standards (PCBs 19, 77, 105, 167, 170, and 194) were added at the beginning of the extraction. The extracts were concentrated under nitrogen gas and transferred to vials for GCMS analysis. Injection standards (PCBs 47, 111, 153, and 178) were added to the vials before running on the GCMS. Standards with known PCB concentrations and pure DCM were run every 5-8 samples to evaluate PCB response factors and background noise at retention times of interest, respectively.

4.4 Results and Discussion

4.4.1 Calculation of Method Precision

Precision was calculated for each sediment site and spike level. Relative errors (i.e., standard deviations divided by means) generally came out around 20% (Tables 4-3 and 4-4). These precision results did not show any trend regarding sediment spike level or PCB congener. Since the precision calculated from five repeat runs of injection and recovery standards was around 15-20%, the observed 20% variation would be expected given our injection and instrument variability.

Correction with PRCs decreased method precision (Table 4-5). The amount of PRCs remaining in the strip relative to the amount of PRCs in the strip with no incubation (0 days) had precision around 20%, but correction of the corresponding target PCBs (e.g., PCB 52 using ^{13}C-labeled PCB 52) by this value increased method precision to 30%-145% (Table 4-5). At first glance, some diminished precision is to be expected as the corrected concentrations use two inputs, both of which have a certain degree of imprecision. Method precision after correction generally increased with increasing congener chlorination. Since the PRC correction (Chapter 2) divides the uncorrected value by one minus the normalized PRC load, variations in normalized PRC load will cause large swings in the correction value if the PRC load is close to 1 (see Table 4-6), as it is for the more chlorinated congeners. Although the uncorrected method precision is promising, the large method precisions seen when correcting with PRCs are undesirable. In order for the value of heavier PRCs to be projected from two lighter congeners, the PE passive samplers must be incubated for long enough for the PRCs to lose at least 20% of their value. However, longer incubation times may be desired in order to encourage loss of the heavier PRCs in the sampler and decrease method precision.

When preparing the passive samplers for incubation, six strips were placed directly into DCM and four strips were briefly dipped into the sediment, cleaned, and then placed into DCM. All strips were then extracted and analyzed following the method in Chapter 2. When integrating the peaks resulting from GCMS analysis, both strips

that had never contacted sediment and those that had briefly contacted sediment did not produce peaks above a background level.

4.4.2 Comparison to Pace Laboratories

In addition to investigating method precision, two PE passive samplers from each sediment matrix/spiking level were removed from the sediment after incubation, cleaned, and sent to Pace Laboratories (Minneapolis, MN) for analysis. The average MIT ng/g PE measured from at least 8 replicates was plotted against the average Pace ng/g PE using two replicates. A 1:1 line was plotted for reference (Figures 4-1, 4-2). The MIT and Pace values agreed within 20% error except for congener 52; mean MIT values divided by the mean Pace values were 2.3±0.5, 1.2±0.2, 1.1±0.2, and 0.90±0.2 for congeners 52, 101, 153, and 180, respectively. It is not clear why these ratios increase for smaller congeners, although this result may indicate a loss of smaller congeners during solvent evaporation at Pace.

4.4.3 Investigation of Method Accuracy

In order to determine the accuracy of the PE passive sampler method, we incubated PE passive samplers in purchased clean sediment with four known amounts of PCBs added. The amount of PCB 52 present in the PE strip was corrected with PRCs to deduce the equilibrated PE concentrations. These were converted to corresponding porewater levels (ng/L porewater) using K_{PEW} and the calculations described in Chapter 2. The passive samplers did not lose enough heavier PRCs (101, 153, and 180) to correct using PRC movement. We believe that the low PRC loss may be due to the low f_{oc} of this sediment (1.16% vs. 14% for sites 1 and 8). Lowering the f_{oc} input in the model by Fernandez et al (2009) [14] lowered PRC loss estimations. Using our measured f_{oc} and sediment porosity (0.9), the two lightest PRCs would be expected to approach 20% loss around 75 days of incubation, longer than our 31 day incubation. The modeled losses for 31 days of incubation were 0.82, 0.91, 0.96, and 0.98 respectively for PCB 52, 101, 153, and 180. This provided a compelling example

of such a model's utility when designing a passive sampler experiment.

The known spike of PCBs added to the sediment matrix was converted to ng/L porewater using the fraction of organic carbon f_{oc} and the organic carbon-water partition coefficent K_{oc}:

$$\frac{ng_{PCB}}{mL_{porewater}} = \frac{ng_{PCB}}{g_{dry\ sed} * f_{oc} * K_{oc}} \tag{4.2}$$

where f_{oc} is the fraction of organic carbon in the sediment (g OC/g dry sediment), K_{oc} is the organic carbon-water partition constant (ml water/g OC), and $f_{oc} * K_{oc}$ is an estimate of the sediment distribution coefficient K_d without the effects of black carbon. The pore water concentration found from PE was plotted against the pore water concentration deduced from the sediment spike, and fitted to a regression line (Figure 4-3):

$$\frac{ng_{PCB\ 52}}{L_{pore\ water\ from\ PE}} = 0.1074 * \frac{ng_{PCB\ 52}}{L_{pore\ water\ from\ spike}} + 0.3583 \tag{4.3}$$

The slope was 0.1074±0.07 and the interecept was 0.3583±2 (95% confidence bounds). The pore water concentrations deduced from the sediment spike were about 10 times greater than the pore water concentrations deduced from the PE passive samplers. As noted in Chapter 3, this supports the need to include the effects of black carbon in the sediment equilibrium partitioning correction. The resulting increase in K_d would decrease the concentration deduced from the sediment spike, so the elevated pore water levels are not unexpected.

4.4.4 Calculation of Method Detection Limit

The MDL was calculated using the method of Hubaux and Vos [18]. A linear regression on the data was done in Matlab, and 99% prediction intervals were calculated and plotted (Figures 4-4, 4-5, 4-6, 4-7). The MDL was obtained graphically by finding the point where the upper prediction interval intersected the y-axis, and following a horizontal line drawn through that point to its intersection with the lower confidence

interval. The x value of this intersection point is the MDL. The MDL was found to be 77 ng/g dry sediment for PCB 52, 720 ng/g dry sediment for PCB 101, 1100 ng/g dry sediment for PCB 153, and 900 ng/g dry sediment for PCB 180. Using the fraction of organic carbon in the sediment, 0.0116, and the organic carbon-water partition coefficient of Hansen [20], these MDLs correspond to 42 ng/L, 103 ng/L, 61 ng/L and 33 ng/L respectively for PCBs 52, 101, 153, and 180. Because these MDLs were calculated using the uncorrected amount of target compound in the PE passive sampler, they are specific to the sediment and incubation time used. When investigating the accuracy of PE passive samplers, we found that pore water concentrations calculated from the sediment spike were consistently about 10 times higher than pore water concentrations deduced from PE passive samplers. In Chapter 5, we found that PE passive sampler results matched directly measured pore water concentrations within a factor of 2. It is possible that since the equilibrium partitioning used to calculated ng/L pore water from the known sediment spike did not account for black carbon, the results are about 10 times higher than directly measured pore water results. In this case, the MDLs for our method would be 4.2 ng/L, 10.3 ng/L 6.1 ng/L, and 3.3 ng/L respectively for PCBs 52, 101, 153, and 180.

4.5 Recommendations

Although PE passive samplers are appealing, such a new method must be able to demonstrably meet quality control standards in order to be transferred to practitioners outside the developer's lab. We investigated data quality measures such as method precision, accuracy, method detection limit, and consistency with a contract laboratory. The method precision results before PRC correction of $\pm 20\%$ suggest that PE passive samplers should be incubated until the lightest PRCs have lost 20% of their original PRC load, so that we are confident loss has occurred. After PRC correction, precision results increased, with the greatest increases seen for the most chlorinated congeners. The PRC correction approaches infinity as PRC levels normalized to the original load approach 1, so small variations in normalized PRC levels for congeners

that show little movement during the incubation period produce large variations in corrected target compound concentration. We suggest PE passive samplers should be deployed until PRC losses of at least two or three PRCs is greater than 20% to ensure that the PRCs-based corrections for target HOCs will be trustworthy. This would require less than 30 days for the sediments used here, but could be longer for sediments with low amounts of organic carbon and black carbon (Table 4-7), as in our experience with a certified clean sediment. Incubating for long periods of time, so that the slowest PRCs have time to move out of the passive sampler, would result in smaller method precision after correction. Since shorter times are desirable in real-life measurement situations, we suggest using thinner polyethylene strips or a different type of polymer that allows faster PRC diffusion for sites where incubation times are an issue.

Two replicate samplers from eight sample sets of at least ten replicates each were sent to Pace Laboratories (Minneapolis, MN) for analysis. The Pace sampler results matched the MIT sampler results within 20% measurement error except for PCB 52, which was consistently lower in the Pace results than MIT measurements. This may reflect a negative method bias at Pace or a positive bias at MIT.

The method accuracy was investigated by spiking a purchased clean sediment with three known amounts of PCBs. The sediment was incubated with PE passive samplers, and pore water concentrations were deduced from the samplers and from the known sediment spike using equilibrium partitioning. The pore water concentrations deduced from the sediment spike were about 10 times higher than the concentrations measured with the PE passive samplers when one assumes a K_d given by $f_{oc} * K_{oc}$. However, the equilibrium partitioning correction for the sediment spike did not include the effects of black carbon, which would decrease the deduced pore water concentrations.

Method detection limits ranged from 4.6 ng/L to 10.3 ng/L, depending on the PCB congener under investigation. These MDLs were calculated using the amount of target compound in the PE passive sampler before correction for PRCs, and are therefore specific to the sediment and incubation time used.

Site 1	25 ug/289.7 g	250 ug/291.7 g	2500 ug/289.7 g
PCB 52	0.0004830	0.00480	0.0483
PCB 101	0.00433	0.0430	0.433
PCB 153	0.00932	0.0926	0.932
PCB 180	0.00614	0.0610	0.614

Table 4.1: Spiked concentrations of PCB 52, 101, 153 and 180 at Site 8

Site 8	25ug/225g	250ug/210g	2500ug/210g
PCB 52	0.000625	0.00483	0.0667
PCB 101	0.00560	0.0433	0.598
PCB 153	0.0121	0.0932	1.29
PCB 180	0.00795	0.0614	0.848

Table 4.2: Spiked concentrations of PCB 52, 101, 153 and 180 at Site 8

	0 μg/323.3g	25 μg/289.7g	250 μg/291.7g	2500 μg/289.7g
PCB 52	17.5%	30.6%	28.5%	20.3%
PCB 101	15.9%	27.1%	28.7%	19.8%
PCB 153	13.9%	27.2%	28.5%	21.5%
PCB 180	19.3%	34.6%	29.0%	21.9%

Table 4.3: Site 1 precision for at least eight replicates at four μg Aroclor 1260/g dry sediment spike levels

	0 μg/250g	25 μg/225g	250 μg/210g	2500 μg/210g
PCB 52	20.5%	26.6%	12.0%	22.1%
PCB 101	19.6%	24.2%	11.4%	21.4%
PCB 153	18.2%	26.8%	12.9%	22.0%
PCB 180	21.0%	21.9%	14.4%	22.7%

Table 4.4: Site 8 precision for at least eight replicates at four μg Aroclor 1260/g dry sediment spike levels

Site 1: No Spike (PCB 52) Sampler #	ng/gPE	PRCs/0 day	Corrrected ng/gPE	ng/L porewater
1	72.90	0.37	116.10	0.32
2	78.26	0.41	131.87	0.37
3	90.68	0.50	180.33	0.50
4	90.15	0.43	158.12	0.44
5	114.23	0.51	233.57	0.65
6	86.19	0.45	155.74	0.43
7	91.15	0.42	156.89	0.44
8	98.36	0.52	203.90	0.57
9	83.07	0.39	135.09	0.38
10	57.65	0.16	68.50	0.19
precision	17.53339604	24.97072147	29.94053794	29.94053794

Site 1: No Spike (PCB 101) Sampler #	ng/gPE	PRCs/0 days	Corrrected ng/gPE	ng/L porewater
1	116.56	0.54	251.16	0.20
2	117.13	0.64	324.02	0.26
3	134.00	0.87	1012.17	0.82
4	124.36	0.82	678.54	0.55
5	125.65	0.82	710.22	0.57
6	158.80	0.82	863.51	0.70
7	117.08	0.64	324.17	0.26
8	109.10	0.71	375.67	0.30
9	135.21	0.60	335.52	0.38
10	83.70	0.25	111.76	0.09
precision	15.91590715	27.62205088	59.32040492	58.7798535

Site 1: No Spike (PCB 153)	ng/gPE	PRC loss/time0	Corrrected ng/gPE	ng/L porewater
1	248.65	0.81	1297.46	0.30
2	267.59	0.88	2265.75	0.53
3	264.48	0.96	6612.09	1.54
4	252.82	0.94	4413.82	1.03
5	266.20	0.94	4834.66	1.13
6	301.51	0.94	5243.71	1.22
7	255.27	0.87	1979.75	0.46
8	216.40	0.90	2207.94	0.51
9	298.27	0.78	1380.40	0.32
10	181.47	0.34	274.13	0.06
precision	13.91274859	22.12818838	67.86106663	67.86106663

Site 1: No Spike (PCB 180) Sampler #	ng/gPE	PRC loss/time 0	Corrrected ng/gPE	ng/L porewater
1	86.21	0.93	1150.69	0.10
2	115.68	0.96	2513.11	0.22
3	113.16	0.99	7880.26	0.67
4	120.05	0.98	5785.47	0.49
5	116.96	0.98	5871.59	0.50
6	106.58	0.98	5114.01	0.43
7	95.23	0.95	1960.23	0.17
8	76.52	0.96	2107.92	0.18
9	120.06	0.91	1401.10	0.12
10	65.83	0.45	119.41	0.01
precision	19.29203679	17.97734004	75.25973698	75.25973698

Site 8: No Spike (PCB 52) Sampler #	ng/gPE	PRCs/0 days	Corrrected ng/gPE	ng/L porewater
1	211.79	0.41	357.91	1.00
2	245.53	0.49	476.93	1.33
3	199.61	0.25	265.09	0.74
4	276.58	0.49	541.97	1.51
5	193.77	0.23	253.24	0.71
6	186.72	0.41	314.90	0.88
7	277.31	0.43	489.24	1.37
8	197.41	0.38	319.03	0.89
9	154.03	0.34	234.77	0.66
10	161.47	0.29	227.35	0.63
precision	20.52441358	24.54188244	33.10220724	33.10220724

Site 8: No Spike (PCB 101) Sampler #	ng/gPE	PRCs/0 days	Corrrected ng/gPE	ng/L porewater
1	161.62	0.67	494.42	0.40
2	209.84	1.05	*PRCs above 1*	
3	165.98	0.56	380.23	0.31
4	218.25	0.94	3361.63	2.71
5	147.52	0.40	247.54	0.20
6	154.67	0.74	587.02	0.47
7	218.20	0.72	789.28	0.64
8	159.14	0.69	521.62	0.42
9	129.94	0.47	243.86	0.20
10	134.92	0.57	311.55	0.25
precision	19.62402181	29.22596912	128.1040847	128.1040847

Site 8: No Spike (PCB 153) Sampler #	ng/gPE	PRCs/0 days	Corrrected ng/gPE	ng/L porewater
1	176.56	0.81	949.78	0.22
2	238.51	1.06	*PRCs above 1*	
3	162.95	0.61	418.16	0.10
4	217.59	0.98	11573.74	2.69
5	163.82	0.66	487.01	0.11
6	179.05	0.80	885.22	0.21
7	204.84	0.91	2218.34	0.52
8	156.49	0.96	3811.15	0.89
9	133.27	0.60	329.37	0.08
10	152.10	0.92	1810.74	0.42
precision	18.21040223	19.62833318	143.4332197	143.4332197

Site 8: No Spike (PCB 180) Sampler #	ng/gPE	PRCs/0 days	Corrrected ng/gPE	ng/L porewater
1	79.40	0.93	1096.42	0.09
2	89.75	1.10	*PRCs above 1*	
3	67.11	0.83	388.18	0.03
4	82.28	0.99	12317.91	1.04
5	63.05	0.86	438.06	0.04
6	63.34	0.92	795.77	0.07
7	108.58	0.97	3184.12	0.27
8	72.81	0.99	4932.65	0.42
9	56.09	0.82	309.19	0.03
10	65.31	0.97	2113.51	0.18
precision	20.97723582	9.208489295	138.4362346	138.4362346

Table 4.5: PRC correction and precision calculations for sites 1 and 8 at four spike concentrations

PRCs/time 0	PRC correction	error of correction	error of corrected ng/g PE
0.3	1.43	0.12	21.73
0.4	1.67	0.22	23.95
0.5	2	0.4	28
0.6	2.5	0.75	36.05
0.7	3.33	1.55	76
0.8	5	4	80
0.9	10	18	180
0.95	20	76	380
0.99	100	1980	1980

Table 4.6: Error propagation for PRC correction

Site number	porosity	foc	fbc
1	0.88	0.14	0.0213
8	0.90	0.14	0.0118
Clean	0.91	0.0116	0.00228

Table 4.7: f_{oc}, f_{bc}, and porosity (ϕ) for sites 1, 8, and clean sediment

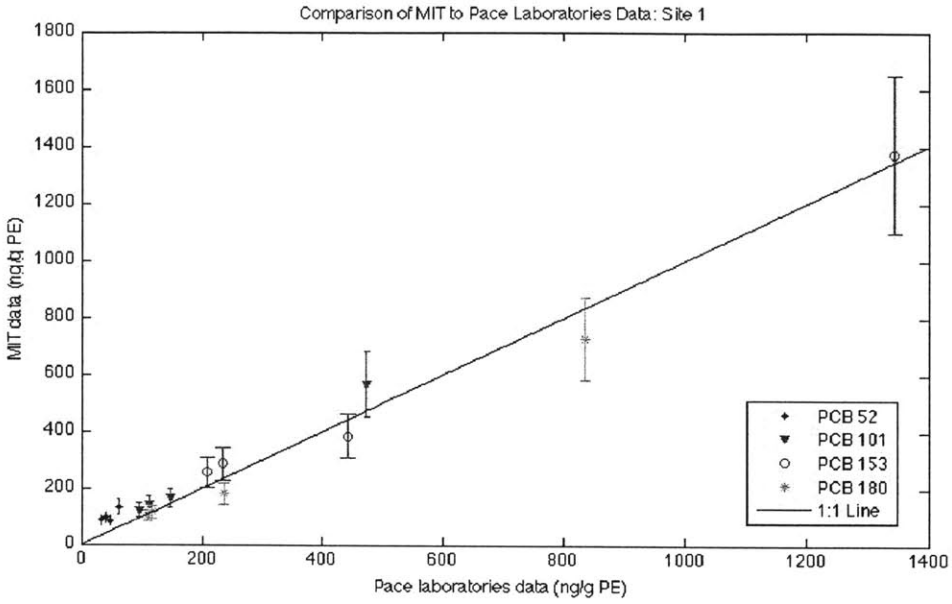


Figure 4-1: Comparison of MIT and Pace results for Site 1

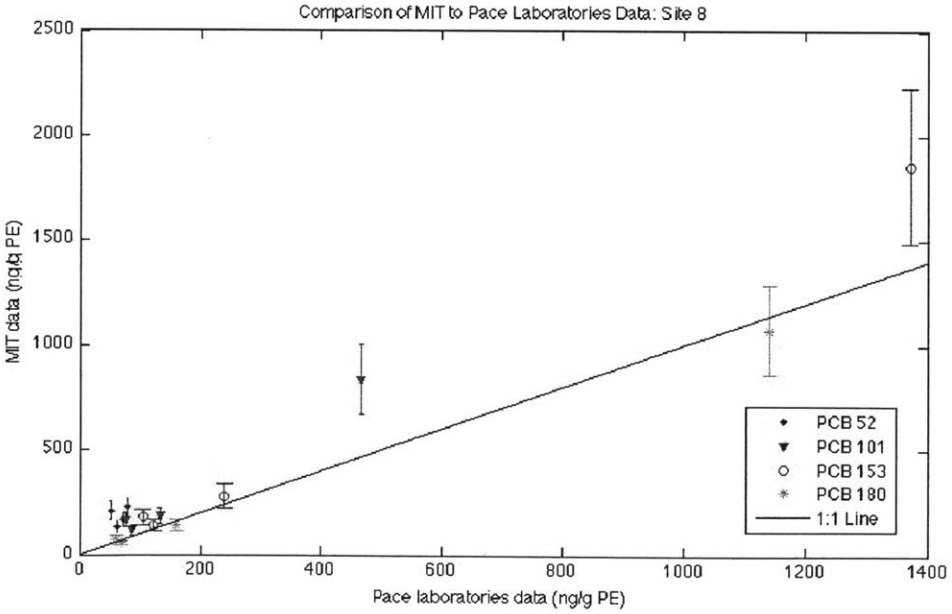


Figure 4-2: Comparison of MIT and Pace results for Site 8

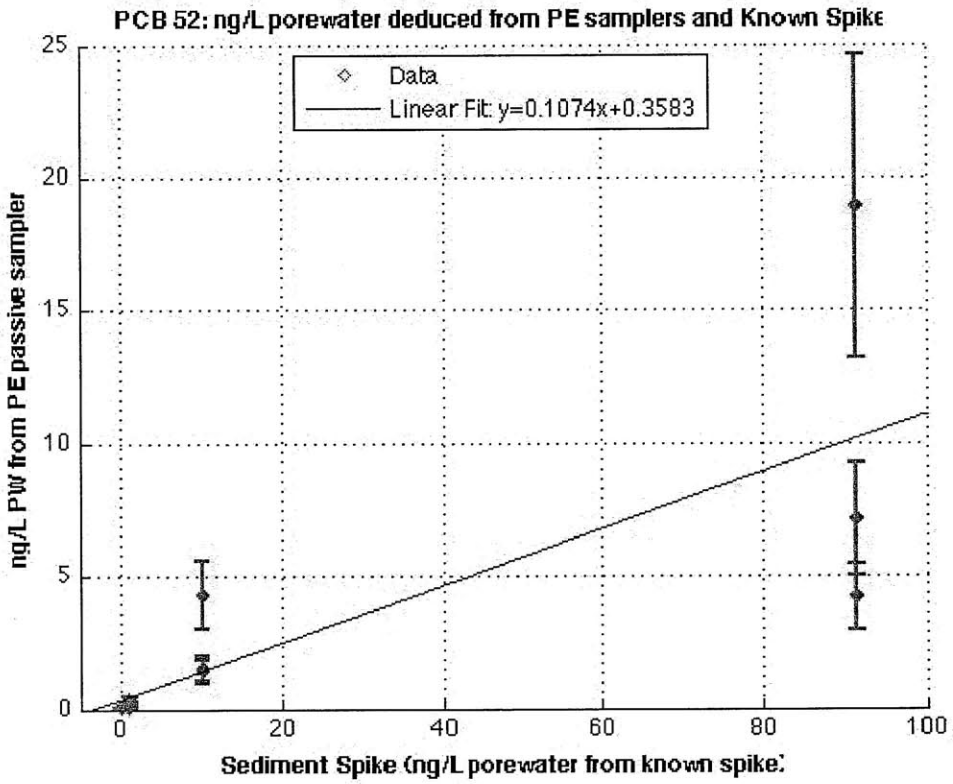


Figure 4-3: Comparison of pore water concentrations deduced from PE passive samplers (ng/L) to pore water concentrations deduced from a known sediment spike

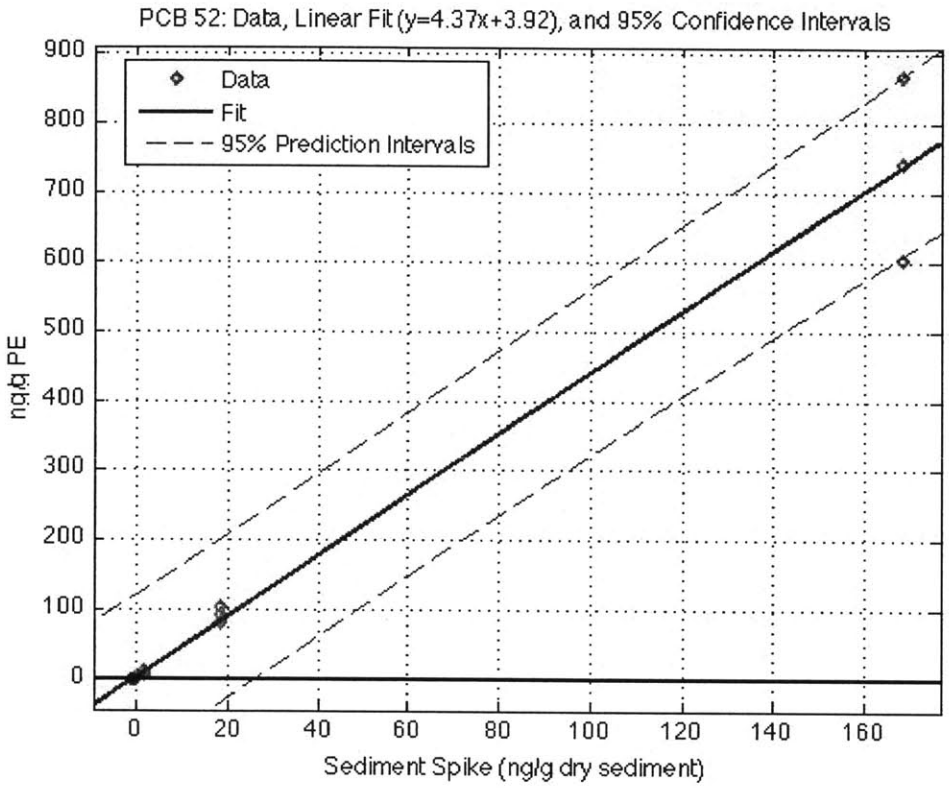


Figure 4-4: Data, linear fit, and 95% confidence intervals for PCB 52 spiked into blank sediment after 31 day incubation

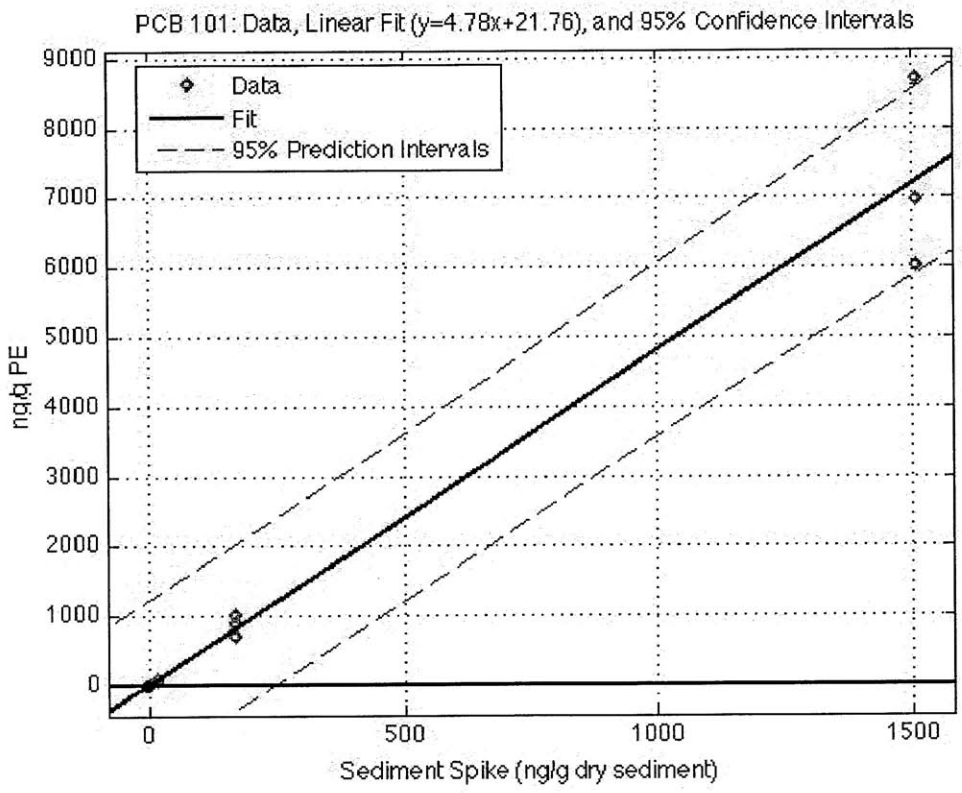


Figure 4-5: Data, linear fit, and 95% confidence intervals for PCB 101 spiked into blank sediment after 31 day incubation

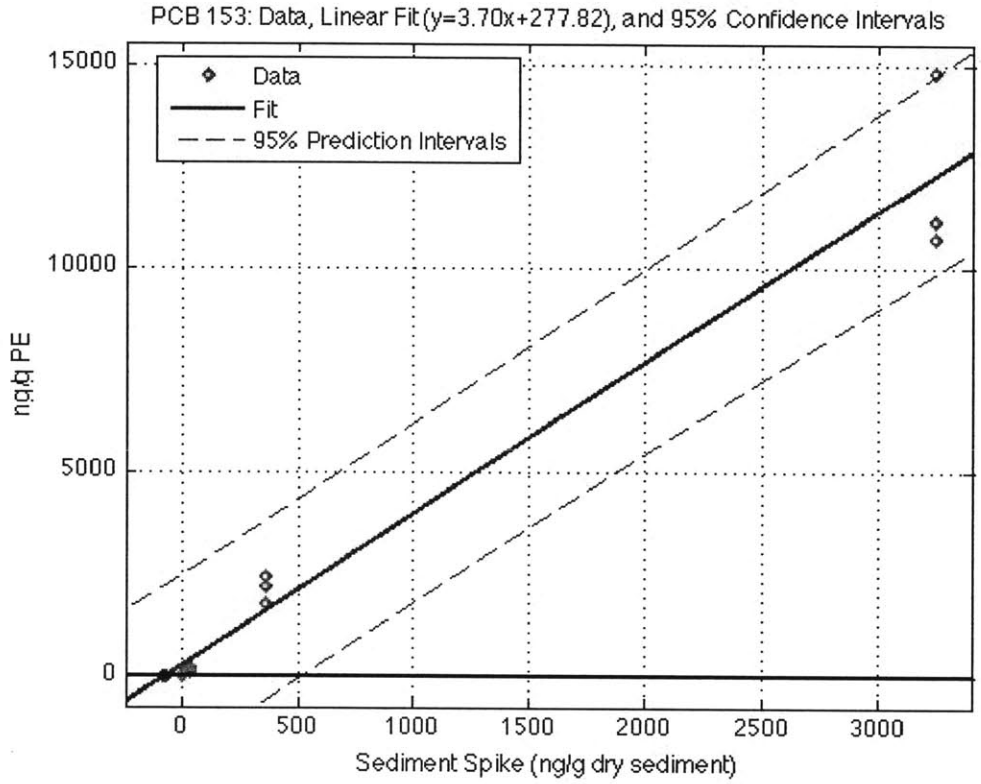


Figure 4-6: Data, linear fit, and 95% confidence intervals for PCB 153 spiked into blank sediment after 31 day incubation

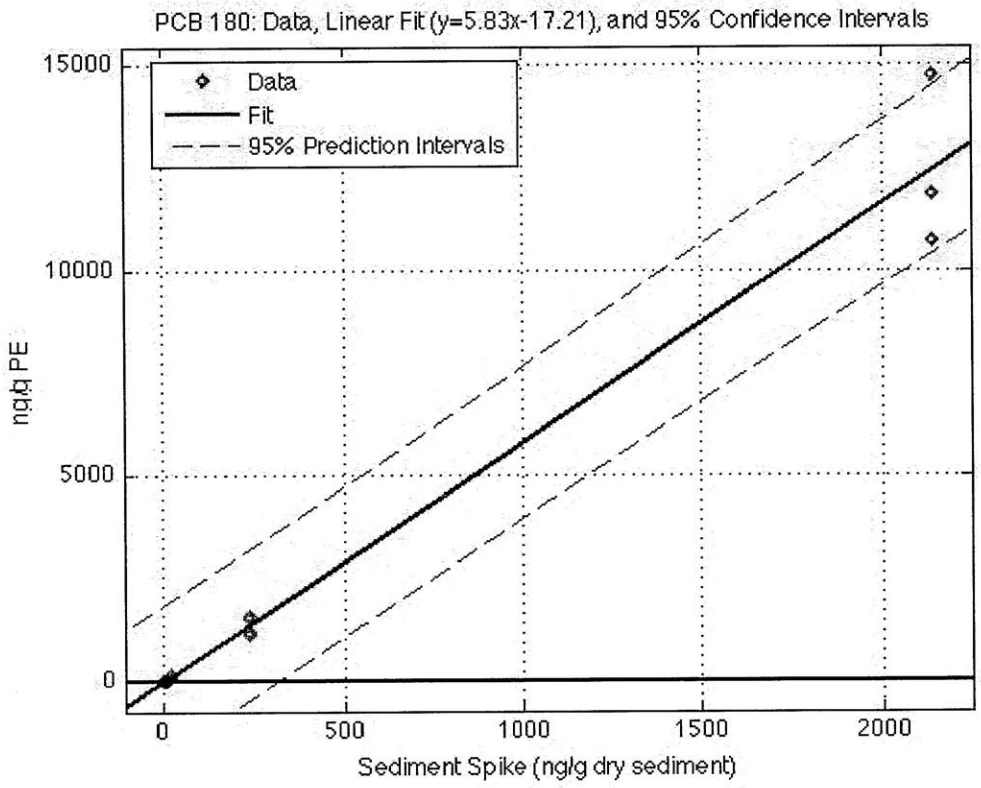


Figure 4-7: Data, linear fit, and 95% confidence intervals for PCB 180 spiked into blank sediment after 31 day incubation

Chapter 5

Accuracy

5.1 Introduction

Since the primary route of PCB exposure to humans is through consumption of contaminated organisms [16], prediction of biaccumulation in benthic organisms is useful when assessing the health risks posed by a contaminated sediment. Previous work has shown that bioaccumulation of PAHs predicted through passive sampling compares much more closely to measured biaccumulation than bioaccumulation factors deduced through solvent extraction and equilibrium partitioning [30]. Moreover, the bioaccumulation of PCBs by mummichog, blue crab, and white perch does not match well with bioaccumulation predictions obtained through sediment extraction and equilibrium partitioning [25] [21]. Work with passive samplers and air bridges has indicated that the pore water concentration deduced from passive samplers compares within a factor of 2 to pore water concentrations obtained through air bridges, while the pore water concentration based on sediment concentrations averaged 7 times too high [19]. Hence, it appears that passive sampling approaches offer one of the best ways to anticipate bioaccumulation by benthic organisms.

In this work, we tested the accuracy of using polyethylene passive samplers for assessing PCB levels in the pore water. This was done using sediment grab samples from a PCB-contaminated lake at 18 sediment sites. Pore water PCB measurements were made using (a) direct porewater extractions, (b) accelerated solvent extractions

of the sediments with equilibrium partitioning calculations to infer the pore water levels, and (c) using PE passive sampling with corrections for disequilibria using PRCs and then using PE-water partitioning to infer the corresponding pore water concentrations.

5.2 Materials and Methods

5.2.1 Sediment Collection, Preparation and Homogenization

Sediment was collected using a grab sampler from two sets of 10 sediment sites in Lake Cochituate (Natick, MA) by ICF International (Chapter 2, Figure 2-1) on November 19, 2009 (sites 1-10) and December 10, 2010 (sites 11-20). Overlying lake water was removed with a clean glass pipette. The sediments were allowed to sit after surface water removal and before continuing the porewater extraction process. This resulted in a thin layer of standing water accumulating on top of the sediment. This water was reincorporated into the sediment with a DCM-rinsed metal spoon.

5.2.2 Polyethylene Passive Samplers

Except for some small alterations in the sediment homogenization procedure, the PE sampler method followed that described in Chapter 2. As explained in Chapter 2, two sets of PRCs were used: PCBs 52,101, 153, and 180 for sites 1-10 and PCBs 47, 111, 153, and 178 for sites 11-20. The first set of PRCs interfered with analysis at Pace Laboratories (Minneapolis, MN), so the second set was introduced. The sediments were not spiked or tumbled prior to PE insertion. Three PE strips were used for each sediment site. The samples were incubated for 29 days, recovered, and analyzed as in Chapter 2. Briefly, the samplers were removed from the sediment, rinsed, and extracted with DCM after adding surrogate standards (PCBs 19, 77, 105, 167, 170, and 194). Injection standards (PCBs 39, 55, 104, 150, and 188) were added to the concentrated extracts. The extracts were run on a GCMS using SIM mode with three groupings. The peak retention times were identified through comparison of an Aroclor

1260 standard run on our GCMS system to the chromatograms of Schulz, Patrick and Dulnker (1989) [31]. The mass chromatogram peaks of the quantitation ions were manually integrated using software options that drew a line from the background level at the peak beginning to the background level at the peak end, so that only the peak itself was integrated. Concentrations in the PE samplers were deduced using daily response factors found by injecting known standard solutions, using the injection standards to adjust for the extract volumes, and correcting for recoveries of the surrogate standards in each case.

5.2.3 Porewater Extraction from Lake Sediments

Sediment was scooped out of the jar and transferred to 200 mL clean glass centrifuge tubes. The samples were centrifuged on a GS-6 Beckman swinging bucket rotor centrifuge for one hour at 2150 rpm, which corresponds to 1000 relative centrifugal force (rcf). The supernatant was transferred with a clean glass graduated pipette to 200 mL clean glass centrifuge tubes. The samples were then treated with alum to remove colloids [22]. We used a 10 percent by weight alum solution–about 5 mL alum to 200 mL pore water–and adjusted the pH to above 5 by 1 M NaOH, using about five drops per 200 mL pore water. The porewater samples were returned to the centrifuge and run for 1 hour at 2150 rpm. The resulting supernatant was clear. The supernatant was transferred to precleaned glass bottles and stored at 4°C until extraction.

5.2.4 Liquid-Liquid Extraction of Organics from Porewater

Recovery standards (PCBs 19, 77, 105, 167, 170, 194) were added to the pore waters before beginning the extraction procedure. The pore water was transferred to a separatory funnel. Dichloromethane (10 percent of the pore water volume) was added. The DCM-sample mixture was shaken for 10 minutes and then allowed to sit for 10 minutes to allow the phases to separate. The DCM, now containing organic compounds from the pore water, was drained from the separatory funnel to a clean glass

round bottomed flask. The DCM addition, shaking, rest, and draining were repeated twice. All three DCM extractions were combined in the same flask. We dried the DCM of any residual water by adding an excess of anhydrous sodium sulfate. When addition of anhydrous sodium sulfate resulted in granules forming in the solution, the anhydrous sodium sulfate was deemed to be in excess. The dried DCM, measuring around 100 mL, was quantitatively transferred to a clean glass round bottomed flask. The flask was rinsed with DCM during transfer. The extract was concentrated on a rotary evaporator to about 2 mL. This concentrated extract was quantitatively transferred to a 2 mL amber Agilent vial. The extract was further concentrated under a gentle stream of nitrogen gas, adjusted so that the liquid surface rippled but did not break, until a thin film of extract (around 100 μL) remained on the bottom of the vial. This was quantitatively transferred to a 250 μL Agilent glass insert. Injection standards (5 ng each of PCBs 104, 155, 150, and 188) were added and the sample was analyzed via gas chromatographymass spectrometry as described in Chapter 2 and above.

5.2.5 Accelerated Solvent Extraction (ASE) of Sediments

About 20 g of sediment from each site was ladled into aluminum boats during the homogenization process (Chapter 2). The boats were dried overnight in a 60°C oven and cooled. The cooled sediment cakes were ground using a mortar and pestle, rinsed with dichloromethane and air-dried inside a fume hood. The sediment cake was emptied into the mortar and ground for 5-10 minutes. The ground sediment was sieved (425 μm aperture) and stored in a cleaned and foiled jar.

Accelerated solvent extraction (ASE) was used to collect the PCBs from the dried sediment samples. The volume of 1 g sediment was found by weighing this material. The ASE cells were filled with clean Ottawa sand. Enough sand was removed from the cell until the vacated volume resembled the volume of dried sediment to be added. Sediment was loaded into the cell with a glass funnel. If vacated space remained in the cell, the space was filled with more sand. Recovery standards (5 ng PCB 19, 77, 105, 167, 170, and 194 in DCM at 100 ng/mL concentration) were pipetted into the

filled cell. Sand grains were carefully blown from the cell threads with an aerosol air pump. Lids were placed on the cells and the cells were inserted into a Dionex ASE 200 extractor. During a run, each cell was filled with a solvent mixture of 45% methanol and 5% dichloromethane to 1500 psi. The oven did not preheat, but heated for 6 minutes and remained static at 125°C for 5 minutes. Three rinses occurred, each flushing 60% of the cell volume. The cell was then purged for 60 seconds to remove all solvent. The resulting solvent-PCB mixture was concentrated under a gentle stream of nitrogen gas until about 1.5 mL of concentrate remained on the bottom of the vial. This concentrate was quantitatively transferred to a 2 mL amber Agilent vial. Injection standards (10 ng each of PCBs 39, 55, 104, 150, and 188 in DCM at 100 ng/mL concentration) were added and the sample was analyzed via gas chromatography–mass spectrometry as described above.

5.3 Results and Discussion

In order to compare the correspondence between porewater concentrations obtained through liquid-liquid extraction and porewater concentrations deduced through sediment extraction and PE passive samplers, each method was used to obtain a porewater concentration at 18 sediment sites (Figure 2-1). The data for PCB 101 was plotted and a robust linear regression, a linear fit that is designed to be less influenced by outliers than least squares regression, was used in Matlab to fit a line to the data (Figure 5-1 Figure 5-2; data in Appendix B). A 1:1 line was plotted for reference to assess the correspondence of the pore water concentration deduced from sediment extraction or PE passive samplers to the pore water concentration measured via liquid-liquid extraction. An accurate method would fit closely to the 1:1 line, while a less accurate method would fit far from the line (Figure 5-4). The root mean squared error for the PE-PW fit was 0.115, while the root mean squared error for the ASE-PW fit was 2.84.

Site 2 was sandy and had a low fraction of organic carbon (0.006) relative to the other sediment sites (typically 0.15). This low f_{oc} caused the equilibrium partitioning

correction of the sediment PCB value to be extremely high, resulting in pore water values of 31 ng/L compared to the liquid-liquid extraction value of 0.16 ng/L. Because the robust linear regression is less sensitive to such outliers, inclusion of Site 2 did not significantly impact the regression line (5.9±0.3 vs. 5.7±0.4). Hence, the porewater estimates deduced from the sediment concentration data were markedly greater (factor of 6) than what was directly measured. This effect has also been reported for PCBs in Hunters Point (San Francisco Bay) by Gschwend et al. (2011) [19]. Overprediction of porewater concentrations for sites with low fractions of organic carbon is a hazard of the sediment extraction with equilibrium partitioning method.

A plot with Site 2 is included for comparison with the PE passive sampler method (Figure 5-3). The ratio of porewater values deduced from PE passive samplers with 20% relative error (Chapter 4) to pore water values obtained via liquid-liquid extraction was 2.3±1.9 (1σ standard deviation). Hence, the PE samplers appear to yield accurate, but somewhat imprecise (factor of 2), porewater estimates.

The average ratio of porewater values deduced from sediment extraction to pore water values obtained via liquid-liquid extraction was 21±44 including Site 2, or 11±7.4 without inclusion of Site 2 (1σ standard deviation). The K_ds used for equilbrium partitioning correction of sediment extracts only accounted for sorption to organic carbon, not black carbon. A correction for black carbon was attempted using pore water values obtained via liquid-liquid extraction for Ciw [32] was used:

$$K_{BC} = 1.6 * log(K_{OW}) - 1.4 \tag{5.1}$$

The porewater values calculated using equlilbrium partitioning with the inclusion of black carbon were generally about 50 times lower than pore water values measured via liquid-liquid extraction, suggesting that this correction need to be better understood.

The pore water concentrations deduced from passive samplers were about a factor of 2 higher than porewater concentrations measured via liquid-liquid extraction, while pore water concentrations deduced via accelerated solvent extraction and equilibrium partitioning were about a factor of 11 higher. Gschwend et al (2011) observed that

PE passive samplers agreed with pore water concentrations obtained via air bridges within a factor of 2, while pore water estimates based on sediment concentrations were a factor of 7 too high [19]. Our observations agree with previous work, suggesting the advantages of PE passive sampling over sediment extraction with equilibrium partitioning Data for PCBs 52, 101, 153 and 180 deduced via liquid-liquid extraction, PE passive samplers, and sediment extraction with equilibrium partitioning is located in Table 5-2.

5.4 Recommendations

The accuracy of PE passive sampler measurements was assessed by comparing the porewater concentration deduced from polyethylene passive samplers at 18 sediment sites to the directly measured porewater concentration at those sites. The polyethylene passive sampler measurements were 2.3±1.9 times higher than pore water concentrations obtained via liquid-liquid extraction. Pore water concentrations estimated from sediment extraction with equilibrium partitioning were 11±7.4 times higher than liquid-liquid extraction results. Inclusion of black carbon effects in the equilibrium partitioning calculation resulted in pore water concentrations several orders of magnitude lower than liquid-liquid extraction results. Until a more realistic correction for black carbon effects is obtained, PE passive samplers present a viable alternative to sediment extraction when a fast, inexpensive method to deduce pore water concentration is desired.

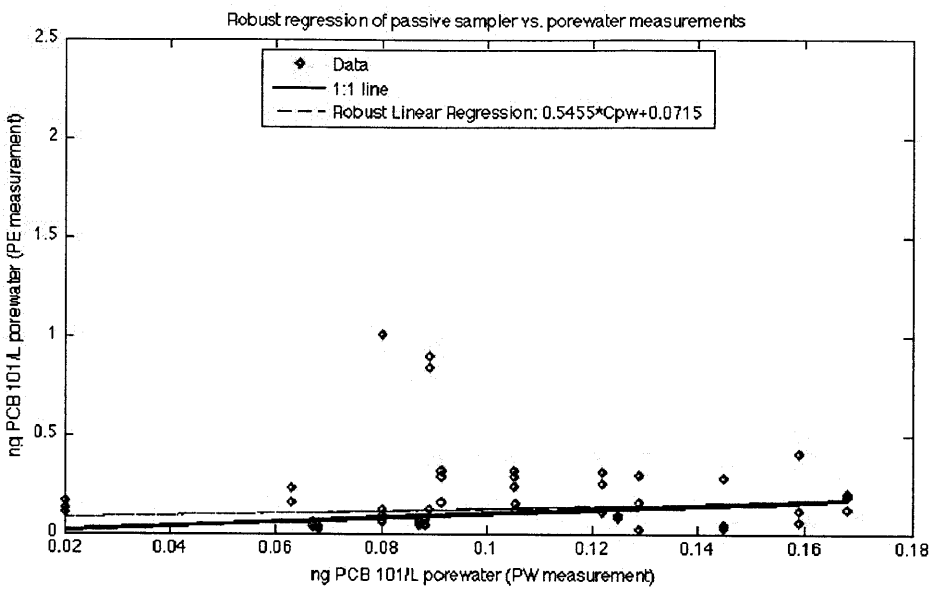


Figure 5-1: Deduced porewater concentrations from polyethylene passive samplers vs. directly measured porewater concentrations at 18 sediment sites

Site Number	ng/L pw	(#101 from sed) ng/L porewater	(#101 from PE) ng/L pw	foc	fbc	Porosity
1	0.129	1.35	0.12	0.14	0.0213	0.881
2	0.159	30.73	0.41	0.006	0.0025	0.554
3	0.125	0.80	0.08	0.16	0.013	0.916
4	0.145	0.45	0.28	0.013	0.00126	0.645
5	0.087	0.48	0.06	0.19	0.013	0.916
6	0.067	2.11	0.05	0.046	0.0068	0.775
7	0.088	0.46	0.07	0.21	0.0174	0.918
8	0.168	2.26	0.15	0.14	0.0118	0.897
9	0.068	0.36	0.03	0.29	0.015	0.932
10	0.08	0.83	0.09	0.15	0.0143	0.923
11	0.08	0.74	0.40	0.093	0.00301	0.964
12	0.02	0.52	0.13	0.15	0.01247	0.943
13	0.10525	1.28	0.28	0.14	0.00785	0.947
14	0.1055	0.84	0.13	0.1	0.00788	0.962
15	0.122	0.98	0.22	0.14	0.02086	0.947
16	0.089	1.34	0.62	0.15	0.0157	0.943
17	0.091	0.97	0.25	0.15	0.00926	0.943
18			0.32	0.17	0.01357	0.936
19	0.063	0.93	0.16	0.19	0.01508	0.929
20			0.16	0.17	0.01641	0.936

Table 5.1: Pore water concentrations (ng/L) of PCB 101 obtained from liquid-liquid extraction, sediment extraction, and PE passive samplers at 20 sites with corresponding f_{oc}, f_{bc}, and ϕ.

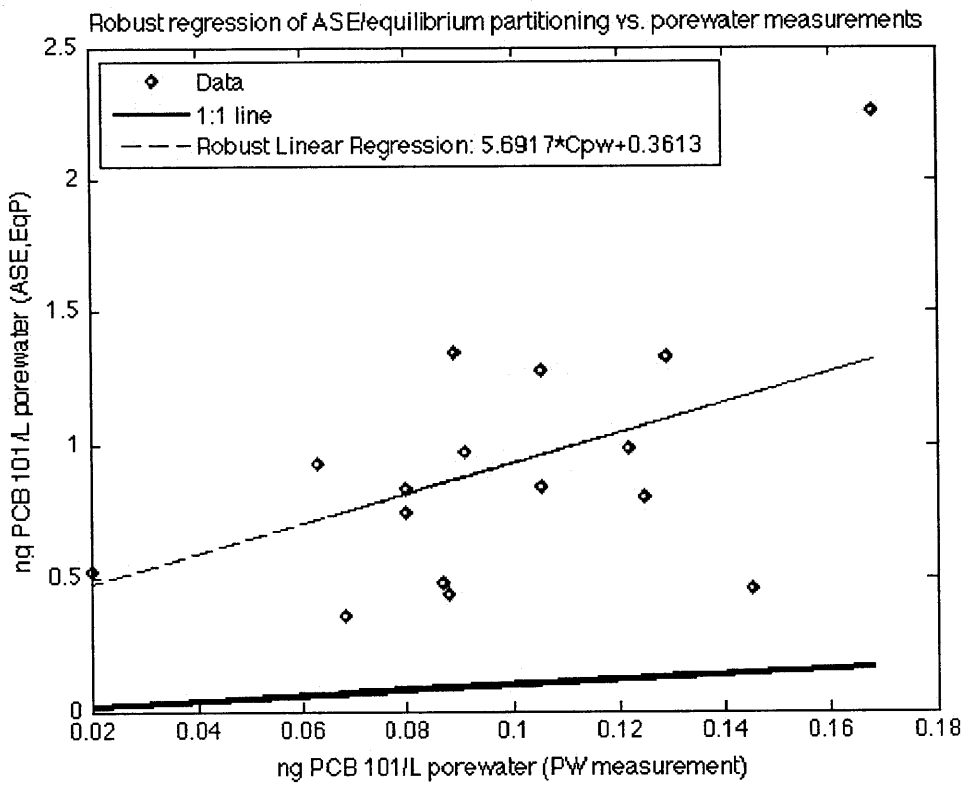


Figure 5-2: Deduced porewater concentrations from accelerated solvent extraction vs. directly measured porewater concentrations at 17 sediment sites

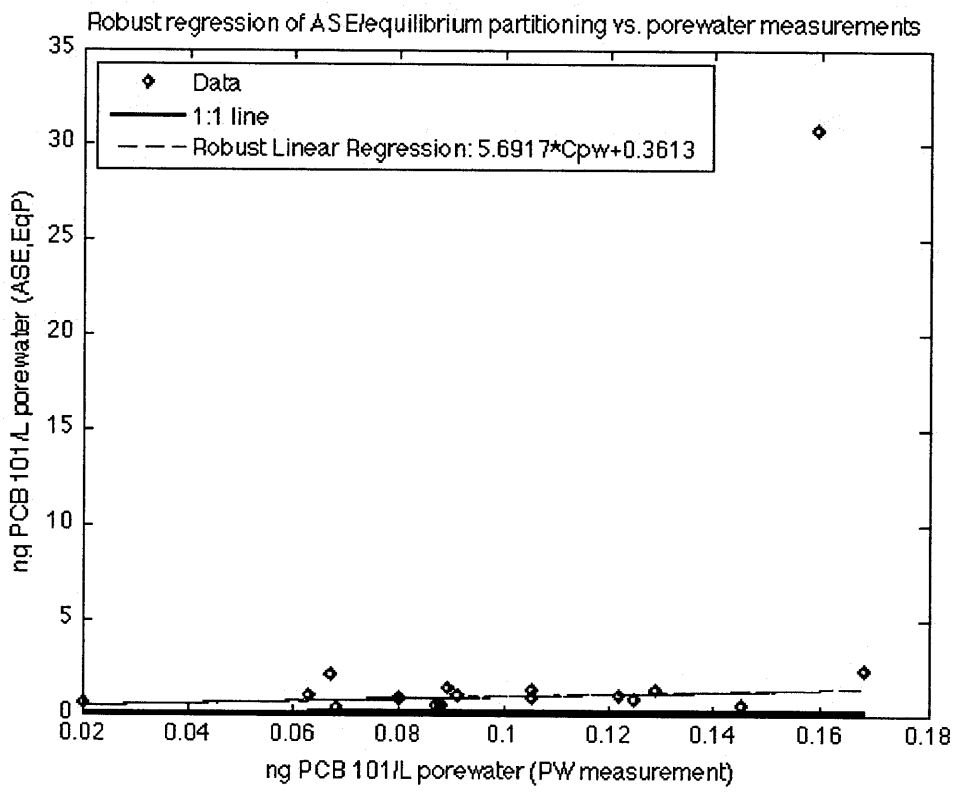


Figure 5-3: Deduced porewater concentrations from accelerated solvent extraction vs. directly measured porewater concentrations at 18 sediment sites

Site	1	2	3	4	5	6	7	8	9	10
ng/L pore water (liquid-liquid extraction)										
PCB 52	0.415	0.690	0.141	0.203	0.113	0.342	0.107	0.680	0.067	0.115
PCB 101	0.129	0.159	0.125	0.145	0.087	0.067	0.088	0.168	0.068	0.08
PCB 153	0.163	0.180	0.115	0.184	0.065	0.054	0.065	0.153	0.049	0.070
PCB 180	0.100	0.127	0.058	0.128	0.038	0.057	0.040	0.096	0.043	0.111
ng/L pore water (accelerated solvent extraction + equilibrium partitioning)										
PCB 52	2.577	61.768	1.150	1.044	0.707	6.586	0.681	6.696	0.575	1.179
PCB 101	1.352	30.675	0.799	0.454	0.478	2.112	0.464	2.258	0.356	0.833
PCB 153	1.305	30.118	0.736	0.432	0.444	1.278	0.464	1.227	0.331	0.793
PCB 180	0.691	15.648	0.391	0.251	0.251	0.805	0.266	0.596	0.183	0.482
ng/L pore water (PE passive samplers)										
PCB 52	0.478	0.331	0.080	0.104	0.057	0.249	0.051	0.417	0.027	0.071
PCB 101	0.199	0.192	0.082	0.114	0.052	0.043	0.047	0.175	0.024	0.066
PCB 153	0.417	0.667	0.180	0.171	0.072	0.051	0.047	0.145	0.021	0.069
PCB 180	0.167	0.392	0.078	0.082	0.032	0.019	0.017	0.053	0.007	0.019

Site	11	12	13	14	15	16	17	18	19	20
ng/L pore water (liquid-liquid extraction)										
PCB 52	0.217	0.094	0.273	0.190	0.183	0.136	0.162		0.113	
PCB 101	0.08	¡0.02	0.10525	0.1055	0.122	0.089	0.091		0.063	
PCB 153	0.085	0.046	0.236	0.089	0.098	0.076	0.084		0.048	
PCB 180	0.048	0.029	0.198	0.042	0.038	0.034	0.043		0.028	
ng/L pore water (accelerated solvent extraction + equilibrium partitioning)										
PCB 52	4.296	0.807	3.097	1.050	1.176	1.606	1.303	1.557	1.305	1.446
PCB 101	1.006	0.520	1.278	0.837	0.982	1.340	0.967	1.088	0.925	1.042
PCB 153	0.730	0.471	0.808	0.605	1.067	1.357	0.917	1.030	0.825	1.020
PCB 180	0.371	0.243	0.397	0.256	0.596	0.706	0.499	0.528	0.412	0.535
ng/L pore water (PE passive samplers)										
PCB 52	0.206	0.066	0.239	0.072	0.111	0.134	0.115	0.137	0.127	0.126
PCB 101	0.396	0.131	0.278	0.134	0.220	0.619	0.252	0.318	0.159	0.158
PCB 153	0.513	0.086	0.196	0.074	0.192	1.352	0.339	0.505	0.116	0.110
PCB 180	0.182	0.069	0.070	0.066	0.068	0.502	0.106	0.181	0.024	0.031

Table 5.2: ng/L pore water for PCBs 52, 101, 153, and 180 at 18-20 sediment sites deduced from liquid-liquid extraction, sediment extraction with equilibrium partitioning, and PE passive samplers

Chapter 6

Surfer

6.1 Introduction

Spatial representation of sediment contamination is useful for selecting additional sampling points and planning the extent of dredging or other remediation techniques. Usually, sediment sampling and chemical analyses are used to locate hot spots containing high levels of contamination. Dredging occurs around these hot spots with the goal of removing the most contaminated sediment, so that the remaining contaminant concentration poses less of a health risk. This process occurred in Lake Cochituate [6]. Dredging occurred at three of four hot spots, and the dredged areas were capped with clean sediment, with the goal of reducing the spatially averaged total PCB concentrations in the affected cove to less than 1 ppm (Figure 2-1). Although the traditional method of manually locating hot spots and defining dredging areas based on these hot spots is useful, contour mapping algorithms could infer information from a limited data set and provide an informed estimate of the location of high concentration areas.

Since part of the objective of using PE passive sampling is to acquire more data than usual, we sought to optimize the use of larger data sets. Hence, we used Surfer®9, a grid-based mapping program, developed by Golden Software (Golden, CO), to create contour maps of PCB contamination over Lake Cochituate as measured by direct pore water measurements, passive samplers, and sediment concentrations.

By comparing these maps, we sought to understand how site evaluation would be affected by the nature of the input data. Also, by using a two-step sampling scheme in which the second round of samples were located after seeing the results from the first round of ten analyses, we wanted to investigate the effect of adding an additional round of ten sampling sites. Such information could help one see some of the value of using the PE passive sampling approach as compared to current practices that chiefly rely on sediment concentration measurements.

6.2 Theory

The Surfer®9 software uses a gridding algorithm to create a dense grid of interpolated points from a set of measured data. Different types of maps, such as concentration contours, 3D surfaces showing relative concentrations in 2D space, and vector maps, may then be plotted using this grid file. Although Surfer®9 offers twelve gridding functions, only four accommodated a fault line, or barrier. A fault line was necessary in our case to simulate the lake shoreline. Of these four methods, two were traditional interpolation algorithms: "Inverse Distance to a Power" and "Minimum Curvature." Minimum Curvature fit our situation best. This algorithm creates the smoothest possible surface that meets the data as closely as possible, as though a thin plate were bent slightly to pass through each of the data points. The algorithm allows input of the measurement precision as part of the Maximum Residual option. If measurement precision is known, as for polyethylene passive samplers, a maximum residual value of 10% of data precision is suggested. Using the results of Chapter 4, in which we found that the precision of polyethylene passive samplers is around 20% relative error, we calculated the precision of each data point and used the average relative error in the maximum residual calculation. In the case where precisions are not known, a default value is used. This is what we used when mapping pore water concentrations deduced from sediment extractions and porewater extractions. The

default residual is given:

$$Default\ Maximum\ Residual = 0.001 * (Z_{max} - Z_{min}) \tag{6.1}$$

where Z_{max} is the maximum data value, and Z_{min} is the minimum data value.

6.3 Materials and Methods

The first round of sampling stations, Sites 1-10 (Figure 2-1), sought to sample the source area (site 6), sediments located downstream of the source area considering prevailing currents (sites 1, 2,3,4,5), a station upsteam of the source area (site 10), and stations distributed across the lake from the source area (sites 7,8,9). The second set of sampling stations were chosen after the results from the first ten sites had been obtained. We chose to investigate one site just outside of the identified source area (site 11), one site in an previously unsampled area close to the northeastern shore (site 12), one site co-located with a previously identified PCB 52 hot spot (site 13), three sites distributed across the lake from the source area in a previously unsampled section (sites 14-16), and 4 closely located sites downstream of the source area (sites 17-20) in an effort to characterize bottom heterogeneity on the 10 meter scale.

An Excel file was prepared with columns of (a) the site numbers, (b) the universal transverse Mercator UTM easting and northing coordinates of each sampling site, porewater concentration (ng/L) at each site as inferred from (c) polyethylene passive samplers, (d) accelerated solvent extraction of sediment samples, and (e) direct measurement. The UTM coordinates, a .bln fault line file with coordinates of the lake shore, and plotting limits were provided by ICF International consultants (Steve Reichenbacher, Lexington MA). One grid file was created for each data set using the Minimum Curvature gridding method.

Since data precision was known for the polyethylene passive samplers, 10% of the average data precision (2% of the average pore water value as inferred from PE passive samplers, or 0.004 ng/L) was used as the maximum residual value. Maps of

pore water concentrations inferred from PE passive samplers created using the default maximum residual value, 0.00059, and 0.004 were compared (Figure 6-1). Inclusion of data precision did not greatly influence the map, although some changes in contours were observed. The contours around sites with elevated concentration became smaller with the inclusion of data precision, and a regions of low concentration in the center of the lake broke into two regions when data precision was included.

Data precisions were not known for the accelerated solvent extractions of sediments and directly measured porewater data sets, so the default maximum residual was allowed. Contour maps were created from the grid files, and a post layer containing the site numbers was added to each contour map. To allow comparison across measurement types, the map coloring was scaled to the maximum and minimum values of the combined data sets (Figures 6-2, 6-3, 6-4).

Six contour maps were created showing the concentration of PCB 101 as measured using (a) liquid-liquid extraction of porewater data, (b) porewater concentrations deduced from polyethylene passive samplers, and (c) sediment analysis with equilibrium partitioning [12] (Figures 6-2, 6-3, 6-4). One set of maps (set a) used the first round of 10 sampling sites, and the second set (set b) added the second round of 10 sampling sites. The porewater concentrations at sites 18 and 20 were not directly measured because these sites were closely located with 17 and 19.

In order to compare the results using different PRC congeners, three maps showing the concentration of PCBs 52, 101, 153 and 180 using directly measured pore water concentrations from 18 sites were created (Figures 6-6, 6-7, 6-8, 6-9).

6.4 Results and Discussion

6.4.1 Comparison of Surfer®9 to Traditional Method

Like the traditional method of locating hot spots and assuming sediment close to that spot contains a high PCB concentration, Surfer®9 contours formed enclosed curved shapes around regions of high concentration (Figure 6-6). However, the additional

information provided by the gridding algorithm altered the shape and centering of these "hot spot rings compared to the centered, circular or elliptical rings that would have been inferred traditionally. At Site 1 (Figure 6-1a), the low spot rings are off center from the sampling site, skewed by the higher concentrations measured at Sites 2, 15 and 16. The higher concentration measured at Sites 8 and 18 produces a small circular ring immediately around the site, but a region of high concentration is also expected in the cove in which the site is located. Information obtained from Surfer®9 follows the pattern of traditional mapping, but incorporates information from the entire sampling set to produce a more informed result.

6.4.2 Comparison of PE Passive Samplers, Sediment Extraction, and Pore Water Extraction

The results of Chapter 5 noted that pore water concentrations inferred from PE passive samplers are about a factor of 2.3±1.9 higher than pore water concentrations obtained through liquid-liquid extraction. Pore water concentrations estimated from sediment extraction and equilibrium partitioning are 11±7.4 times higher than liquid-liquid extractions results. They are 21±44 times higher if Site 2, a site whose low organic carbon fraction (0.006) produces an estimated pore water concentration 200 times higher than the liquid-liquid extraction result, is included. The higher estimated pore water concentrations and large variation between sites found through sediment extraction are apparent in the Surfer®9 maps (Figures 6-2, 6-3, 6-4). Maps created from sediment extraction data show hot spots at Sites 8/13 (2.3/1.3 ng/L) and 6 (2.1 ng/L) that would be concerning if the PE passive sampler (8/13: 0.15/0.28 ng/L; 6: 0.05 ng/L) and pore water (8/13: 0.14/0.14 ng/L; 6: 0.05 ng/L) were not known. Inclusion of Site 2 in the contour map (Figure 6-5; map coloring not scaled to PE passive sampler and pore water maps) indicates the large hot spot seen in sediment extraction results, but not seen in results from PE passive samplers or direct pore water measurements.

6.4.3 Incorporation of an Additional 10 Sampling Sites

In order to investigate the effect of adding an additional round of 10 sampling sites, sediment was collected from Lake Cochituate in two rounds of ten samples each. The additional ten samples do not fundamentally change the map, but result in bumpier contour lines (Figures 6-2, 6-3, 6-4). Although it would seem logical to locate future sampling points in areas that show a lot of variation, the addition of Sites 15 and 16 in a previously unsampled, but low-variation areas, resulted in areas of large variation around Site 15 in the PE passive sample map. The pore water map increased only somewhat, as the directly measured pore water concentration at Site 15 is 0.14 ng/L relative to 0.22 deduced from PE passive samplers. Both maps showed increased variation along the western lake shore.

6.4.4 Comparison of Congeners 52, 101, 153, and 180

To examine the concentrations of different PCB congeners in Lake Cochituate, contour maps were created from directly measured pore water concentrations (ng/L) at 18 sampling sites. The map coloring was normalized to the maximum and minimum pore water concentrations of all four congeners (Figures 6-6, 6-7, 6-8, and 6-9). Given the historical contamination of Lake Cochituate by Aroclor 1260, (0.56% PCB 52, 5.02% PCB 101, 10.8% PCB 153, 7.12% PCB 180 [31]), we expected the values of PCB 101 and 153 in the pore water to be higher than PCB 52 (due to its low presence in Aroclor 1260) and PCB 180 (due to its affinity for organic carbon and black carbon). However, the map of PCB 52 shows unexpected hot spots for this congener (0.69 ng/L at Site 2 and 0.68 ng/L at Site 8) which are weakly reflected in the PCB 101, 153 and 180 maps. Due to the low presence of PCB 52 in Aroclor 1260, we suspect that the sampling sites may reflect a non-Aroclor 1260 source of PCB contamination.

6.4.5 Monte Carlo Test of Contour Maps

Although the Minimum Curvature mapping algorithm accounts for measurement method precision, we wanted to investigate what would have happened if we had analyzed a set of replicate samples which produced values within the experimental error of our current pore water concentrations. We chose to investigate pore water values for PCB 52 due to its intriguing hot spot behavior. Replicate pore water values were measured at sites 11, 12, 13, 14, and 17. The method precision calculated from these replicates was about 8%. A Monte Carlo method was used by randomly choosing a value within method precision of the previously measured values for 18 sites in Excel, and then creating a map in Surfer®9 from the randomly chosen data. This procedure was repeated 10 times. The maps with maximum and minimum area of high concentration (above 0.5 ng/L) were chosen manually (Figures 6-9, 6-10). The minimum and maximum maps look reassuringly similar, indicating that a remediation decision based on Surfer®9 maps would not have changed very much if a replicate set of pore water measurements was conducted.

6.5 Conclusions

A grid-based mapping software, Surfer®9, was used to visualize porewater concentrations directly measured via liquid-liquid extraction of porewater samples, deduced from PE passive samplers, and estimated from sediment after extraction and calculations with equilibrium partitioning [12]. Like traditional mapping techniques of locating a hot spot and assuming that sediment near a hot spot is also contaminated, Surfer®9 showed that sediment around a sampling site with high concentration would also be identified as "highly contaminated." However, the size and shape of this area deviated from the traditional circle depending on the values of neighboring sampling sites. The additional information incorporated by Surfer®9 could inform remediation decisions.

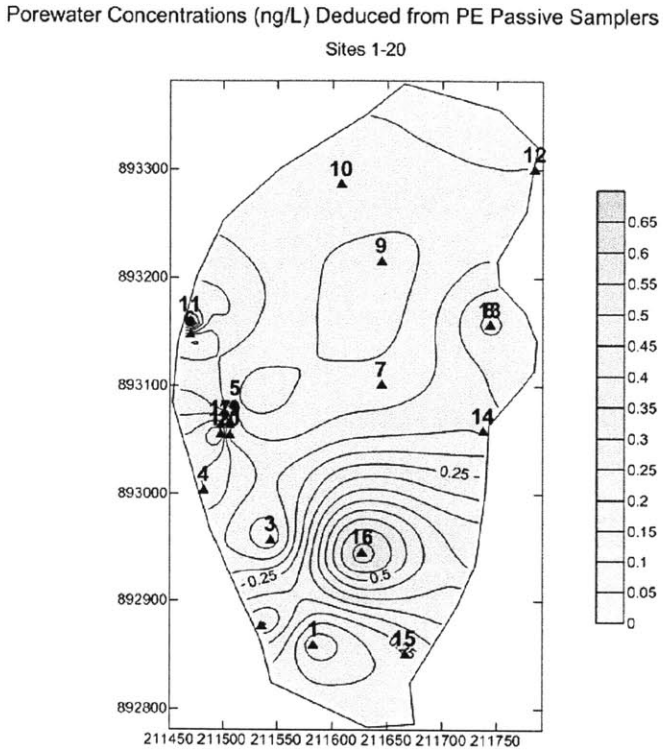
Results from Chapter 5 suggest that porewater concentrations estimated from sediment extraction are elevated compared to porewater concentrations deduced from PE

passive samplers and liquid-liquid extraction of pore water, itself. As expected (due to neglecting impacts of BC), the sediment extraction with equilibrium partitioning map showed higher concentrations than the results of PE passive samplers and liquid-liquid extraction. Although the hot spots identified by sediment extraction (sites 2,6,8/13 (collocated)) were also identified by PE passive samplers and direct pore water measurement, the hot spots measured via sediment extraction were significantly elevated compared to the PE passive sampler and pore water results.

Sediment samples were collected in two rounds of 10 sites each. We chose the second round of sampling sites to cover areas with low sampling site density and to resample areas identified as hot spots in Round 1. The second round of sampling sites did not fundamentally change the map, but resulted in bumpier contour lines due to the added information. This introduced areas of variation in areas with previous low sampling site density, although such variation may not be important if all the values fall below or above key clean up criteria.

The presence of PCBs 52, 101, 153 and 180 in Lake Cochituate was investigated by creating Surfer®9 maps with porewater concentrations (ng/L) measured via liquid-liquid extraction of that water. Although PCB 52 comprises only 0.56% of Aroclor 1260, regions of high (0.7 ng/L) PCB 52 concentration were found at Sites 2 and 8/13 (collocated). The hot spots are weakly reflected in the PCB 101, 153, 52, and 180 maps. We suspect that these results may reflect a source of non-Aroclor 1260 contamination.

A Monte Carlo method was used to investigate the effect of method precision on Surfer®9 maps. The method precision of PCB 52 measured via liquid-liquid extraction of porewater was calculated (8%) and a new value within method precision of the original PCB 52 concentration was randomly chosen. Ten maps were created using randomly chosen data within method precision. The maps with maximum and minimum areas of high concentration were identified and examined. The maps did not differ significantly from one another, suggesting that Surfer®9 results would have been similar if a replicate set of samples was extracted.



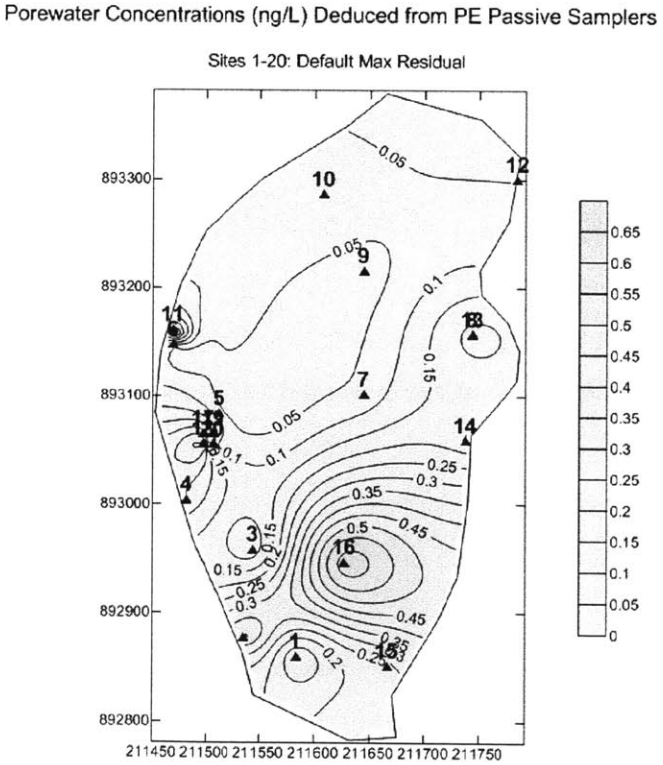


Figure 6-1: Contour map of porewater concentrations deduced from PE passive samplers for PCB 101 at 20 sites using the default max residual (a) and data precision (b) options

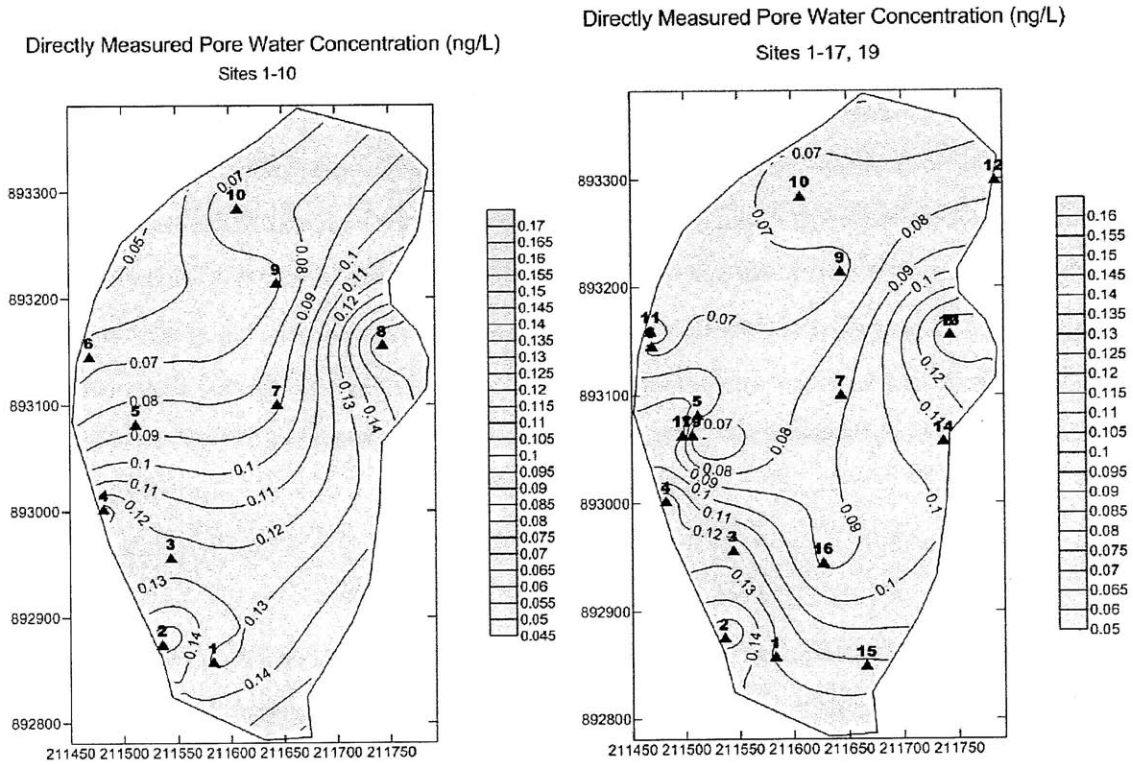
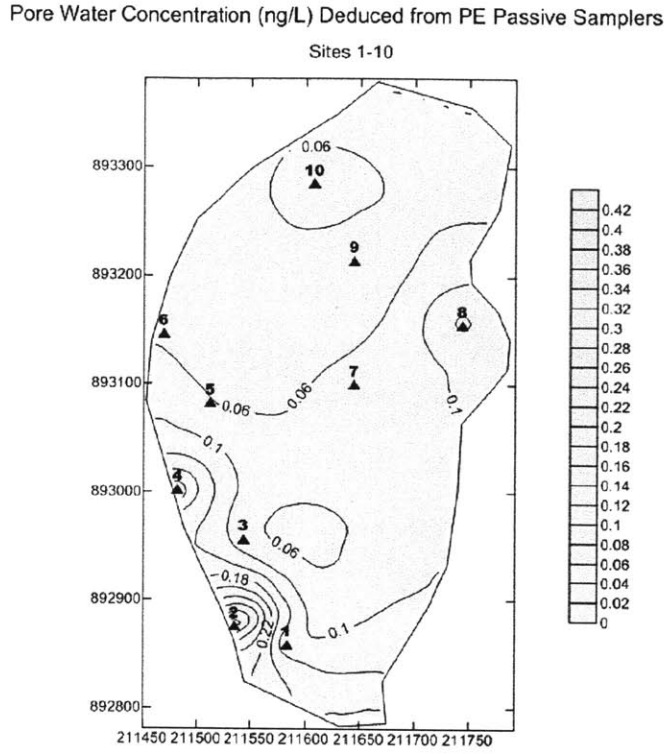


Figure 6-2: Contour map of directly measured porewater concentrations for PCB 101 using 10 (a) and 18 (b) sites



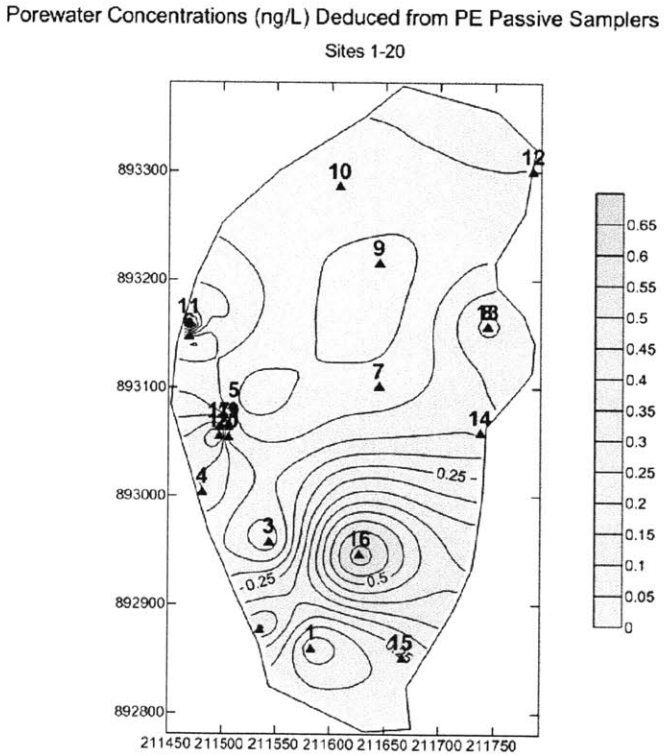


Figure 6-3: Contour map of porewater concentrations deduced from polyethylene passive samplers for PCB 101 using 10 (a) and 20 (b) sites

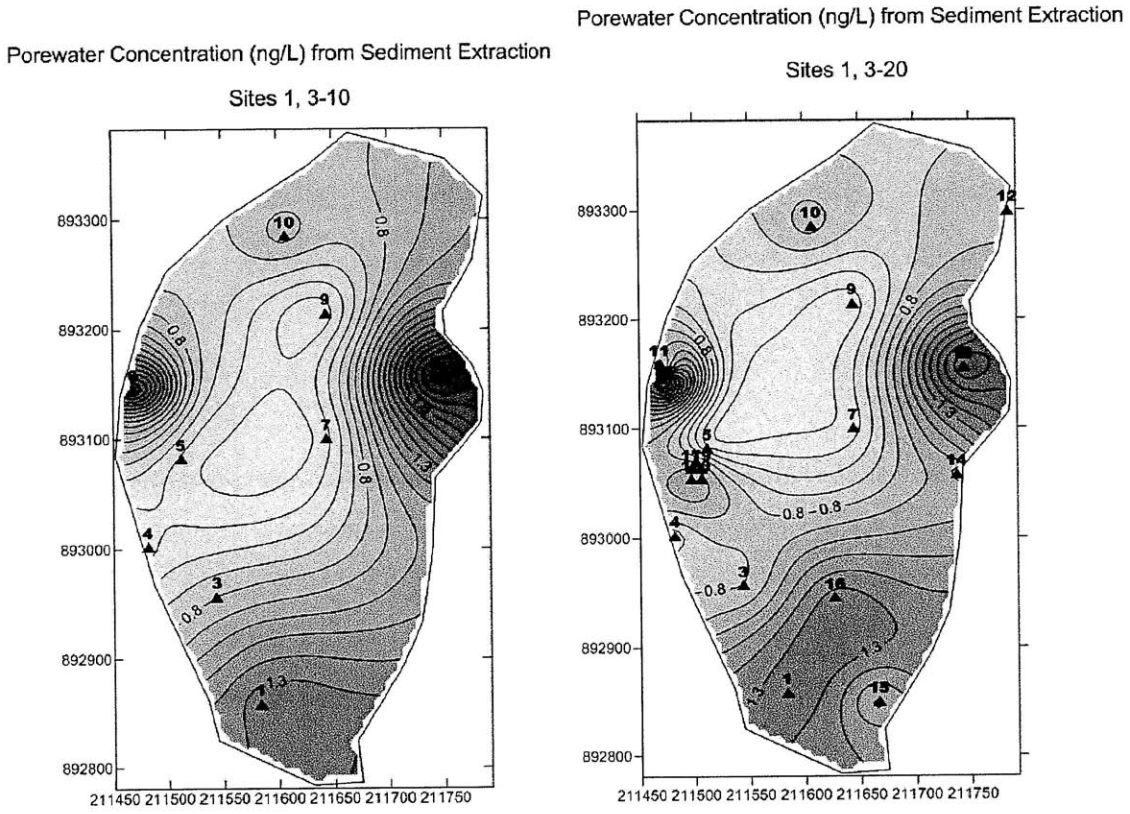


Figure 6-4: Contour map of porewater concentrations deduced using accelerated solvent extraction and equilibrium partitioning for PCB 101 using 9 (a) and 19 (b) sites

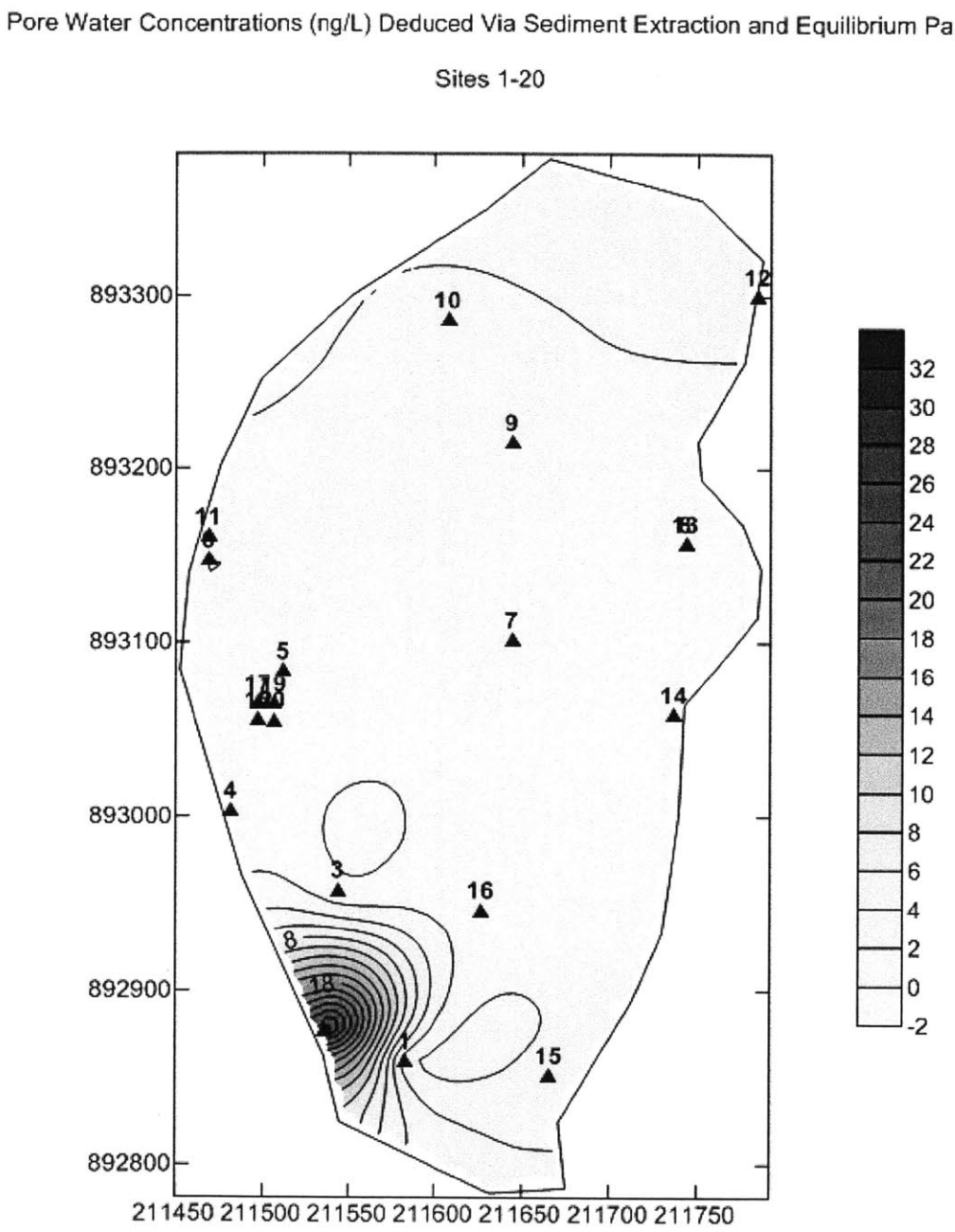


Figure 6-5: Map of porewater concentrations (ng/L) deduced by sediment extraction from 20 sites, including an unexpectedly high concentration at Site 2

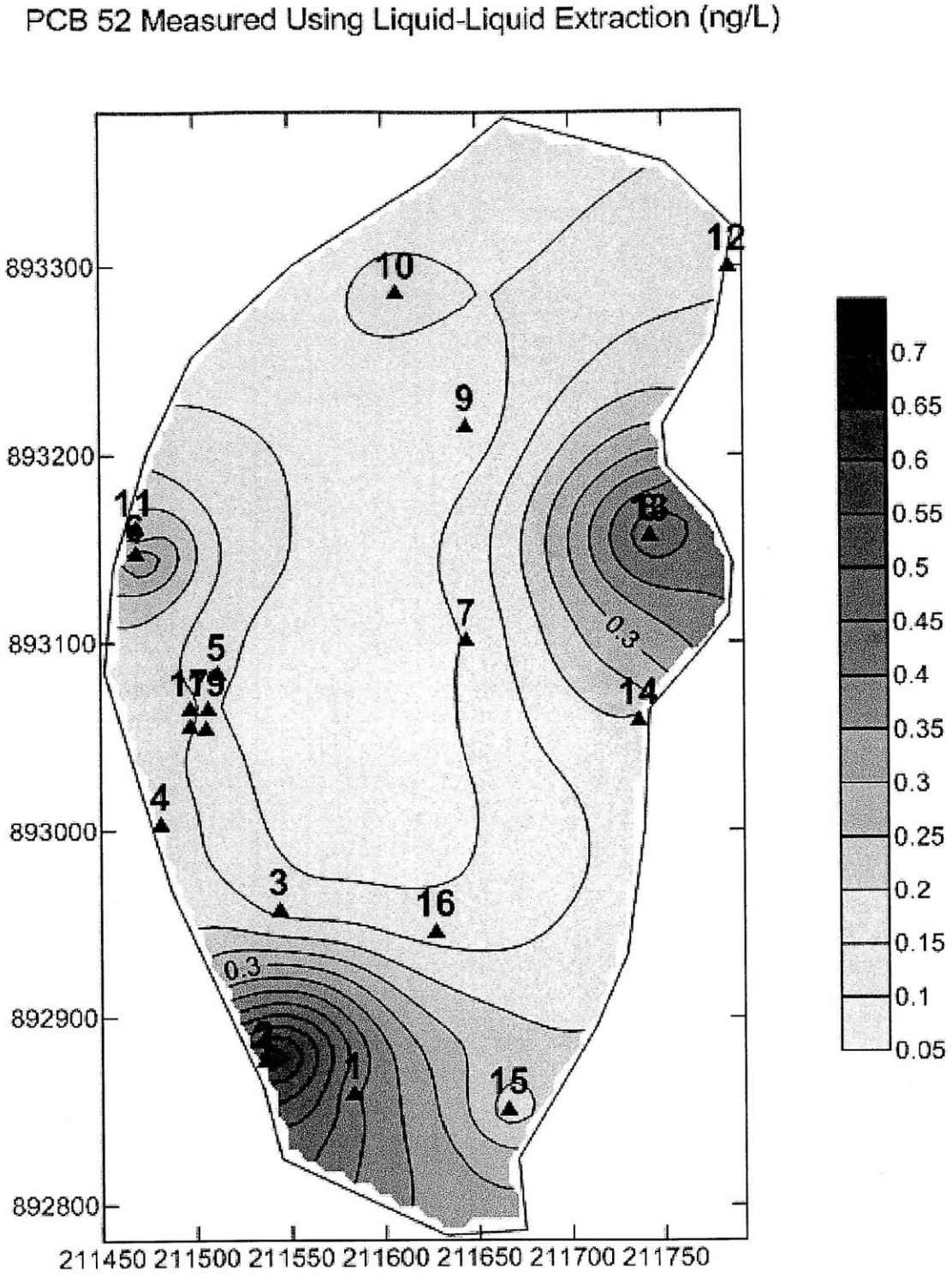


Figure 6-6: Map of PCB 52 concentration in pore water (ng/L) measured via liquid-liquid extraction

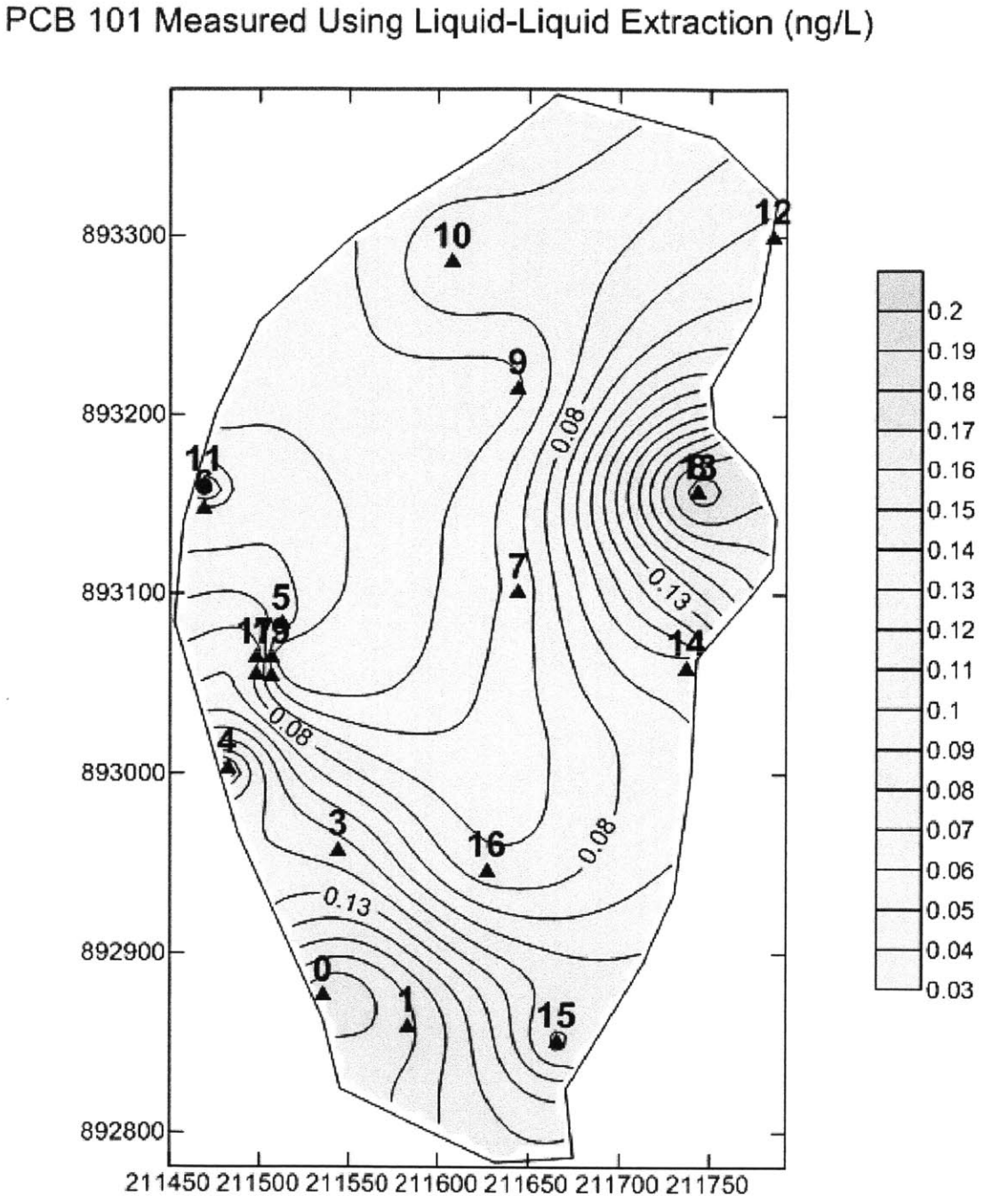


Figure 6-7: Map of PCB 101 concentration in pore water (ng/L) measured via liquid-liquid extraction

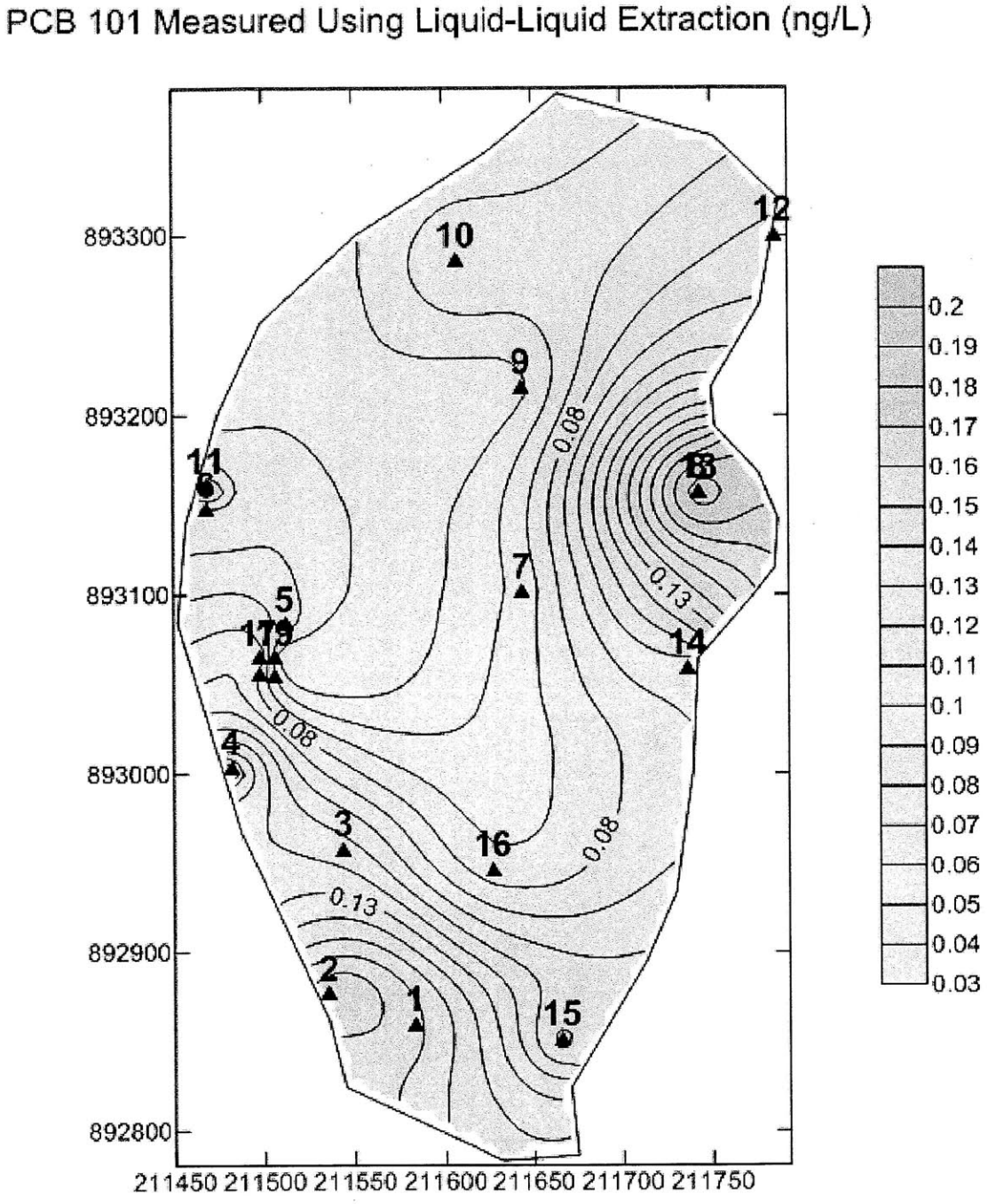


Figure 6-8: Map of PCB 153 concentration in pore water (ng/L) measured via liquid-liquid extraction

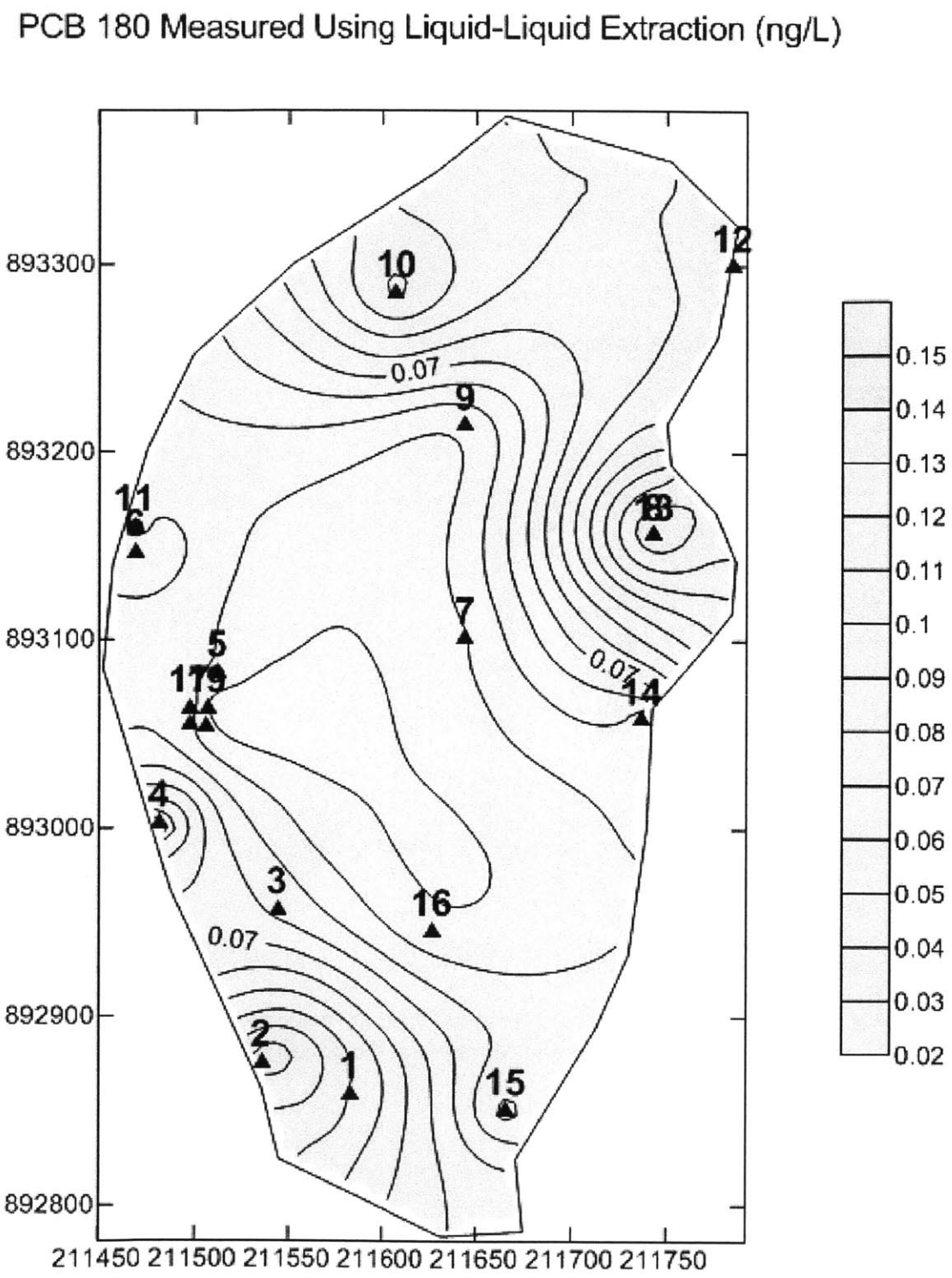


Figure 6-9: Map of PCB 180 concentration in pore water (ng/L) measured via liquid-liquid extraction

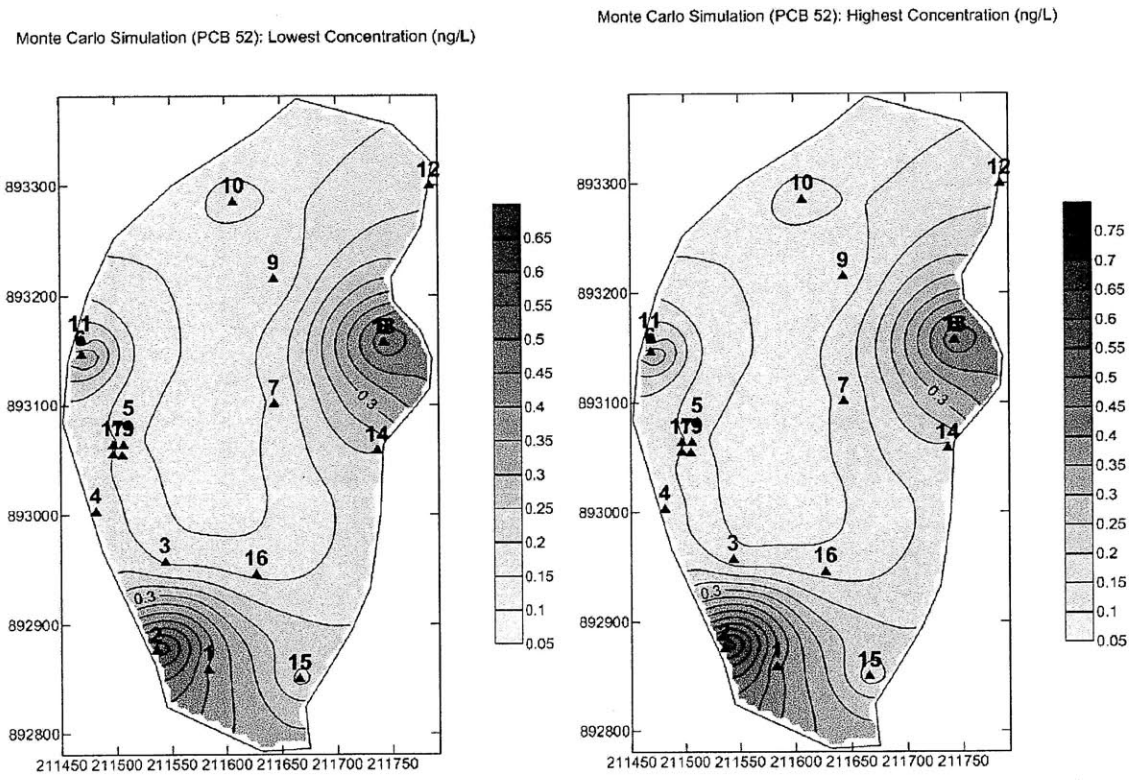


Figure 6-10: PCB 52: Minimum (a) nd maximum (b) regions of high concentration (ng/L) obtained through a 10-sample Monte Carlo simulation

Chapter 7

Conclusion

Polychlorinated biphenyl compounds (PCBs) can cause liver damage and acne-like symptoms in adult humans and impaired cognition in children exposed in utero. Since PCBs sorb strongly to organic carbon and black carbon in sediments, thus remaining shielded from rapid transport and decay [2][3], sediment contaminated with PCBs can pose a human health hazard for decades, as in the Hudson River PCBs Superfund Site [1].

In general, assessing the hazard posed by such contaminants appears to be best accomplished by measuring those chemicals' presence in the sediment's pore water. A variety of methods have been established for deduction of PCB concentrations in the pore water of contaminated sediments. Direct measurement of PCB concentration via liquid-liquid extraction of the pore water itself can be time consuming and expensive, often requiring large volumes of water and solvent [7]. Solvent extraction of sediment samples with equilibrium partitioning calculations is complicated by the correction for black carbon behavior, which is dependent on the pore water concentration [2] [3], as well as knowledge of the relevant K_{BC} values. Measurement of bioaccumulation in benthic organisms such as mussels is a messy, time-consuming process and depends on the conditions of incubation and organism used [25].

Passive sampling has been presented as an alternative to bioaccumulation measures, sediment extraction, and direct pore water measurement. Performance reference compounds (PRCs) are used to measure the passive samplers' approach to

equilibrium [10] [14]. PE passive samplers have been used to deduce pore water concentrations in Boston Harbor and San Francisco Bay [15] [33] [28]. In order to demonstrate the potential of PE passive samplers to accurately and inexpensively measure sediment porewater concentrations, we sought to identify difficulties with the method and attempt to resolve them, determine key data metrics and begin involving industry elements in PE passive sampler use, compare PE passive samplers to sediment extraction with equilibrium partitioning and direct pore water measurement, and investigate the use of contour mapping software in visualizing sediment concentrations.

In order to compare actual PRC behavior with predictions based on the mass transfer model of Fernandez et al. (2009)[14], we incubated PE passive samplers in two sample matrices and removed passive samplers at six time points over 476 days. PRC movement followed the expected pattern of lighter congeners moving faster than slower congeners. The movement of PCBs 52 and 101 was severely underpredicted by the model over 476 days. This may be due to the effects of black carbon, which were not included in the model to the complex nature of these interactions.

To promote use of PE passive samplers as a measurement method for real-world contamination sites, we characterized key data metrics including precision, method detection limit, accuracy relative to a known spike, and consistency with a contract laboratory (Pace Laboratories, Minneapolis, MN). Method precision results were around 20% for PE passive samplers before PRC correction, while method precision after PRC correction ranged from 30% for PCB 52 to 145% for heavier PRCs. The PRC correction becomes error-prone as the amount of PRCs remaining in the PE passive sampler relative to the original PE concentration is still near 1 after deployment. An incubation time long enough to observe some loss of the slowest PRCs is therefore desirable. PE passive samplers that were randomly chosen from sets of at least ten replicates and sent to Pace Laboratories for analysis were consistent with MIT data within method precision, except for PCB 52, which was consistently reported high in the MIT results relative to Pace results. Method accuracy was considered by spiking a clean sediment matrix with known amounts of PCBs and comparing the pore wa-

ter concentration deduced from PE passive samplers to the pore water concentration found through equilibrium partitioning of the known spike. Porewater concentrations deduced from the spike were about 10 times higher than concentrations deduced from PE passive samplers. The elevated levels of pore water concentration could be due to the effects of black carbon, which were not accounted for by equilibrium partitioning. Method detection limit was calculated using the method of Hubaux and Vox [18] and found to be about 4.6 ng/L, 10.3, ng/L, 6.2 ng/L, and 3.3 ng/L respectively for PCBs 52, 101, 153, and 180. These MDLs were calculated using the amount of target compound in the passive sampler before PRC correction, and are specific to the sediment and incubation time used.

Previous work has shown that pore water concentrations deduced from passive samplers compare within a factor of 2 to pore water concentrations obtained through air bridges, while pore water concentrations estimated through sediment extraction and equilibrium partitioning calculations average 7 times too high [19]. We measured the pore water concentration of PCB 101 in 18 lake sediment samples through (a) direct liquid-liquid extraction of pore water, (b) incubation of sediment with PE passive samplers, and (c) sediment extraction with equilibrium partitioning. The pore water concentrations deduced from PE passive samplers were about two times higher than directly measured pore water concentrations. Pore water concentrations obtained through solvent extraction and equilibrium partitioning were about 11 times higher than directly measured pore water concentrations, suggesting the advantages of PE passive sampling over sediment extraction with equilibrium partitioning.

Traditional sediment mapping techniques locate sites with elevated concentrations via sediment sampling and assume that sediment located close to such "hot spots" are also contaminated. This technique can be improved upon by use of contour mapping software such as Surfer®9. Maps were created using pore water concentrations deduced from PE passive samplers, sediment extraction with equilibrium partitioning, and direct pore water measurement at 20 sites. Like traditional techniques, Surfer®9 identified regions of elevated concentration, but the shape and extent of these regions depended on surrounding sediment concentration. A Monte Carlo method was used

to investigate the change in contour lines if the map was created from a new set of pore water concentration values chosen within method precision. The map did not change significantly over 10 such data sets (liquid-liquid extraction method precision 8%), suggesting that the hot spot areas can be reasonably trusted.

As noted in Chapter 3, the correction for equilibrium using PRCs becomes error-prone as the PRC load relative to the pre-incubation load remains near 1. Future efforts should encourage PRC loss through longer incubations, thinner passive samplers, or non-PE materials that promote faster PRC migration. Future efforts could also endeavor to obtain an MDL based on directly measured pore water concentrations, not pore water concentrations as deduced from a known sediment spike as in Chapter 4. Incorporation of the effects of black carbon into the model of Fernandez et al. (2009) would be a valuable addition to the passive sampler method.

Appendix A

Excel Macros

A.1 Instructions for running Excel macros

Your Excel sheet needs to have a Standards, Extracts, and Constants worksheet.

First, run build_standardslog:

1. Go to the standards worksheet.

2. Click on the Developer tab, then the macros icon.

3. The macro dialogue box pops up. Choose build_standardslog.

4. The macro will ask you for the starting row. Pick your favorite row (preferably vacant).

5. The macro will ask you for the run date. I use the format monthdate (0719), but you can use whatever you want, as long as its consistent.

6. The macro asks you how many DCM, injection, recovery, PRC, target standards, and time 0 strips you want.

7. The macro creates boxes for the DCM blanks and recovery, PRC, injection, and Aroclor standards.

8. The macro will ask you for the mass of the time 0 strips and the concentrations/ng added of the standards solutions. This information is entered into the Constants worksheet and the macro creates boxes for the time 0 strips.

9. Now you can enter the peak areas and backgrounds, elution times, etc. from the GCMS software.

Now that you have standards, run build_datalog:

1. Go to the Extracts worksheet.

2. Click on the Developer tab, then the macros icon.

3. Choose build_datalog from the dialogue box.

4. The macro will ask you how many PE strips you want the macro to make data entry boxes for (I usually make boxes for an entire run at once, since they all have the same recovery/injection/PRC standards). Any number (except 0) is fine.

5. The macro will ask you for the run date. This has to be entered in the same format as you entered it in the build_standardslog macrothe macro will use the date to find the standards average peak area values.

6. The macro will ask you for the ng/mL of the recovery standard, ng recovery compounds added to the sample, ng/mL of the PRC standard, ng/mL of the injection standard, ng injection compounds added to the sample, and ng/mL of the target compound standard.

7. The macro will ask you for the strip name (short abbreviation that goes after the date), the strip description (long name that can include site number, experiment, etc.), and strip mass (g).

8. The macro will ask you for the starting rowthe row that you want the data boxes to start at.

9. The macro creates boxes for the PE strips and enters the calculations.

A.2 Standards Organization (run first)

```
Sub build_standardslog()
'get info from user
    startRow = Application.InputBox("Enter Starting Row", "
       Starting Row", , , , , , 1)
    rundate = Application.InputBox("Enter run date", "Run
       Date", , , , , , 1)
```

```
    numDCM = Application.InputBox("Enter number of DCM
        samples", "DCM samples", , , , , 1)
    numInj = Application.InputBox("Enter number of injection
        standard samples", "Injection standards", , , , , , 1)
    numRec = Application.InputBox("Enter number of recovery
        standard samples", "Recovery standards", , , , , , 1)
    numPRC = Application.InputBox("Enter number of PRC
        standard samples", "PRC standards", , , , , , 1)
    numEPA = Application.InputBox("Enter number of target
        standard samples", "Target standards", , , , , 1)
    numBlank = Application.InputBox("Enter number of Time 0
        strips", "Time 0 Strips", , , , , , 1)
'make title box
    Call build_title(startRow)
'make dcm inputs
    For dcm = 1 To numDCM
        If dcm = 1 Then
            pasterow = startRow + (dcm + 4)
            Call build_dcm(startRow)
            Range("A" & (startRow + 5)).Value = rundate & "
                DCM"
            Range("A" & (startRow + 5)).Font.Bold = True
        Else
            Worksheets("Standards").Range("A" & (startRow +
                5), "J" & (startRow + 5)).Copy Destination:=
                Range("A" & pasterow)
            Range("A" & pasterow).Value = rundate & "DCM" & (
                dcm - 1)
            Range("A" & pasterow).Font.Bold = True
        End If
```

```
        pasterow = pasterow + 1
    Next dcm
    Call dcm_borders(startRow, numDCM)
    pasterow = pasterow + 1
'make injection standard inputs
    For inj = 1 To numInj
        If inj = 1 Then
            injstartrow = pasterow
            Call build_box(pasterow, 5)
            For num = 1 To 5
                Range("B" & (pasterow + num + 1)).Value = (
                  num + 2) & " Cl"
                Range("F" & (pasterow + num + 1)).Value = "=E
                  " & (pasterow + num + 1) & "/D" & (
                  pasterow + num + 1)
            Next num
            Range("A" & (pasterow + 2)).Value = "d17-39"
            Range("A" & (pasterow + 3)).Value = "d34-55"
            Range("A" & (pasterow + 4)).Value = "d22-104"
            Range("A" & (pasterow + 5)).Value = "d40-150"
            Range("A" & (pasterow + 6)).Value = "d52-188"
        Else
            Worksheets("Standards").Range("A" & injstartrow,
              "H" & (injstartrow + 6)).Copy Destination:=
              Range("A" & pasterow)
        End If
        Range("A" & pasterow).Value = rundate & "INJ" & inj
        Range("A" & pasterow).Font.Bold = True
        pasterow = pasterow + 7
    Next inj
```

```
    Worksheets("Standards").Range("A" & injstartrow, "H" & (
       injstartrow + 6)).Copy Destination:=Range("I" & (
       pasterow - 7))
    Range("I" & (pasterow - 7)).Font.Bold = True
    Range("I" & (pasterow - 7)).Value = "Average Injection
       Standards"
    For Count = 1 To 5
        Range("L" & (pasterow - (6 - Count))).Value = "
           Average("
        For num = 1 To numInj
            If num = numInj Then
                Range("L" & (pasterow - (6 - Count))).Value =
                    Range("L" & (pasterow - (6 - Count))).
                   Value & "D" & (pasterow - ((6 - Count) + 7
                    * (num - 1))) & ")"
            Else
                Range("L" & (pasterow - (6 - Count))).Value =
                    Range("L" & (pasterow - (6 - Count))).
                   Value & "D" & (pasterow - ((6 - Count) + 7
                    * (num - 1))) & ","
            End If
        Next num
        Range("L" & (pasterow - (6 - Count))).Value = "=" &
           Range("L" & (pasterow - (6 - Count))).Value
    Next Count
    For num = 0 To 4
        Names.Add Name:=("avginj" & rundate & num), RefersTo
           :=Range("L" & (pasterow - 5 + num))
    Next
'make recovery standards entries
```

```
pasterow = pasterow + 1
   For rec = 1 To numRec
        If rec = 1 Then
            recstartrow = pasterow
            Call build_box(pasterow, 6)
            For num = 1 To 6
                Range("B" & (pasterow + num + 1)).Value = (
                   num + 2) & " Cl"
                Range("F" & (pasterow + num + 1)).Value = "=E
                   " & (pasterow + num + 1) & "/D" & (
                   pasterow + num + 1)
            Next num
            Range("A" & (pasterow + 2)).Value = "d5-19"
            Range("A" & (pasterow + 3)).Value = "d8-77"
            Range("A" & (pasterow + 4)).Value = "d54-105"
            Range("A" & (pasterow + 5)).Value = "d64-167"
            Range("A" & (pasterow + 6)).Value = "d77-170"
            Range("A" & (pasterow + 7)).Value = "d84-194"
        Else
            Worksheets("Standards").Range("A" & recstartrow,
               "H" & (recstartrow + 7)).Copy Destination:=
               Range("A" & pasterow)
        End If
        Range("A" & pasterow).Value = rundate & "REC" & rec
        Range("A" & pasterow).Font.Bold = True
        pasterow = pasterow + 8
    Next rec
    Worksheets("Standards").Range("A" & recstartrow, "H" & (
       recstartrow + 7)).Copy Destination:=Range("I" & (
       pasterow - 8))
```

```
    Range("I" & (pasterow - 8)).Font.Bold = True
    Range("I" & (pasterow - 8)).Value = "Average Recovery
       Standards"
    For Count = 1 To 6
        Range("L" & (pasterow - (7 - Count))).Value = "
           Average("
        For num = 1 To numInj
            If num = numRec Then
                Range("L" & (pasterow - (7 - Count))).Value =
                    Range("L" & (pasterow - (7 - Count))).
                   Value & "D" & (pasterow - ((7 - Count) + 8
                    * (num - 1))) & ")"
            Else
                Range("L" & (pasterow - (7 - Count))).Value =
                    Range("L" & (pasterow - (7 - Count))).
                   Value & "D" & (pasterow - ((7 - Count) + 8
                    * (num - 1))) & ","
            End If
        Next num
        Range("L" & (pasterow - (7 - Count))).Value = "=" &
           Range("L" & (pasterow - (7 - Count))).Value
    Next Count
    For num = 0 To 5
        Names.Add Name:=("avgrec" & rundate & num), RefersTo
           :=Range("L" & (pasterow - 6 + num))
    Next
'Add PRC entries
    pasterow = pasterow + 1
   For prc = 1 To numPRC
        If prc = 1 Then
```

```
            prcstartrow = pasterow
            Call build_box(pasterow, 4)
            For num = 1 To 4
                Range("B" & (pasterow + num + 1)).Value = (
                    num + 3) & " Cl"
                Range("F" & (pasterow + num + 1)).Value = "=E
                    " & (pasterow + num + 1) & "/D" & (
                    pasterow + num + 1)
            Next num
            Range("A" & (pasterow + 2)).Value = "d19-52"
            Range("A" & (pasterow + 3)).Value = "d38-101"
            Range("A" & (pasterow + 4)).Value = "d54-153"
            Range("A" & (pasterow + 5)).Value = "d72-180"
        Else
            Worksheets("Standards").Range("A" & prcstartrow,
                "H" & (prcstartrow + 5)).Copy Destination:=
                Range("A" & pasterow)
        End If
        Range("A" & pasterow).Value = rundate & "PRC" & prc
        Range("A" & pasterow).Font.Bold = True
        pasterow = pasterow + 6
    Next prc
    Worksheets("Standards").Range("A" & prcstartrow, "H" & (
        prcstartrow + 5)).Copy Destination:=Range("I" & (
        pasterow - 6))
    Range("I" & (pasterow - 6)).Font.Bold = True
    Range("I" & (pasterow - 6)).Value = "Average PRC
        Standards"
    prcrow = pasterow - 6
    For Count = 1 To 4
```

```
    Range("L" & (pasterow - (5 - Count))).Value = "Average("
        For num = 1 To numPRC
            If num = numInj Then
                Range("L" & (pasterow - (5 - Count))).Value =
                    Range("L" & (pasterow - (5 - Count))).
                    Value & "D" & (pasterow - ((5 - Count) + 6
                    * (num - 1))) & ")"
            Else
                Range("L" & (pasterow - (5 - Count))).Value =
                    Range("L" & (pasterow - (5 - Count))).
                    Value & "D" & (pasterow - ((5 - Count) + 6
                    * (num - 1))) & ","
            End If
        Next num
        Range("L" & (pasterow - (5 - Count))).Value = "=" &
            Range("L" & (pasterow - (5 - Count))).Value
    Next Count
    For num = 0 To 3
        Names.Add Name:=("avgprc" & rundate & num), RefersTo
            :=Range("L" & (pasterow - 4 + num))
    Next
'add target standard entries
    pasterow = pasterow + 1
   For epa = 1 To numEPA
        If epa = 1 Then
            epastartrow = pasterow
            Call build_box(pasterow, 4)
            For num = 1 To 4
                Range("B" & (pasterow + num + 1)).Value = (
                    num + 3) & " Cl"
```

```
                Range("F" & (pasterow + num + 1)).Value = "=E
                    " & (pasterow + num + 1) & "/D" & (
                    pasterow + num + 1)
            Next num
            Range("A" & (pasterow + 2)).Value = "d19-52"
            Range("A" & (pasterow + 3)).Value = "d38-101"
            Range("A" & (pasterow + 4)).Value = "d54-153"
            Range("A" & (pasterow + 5)).Value = "d72-180"
        Else
            Worksheets("Standards").Range("A" & epastartrow,
                "H" & (epastartrow + 5)).Copy Destination:=
                Range("A" & pasterow)
        End If
        Range("A" & pasterow).Value = rundate & "EPA" & epa
        Range("A" & pasterow).Font.Bold = True
        pasterow = pasterow + 6
    Next epa
    Worksheets("Standards").Range("A" & epastartrow, "H" & (
        epastartrow + 5)).Copy Destination:=Range("I" & (
        pasterow - 6))
    Range("I" & (pasterow - 6)).Font.Bold = True
    Range("I" & (pasterow - 6)).Value = "Average Target
        Standards"
    For Count = 1 To 4
    Range("L" & (pasterow - (5 - Count))).Value = "Average("
        For num = 1 To numEPA
            If num = numInj Then
                Range("L" & (pasterow - (5 - Count))).Value =
                    Range("L" & (pasterow - (5 - Count))).
                    Value & "D" & (pasterow - ((5 - Count) + 6
```

```
                    * (num - 1))) & ")"
            Else
                Range("L" & (pasterow - (5 - Count))).Value =
                    Range("L" & (pasterow - (5 - Count))).
                    Value & "D" & (pasterow - ((5 - Count) + 6
                    * (num - 1))) & ","
            End If
        Next num
        Range("L" & (pasterow - (5 - Count))).Value = "=" &
            Range("L" & (pasterow - (5 - Count))).Value
    Next Count
    For num = 0 To 3
        Names.Add Name:=("avgaro" & rundate & num), RefersTo
            :=Range("L" & (pasterow - 4 + num))
    Next

'add Time 0 strip entries
pasterow = pasterow + 1
Call builddatalog(rundate, pasterow, numBlank)
    Worksheets("Standards").Range("A" & prcrow, "H" & (prcrow
        + 5)).Copy Destination:=Range("K" & pasterow + 9)
    Range("K" & (pasterow + 9)).Font.Bold = True
    Range("K" & (pasterow + 9)).Value = "Average Time 0 PRCs"
    Range("N" & (pasterow + 10)).Value = "ng PRC/gPE"
    For Count = 1 To 4
    Range("N" & (pasterow + (10 + Count))).Value = "Average("
    For num = 1 To numPRC
            If num = numInj Then
                Range("N" & (pasterow + (10 + Count))).Value
                    = Range("N" & (pasterow + (10 + Count))).
```

```
                Value & "H" & (pasterow + ((10 + Count) +
                28 * (num - 1))) & ")"
            Else
                Range("N" & (pasterow + (10 + Count))).Value
                = Range("N" & (pasterow + (10 + Count))).
                Value & "H" & (pasterow + ((10 + Count) +
                28 * (num - 1))) & ","
            End If
        Next num
        Range("N" & (pasterow + (10 + Count))).Value = "=" &
            Range("N" & (pasterow + (10 + Count))).Value
    Next Count
    For num = 0 To 3
        Names.Add Name:=("avgblk" & rundate & num), RefersTo
            :=Range("N" & (pasterow + 11 + num))
    Next num
End Sub
Sub build_title(startRow)
    Range("A" & startRow, "J" & (startRow + 3)).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
```

```
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & startRow, "A" & (startRow + 3)).Select
    Selection.Font.Bold = True
    Range("D" & startRow).Select
    Selection.Font.Bold = True
    Range("A" & startRow).Select
    ActiveCell.FormulaR1C1 = "Name"
    Range("A" & (startRow + 1)).Select
    ActiveCell.FormulaR1C1 = "Run Date"
    Range("A" & (startRow + 2)).Select
    ActiveCell.FormulaR1C1 = "Experiment"
    Range("A" & (startRow + 3)).Select
    ActiveCell.FormulaR1C1 = "File Type"
    Range("D" & startRow).Select
    ActiveCell.FormulaR1C1 = "Notes"
End Sub
```

A.3 Organize Samples and Calculations

```
Sub builddatalog(Optional rundate As Variant, Optional
   startRow As Variant, Optional numStrips As Variant)
Dim nameArray() As String
Dim descArray() As String
Dim massArray() As Variant
Dim volArray6() As Variant
Dim volarray4() As Variant
Dim conversion As Double
ReDim volArray6(1 To 6) As Variant
ReDim volarray4(1 To 4) As Variant
Dim KpewArray(1 To 4) As Variant

If IsMissing(rundate) = True Or IsMissing(pasterow) = True Or
    IsMissing(numBlank) = True Then
    numStrips = Application.InputBox("How many samples do you
        want to process?", "Enter Sample Number", , , , , ,
       1)
    rundate = Application.InputBox("Enter date of run", "
       Enter date", , , , , 1)
    startRow = Application.InputBox("Enter Starting Row", "
       Starting Row", , , , , 1)
    ReDim nameArray(1 To numStrips)
    ReDim descArray(1 To numStrips)
    ReDim massArray(1 To numStrips)
    For strip = 1 To numStrips
        Name = Application.InputBox("Enter strip " & strip &
           " name", "strip name")
        nameArray(strip) = rundate & Name
```

```
        descArray(strip) = InputBox("Enter strip " & strip &
            " description", "strip description")
        massArray(strip) = InputBox("Enter strip " & strip &
            " mass (g)", "strip mass")
    Next strip
Else
    ReDim nameArray(1 To numStrips)
    ReDim descArray(1 To numStrips)
    ReDim massArray(1 To numStrips)
    For strip = 1 To numStrips
        nameArray(strip) = rundate & "T0" & strip
        descArray(strip) = "Time 0 Strip " & strip
        massArray(strip) = InputBox("Enter strip " & strip &
            " mass (g)", "strip mass")
     Next strip
End If

'get whole batch info
recngml = Application.InputBox("enter ng/mL of rec standard",
    "rec std ng/mL", , , , , , 1)
ngrec = Application.InputBox("Enter ng rec added", "ng rec",
   , , , , , 1)
PRCngml = Application.InputBox("enter ng/mL of prc standard",
    "prc std ng/mL", , , , , , 1)
injngml = Application.InputBox("enter ng/mL of inj standard",
    "inj std ng/mL", , , , , , 1)
nginj = Application.InputBox("Enter ng inj added", "ng inj",
   , , , , , 1)
arongml = Application.InputBox("enter ng/mL of target
   compound standard", "ng target", , , , , 1)
```

```
'get per-strip info

'enter Kpew info
KpewArray(1) = 5.554
KpewArray(2) = 6.093
KpewArray(3) = 6.633
KpewArray(4) = 7.073

'get starting rows
Perow = Application.InputBox("Enter Next Vacant Row in PE
   Mass Worksheet", "PE  mass row", , , , , 1)

'set up constants worksheet
Worksheets("Constants").Range("D" & Perow).Value = nameArray
   (1) & " to " & nameArray(numStrips)
Worksheets("Constants").Range("D" & Perow).Font.Bold = True
Worksheets("Constants").Range("D" & (Perow + 1)).Value = "Rec
    Concentration (ng/mL)"
Worksheets("Constants").Range("D" & (Perow + 2)).Value = "ng
   rec added"
Worksheets("Constants").Range("D" & (Perow + 3)).Value = "PRC
    concentration (ng/mL)"
Worksheets("Constants").Range("D" & (Perow + 4)).Value = "Inj
    concentration (ng/mL)"
Worksheets("Constants").Range("D" & (Perow + 5)).Value = "ng
   inj added"
Worksheets("Constants").Range("D" & (Perow + 6)).Value = "
   Target Concentration (ng/mL)"
Worksheets("Constants").Range("E" & (Perow + 1)).Value =
```

```
    recngml
Worksheets("Constants").Range("E" & (Perow + 2)).Value =
    ngrec
Worksheets("Constants").Range("E" & (Perow + 3)).Value =
    PRCngml
Worksheets("Constants").Range("E" & (Perow + 4)).Value =
    injngml
Worksheets("Constants").Range("E" & (Perow + 5)).Value =
    nginj
Worksheets("Constants").Range("E" & (Perow + 6)).Value =
    arongml

For strip = 1 To numStrips
    If strip = 1 Then
    'build first box from scratch, using subfunction
        Call build_firstentry(startRow)
        pasterow = startRow
    Else
    'copy first data box to build the rest of the boxes
        pasterow = startRow + (strip - 1) * 28
        Range("A" & startRow, "J" & (startRow + 27)).Copy
            Destination:=Range("A" & pasterow)
    End If

    'enter strip name and description
    Range("A" & pasterow).Value = nameArray(strip)
    Range("B" & pasterow).Value = descArray(strip)
    Range("A" & pasterow, "B" & pasterow).Font.Bold = True
    Worksheets("Constants").Range("A" & (Perow + strip - 1)).
        Value = nameArray(strip)
```

```
Worksheets("Constants").Range("B" & (Perow + strip - 1)).
    Value = massArray(strip)

'calculate sample volume
offnum = 0
For num = 17 To 21
Range("H" & (pasterow + num)).Formula = "=avginj" &
    rundate & offnum & "*'Constants'!E" & (Perow + 5) &
    "*1000/('Constants'!E" & (Perow + 4) & "*D" & (
    pasterow + num) & ")"
offnum = offnum + 1
Next
Range("I" & (pasterow + 21)).Formula = "=SUM(H" & (
    pasterow + 17) & ":H" & (pasterow + 21) & ")"
'rec calculations
offnum = 0
For num = 3 To 8
Range("H" & (pasterow + num)).Formula = "='Constants'!E"
    & (Perow + 1) & "*D" & (pasterow + num) & "*I" & (
    pasterow + 21) & "*0.001/('Constants'!E" & (Perow + 2)
     & "*avgrec" & rundate & offnum & ")"
offnum = offnum + 1
Next
'PRC calculations
offnum = 0
For num = 11 To 14
Range("H" & (pasterow + num)).Value = "=I" & (pasterow +
    21) & "*D" & (pasterow + num) & "*0.001/('Constants'!B
    " & (Perow + strip - 1) & "*avgPRC" & rundate & offnum
     & "/('Constants'!E" & (Perow + 3) & "))"
```

```
    Range("I" & (pasterow + num)).Value = "=H" & (pasterow +
       num) & "/avgblk" & rundate & (num - 11)
    offnum = offnum + 1
    Next
    'Aroclor calculations
    offnum = 0
    For num = 24 To 27
    Range("H" & (pasterow + num)).Value = "='Constants'!E" &
       (Perow + 6) & "*D" & (pasterow + num) & "*I" & (
       pasterow + 21) & "*0.001/(avgaro" & rundate & offnum &
        "*" & "'Constants'!B" & (Perow + strip - 1) & ")"
    offnum = offnum + 1
    Range("I" & (pasterow + num)).Value = "=H" & (pasterow +
       num) & "/(1-I" & (pasterow + (num - 13)) & ")"
    Range("J" & (pasterow + num)).Value = "=I" & (pasterow +
       num) & "*1000/" & KpewArray(num - 23)
    Next
Next strip

End Sub
```

A.4 build_dcm (sub of build_standardslog)

```
Sub build_dcm(startRow)
    With Range("A" & (startRow + 5), "J" & (startRow + 5)).
       Interior
        .Pattern = xlSolid
        .PatternColorIndex = xlAutomatic
        .ThemeColor = xlThemeColorDark1
        .TintAndShade = -0.499984740745262
```

```
        .PatternTintAndShade = 0
    End With
End Sub
```

A.5 dcm_borders(sub of build_standardslog)

```
Sub dcm_borders(startRow, numDCM)
    Range("A" & (startRow + 5), "J" & (startRow + 4 + numDCM)
        ).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
```

```
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
End Sub
```

A.6 build_box (sub of build_standardslog)

```
Sub build_box(pasterow, congnum)
    Range("A" & pasterow, "H" & pasterow).Select
    With Selection.Interior
        .Pattern = xlSolid
        .PatternColorIndex = xlAutomatic
        .ThemeColor = xlThemeColorDark1
        .TintAndShade = -0.499984740745262
        .PatternTintAndShade = 0
    End With
    Range("A" & (pasterow + 1), "H" & (pasterow + 1)).Select
    With Selection.Interior
        .Pattern = xlSolid
        .PatternColorIndex = xlAutomatic
        .ThemeColor = xlThemeColorDark1
        .TintAndShade = -0.249977111117893
        .PatternTintAndShade = 0
    End With
    Range("A" & pasterow, "H" & (pasterow + congnum + 1)).
       Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
```

```
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone

    Range("A" & pasterow, "H" & pasterow).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeTop)
```

```
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (pasterow + 1), "H" & (pasterow + 1)).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeBottom)
```

```
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (pasterow + 1), "J" & (pasterow + 1)).Select
    Selection.Font.Italic = True
    With Selection.Font
        .Name = "Calibri"
        .Size = 8
        .StrikeThrough = False
        .Superscript = False
        .Subscript = False
        .OutlineFont = False
        .Shadow = False
        .Underline = xlUnderlineStyleNone
        .ThemeColor = xlThemeColorLight1
        .TintAndShade = 0
        .ThemeFont = xlThemeFontMinor
    End With
    Range("A" & (pasterow + 1)).Value = "domain-congener"
    Range("B" & (pasterow + 1)).Value = "Cl number"
    Range("C" & (pasterow + 1)).Value = "elution time"
    Range("D" & (pasterow + 1)).Value = "peak area"
```

```
    Range("E" & (pasterow + 1)).Value = "background"
    Range("F" & (pasterow + 1)).Value = "back/peak"
    Range("G" & (pasterow + 1)).Value = "scans integrated"
End Sub
```

A.7 build_firstentry (sub of builddatalog)

```
Sub build_firstentry(startRow)
    Range("A" & startRow, "J" & startRow).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
```

```
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (startRow + 1), "J" & (startRow + 2)).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
```

```
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (startRow + 3), "J" & (startRow + 8)).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .ColorIndex = 0
```

```
        .TintAndShade = 0
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (startRow + 9), "J" & (startRow + 10)).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
```

```
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (startRow + 11), "J" & (startRow + 14)).
       Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
```

```
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (startRow + 15), "J" & (startRow + 16)).
       Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
```

```
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (startRow + 17), "J" & (startRow + 21)).
       Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
```

```
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (startRow + 22), "J" & (startRow + 23)).
       Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
```

```
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & (startRow + 24), "J" & (startRow + 27)).
       Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    With Selection.Borders(xlEdgeLeft)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeTop)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
        .Weight = xlThin
    End With
    With Selection.Borders(xlEdgeRight)
        .LineStyle = xlContinuous
        .ColorIndex = 0
        .TintAndShade = 0
```

```
        .Weight = xlThin
    End With
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("A" & startRow, "J" & startRow).Select
    With Selection.Interior
        .Pattern = xlSolid
        .PatternColorIndex = xlAutomatic
        .ThemeColor = xlThemeColorDark1
        .TintAndShade = -0.499984740745262
        .PatternTintAndShade = 0
    End With
    Range("A" & (startRow + 1), "J" & (startRow + 2)).Select
    With Selection.Interior
        .Pattern = xlSolid
        .PatternColorIndex = xlAutomatic
        .ThemeColor = xlThemeColorDark1
        .TintAndShade = -0.249977111117893
        .PatternTintAndShade = 0
    End With
    Range("A" & (startRow + 9), "J" & (startRow + 10)).Select
    With Selection.Interior
        .Pattern = xlSolid
        .PatternColorIndex = xlAutomatic
        .ThemeColor = xlThemeColorDark1
        .TintAndShade = -0.249977111117893
        .PatternTintAndShade = 0
    End With
    Range("A" & (startRow + 15), "J" & (startRow + 16)).
       Select
```

```
With Selection.Interior
    .Pattern = xlSolid
    .PatternColorIndex = xlAutomatic
    .ThemeColor = xlThemeColorDark1
    .TintAndShade = -0.249977111117893
    .PatternTintAndShade = 0
End With
Range("A" & (startRow + 15), "J" & (startRow + 16)).
   Select
With Selection.Interior
    .Pattern = xlSolid
    .PatternColorIndex = xlAutomatic
    .ThemeColor = xlThemeColorDark1
    .TintAndShade = -0.249977111117893
    .PatternTintAndShade = 0
End With
    Range("A" & (startRow + 22), "J" & (startRow + 23)).
       Select
With Selection.Interior
    .Pattern = xlSolid
    .PatternColorIndex = xlAutomatic
    .ThemeColor = xlThemeColorDark1
    .TintAndShade = -0.249977111117893
    .PatternTintAndShade = 0
End With
Range("A" & (startRow + 1)).Select
Selection.Font.Italic = True
With Selection.Font
    .Name = "Calibri"
    .Size = 10
```

```
        .StrikeThrough = False
        .Superscript = False
        .Subscript = False
        .OutlineFont = False
        .Shadow = False
        .Underline = xlUnderlineStyleNone
        .ThemeColor = xlThemeColorLight1
        .TintAndShade = 0
        .ThemeFont = xlThemeFontMinor
    End With
    ActiveCell.FormulaR1C1 = """Recovery Compounds"""
    Range("A" & (startRow + 9)).Select
    Selection.Font.Italic = True
    With Selection.Font
        .Name = "Calibri"
        .Size = 10
        .StrikeThrough = False
        .Superscript = False
        .Subscript = False
        .OutlineFont = False
        .Shadow = False
        .Underline = xlUnderlineStyleNone
        .ThemeColor = xlThemeColorLight1
        .TintAndShade = 0
        .ThemeFont = xlThemeFontMinor
    End With
    ActiveCell.FormulaR1C1 = """Performance Reference
       Compounds"""
    Range("A" & (startRow + 15)).Select
    Selection.Font.Italic = True
```

```
With Selection.Font
    .Name = "Calibri"
    .Size = 10
    .StrikeThrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
    .TintAndShade = 0
    .ThemeFont = xlThemeFontMinor
End With
ActiveCell.FormulaR1C1 = """Injection Compounds"""
Range("A" & (startRow + 22)).Select
With Selection.Font
    .Name = "Calibri"
    .Size = 10
    .StrikeThrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
    .TintAndShade = 0
    .ThemeFont = xlThemeFontMinor
End With
Selection.Font.Italic = True
ActiveCell.FormulaR1C1 = """Aroclor Compounds"""
```

```
Range("A" & (startRow + 2)).Select
With Selection.Font
    .Name = "Calibri"
    .Size = 8
    .StrikeThrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
    .TintAndShade = 0
    .ThemeFont = xlThemeFontMinor
End With
Selection.Font.Italic = True
ActiveCell.FormulaR1C1 = "domain-congener"
Range("B" & (startRow + 2)).Select
ActiveCell.FormulaR1C1 = ""
Range("A" & (startRow + 2), "J" & (startRow + 2)).Select
Selection.Font.Italic = True
With Selection.Font
    .Name = "Calibri"
    .Size = 8
    .StrikeThrough = False
    .Superscript = False
    .Subscript = False
    .OutlineFont = False
    .Shadow = False
    .Underline = xlUnderlineStyleNone
    .ThemeColor = xlThemeColorLight1
```

```
        .TintAndShade = 0
        .ThemeFont = xlThemeFontMinor
    End With
    Range("B" & (startRow + 2)).Select
    ActiveCell.FormulaR1C1 = "Cl number"
    Range("C" & (startRow + 2)).Select
    ActiveCell.FormulaR1C1 = "elution time"
    Range("D" & (startRow + 2)).Select
    ActiveCell.FormulaR1C1 = "peak area"
    Range("E" & (startRow + 2)).Select
    ActiveCell.FormulaR1C1 = "background"
    Range("F" & (startRow + 2)).Select
    ActiveCell.FormulaR1C1 = "back/peak"
    Range("G" & (startRow + 2)).Select
    ActiveCell.FormulaR1C1 = "scans integrated"
    Range("H" & (startRow + 2)).Select
    ActiveCell.FormulaR1C1 = "% recovery"
    Range("A" & (startRow + 2), "J" & (startRow + 2)).Select
    Selection.Copy
    Range("A" & (startRow + 10)).Select
    ActiveSheet.Paste
    Range("A" & (startRow + 16)).Select
    ActiveSheet.Paste
    Range("A" & (startRow + 23)).Select
    ActiveSheet.Paste
    Application.CutCopyMode = False
    Range("H" & (startRow + 10)).Select
    ActiveCell.FormulaR1C1 = "ng PRC/g PE"
    Range("H" & (startRow + 16)).Select
    ActiveCell.FormulaR1C1 = "sample volume"
```

```
  Range("H" & (startRow + 2)).Select
ActiveCell.FormulaR1C1 = "ng target/gPE"
Range("I" & (startRow + 10)).Value = "PRCs/time 0 value"
Range("I" & (startRow + 16)).Value = "avg.sample volume (
  uL)"
Range("I" & (startRow + 23)).Value = "PRC corrected"
Range("J" & (startRow + 23)).Value = "ng target/L PW"
Range("J" & (startRow + 10)).Value = "modeled PRC values"
Range("A" & (startRow + 3)).Select
ActiveCell.FormulaR1C1 = "d5-19"
Range("A" & (startRow + 4)).Select
ActiveCell.FormulaR1C1 = "d46-77"
Range("A" & (startRow + 5)).Select
ActiveCell.FormulaR1C1 = "d54-105"
Range("A" & (startRow + 6)).Select
ActiveCell.FormulaR1C1 = "d64-167"
Range("A" & (startRow + 7)).Select
ActiveCell.FormulaR1C1 = "d77-170"
Range("A" & (startRow + 8)).Select
ActiveCell.FormulaR1C1 = "d84-194"
Range("A" & (startRow + 11)).Select
ActiveCell.FormulaR1C1 = "d21-47"
Range("A" & (startRow + 12)).Select
ActiveCell.FormulaR1C1 = "d43-111"
Range("A" & (startRow + 13)).Select
ActiveCell.FormulaR1C1 = "d54-153"
Range("A" & (startRow + 14)).Select
ActiveCell.FormulaR1C1 = "d59-178"
Range("A" & (startRow + 17)).Select
ActiveCell.FormulaR1C1 = "d17-39"
```

```
Range("A" & (startRow + 18)).Select
ActiveCell.FormulaR1C1 = "d34-55"
Range("A" & (startRow + 19)).Select
ActiveCell.FormulaR1C1 = "d22-104"
Range("A" & (startRow + 20)).Select
ActiveCell.FormulaR1C1 = "d40-150"
Range("A" & (startRow + 21)).Select
ActiveCell.FormulaR1C1 = "d52-188"
Range("A" & (startRow + 24)).Select
ActiveCell.FormulaR1C1 = "d19-52"
Range("A" & (startRow + 25)).Select
ActiveCell.FormulaR1C1 = "d38-101"
Range("A" & (startRow + 26)).Select
ActiveCell.FormulaR1C1 = "d54-153"
Range("A" & (startRow + 27)).Select
ActiveCell.FormulaR1C1 = "d72-180"
Range("B" & (startRow + 3)).Select
ActiveCell.FormulaR1C1 = "3  Cl"
Range("B" & (startRow + 4)).Select
ActiveCell.FormulaR1C1 = "4   Cl"
Range("B" & (startRow + 5)).Select
ActiveCell.FormulaR1C1 = "5  Cl"
Range("B" & (startRow + 6)).Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
Selection.Borders(xlEdgeTop).LineStyle = xlNone
Selection.Borders(xlEdgeBottom).LineStyle = xlNone
Selection.Borders(xlEdgeRight).LineStyle = xlNone
Selection.Borders(xlInsideVertical).LineStyle = xlNone
```

```
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
ActiveCell.FormulaR1C1 = "6 C1"
Range("B" & (startRow + 7)).Select
Selection.Interior.ColorIndex = xlNone
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
Selection.Borders(xlEdgeTop).LineStyle = xlNone
Selection.Borders(xlEdgeBottom).LineStyle = xlNone
Selection.Borders(xlEdgeRight).LineStyle = xlNone
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
ActiveCell.FormulaR1C1 = "7 C1"
Range("B" & (startRow + 8)).Select
Selection.Interior.ColorIndex = xlNone
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
Selection.Borders(xlEdgeTop).LineStyle = xlNone
Selection.Borders(xlEdgeBottom).LineStyle = xlNone
Selection.Borders(xlEdgeRight).LineStyle = xlNone
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
ActiveCell.FormulaR1C1 = "8 C1"
Range("B" & (startRow + 4), "B" & (startRow + 7)).Select
Selection.Copy
Range("B" & (startRow + 11)).Select
ActiveSheet.Paste
Range("B" & (startRow + 24)).Select
ActiveSheet.Paste
```

```
Range("B" & (startRow + 3), "B" & (startRow + 7)).Select
Application.CutCopyMode = False
Selection.Copy
Range("B" & (startRow + 17)).Select
ActiveSheet.Paste
Range("C" & (startRow + 4)).Select
    Range("A" & (startRow + 2)).Select
Application.CutCopyMode = False
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
Selection.Borders(xlEdgeTop).LineStyle = xlNone
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = xlAutomatic
End With
Selection.Borders(xlEdgeRight).LineStyle = xlNone
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
Range("B" & (startRow + 9), "B" & (startRow + 10)).Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
With Selection.Borders(xlEdgeTop)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = xlAutomatic
End With
Selection.Borders(xlEdgeBottom).LineStyle = xlNone
```

```
Selection.Borders(xlEdgeRight).LineStyle = xlNone
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
With Selection.Borders(xlEdgeTop)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = 1
End With
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = xlAutomatic
End With
Selection.Borders(xlEdgeRight).LineStyle = xlNone
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
Range("B" & (startRow + 16)).Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
Selection.Borders(xlEdgeTop).LineStyle = xlNone
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = xlAutomatic
End With
Selection.Borders(xlEdgeRight).LineStyle = xlNone
```

```
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
Range("B" & (startRow + 23)).Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
Selection.Borders(xlEdgeTop).LineStyle = xlNone
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = xlAutomatic
End With
Selection.Borders(xlEdgeRight).LineStyle = xlNone
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
Range("B" & (startRow + 27)).Select
Selection.Borders(xlDiagonalDown).LineStyle = xlNone
Selection.Borders(xlDiagonalUp).LineStyle = xlNone
Selection.Borders(xlEdgeLeft).LineStyle = xlNone
Selection.Borders(xlEdgeTop).LineStyle = xlNone
With Selection.Borders(xlEdgeBottom)
    .LineStyle = xlContinuous
    .Weight = xlThin
    .ColorIndex = xlAutomatic
End With
Selection.Borders(xlEdgeRight).LineStyle = xlNone
Selection.Borders(xlInsideVertical).LineStyle = xlNone
Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
Range("D" & (startRow + 27), "E" & (startRow + 27)).
  Select
```

```
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    Selection.Borders(xlEdgeLeft).LineStyle = xlNone
    Selection.Borders(xlEdgeTop).LineStyle = xlNone
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    Selection.Borders(xlEdgeRight).LineStyle = xlNone
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
    Range("G" & (startRow + 27)).Select
    Selection.Borders(xlDiagonalDown).LineStyle = xlNone
    Selection.Borders(xlDiagonalUp).LineStyle = xlNone
    Selection.Borders(xlEdgeLeft).LineStyle = xlNone
    Selection.Borders(xlEdgeTop).LineStyle = xlNone
    With Selection.Borders(xlEdgeBottom)
        .LineStyle = xlContinuous
        .Weight = xlThin
        .ColorIndex = 1
    End With
    Selection.Borders(xlEdgeRight).LineStyle = xlNone
    Selection.Borders(xlInsideVertical).LineStyle = xlNone
    Selection.Borders(xlInsideHorizontal).LineStyle = xlNone
End Sub
```

Appendix B

Matlab Code

B.1 find_K_d_iteration.m

```
%Elizabeth Finn, 1/7/2011 (efinn@mit.edu)
%Modified chrysene_case (from Loretta Fernandez)
%Projects normalized mass of heaviest PRC from 3 lighter PRCS
    with known
%masses

%prompt user for inputs
disp(' ')
disp('This progam calculates the mass left of PCB 72-180
   based on data for 19-52,38-101, and 54-153 after
   incubation')
disp(' ')
%days=input('Please enter strip incubation time in days: ');
   %time (days)
%phi=input('Please enter sediment porosity: '); %porosity
numStrips=input('How many PE strips do you want to process?
   ');
```

```
numExpt=input('Which experiment? Enter 1 for QA/QC, 2 for SM,
    3 for Sed Blank: ');
if ismember(numExpt,[1,2,3])==0
    numExpt=input('Enter number: ');
end
numArray=1:1:numStrips;
MpeArray=zeros(numStrips,4);
possiblePhis
   =[0.87223686,0.53338921,0.90908648,0.62579978,0.90908648,0.76054732,0.

    0.88906024,0.92660751,0.91663052,0.90231598,0.94454073,0.94827586,0.9

    0.93212869,0.94360087,0.93790993,0.9440711,0.94454074,0.94547815];

possibleSites=1:1:20;
phiArray=zeros(numStrips);
dayArray=[39,29,31]; %enter days of incubation
%days=dayArray(numExpt);
days=input('Enter days of incubation');
congArray=zeros(numStrips);
for strip=numArray
    %determine site porosity of each PE strip
    if numExpt==3
        phiArray(strip)=0.56586638; %enter actual phi
    elseif ismember(numExpt,[1,2])==1
        disp(['Enter data for Strip ',num2str(strip),':'])
        site=input('Sediment site: ');
        if ismember(site,possibleSites)==0
        site=input('This site does not exist. Enter sediment
           site: ');
```

```
        end
        phiArray(strip)=possiblePhis(site);
    end
    %enter congeners
    congArray(strip)=input('Base projection on 2 or 3
       congeners? ');
    if ismember(congArray(strip),[2,3])==0
        congArray(strip)=input('Please enter 2 or 3: ');
    end
    %process inputs
    if congArray(strip)==3
        MpeArray(strip,1)=input('19-52: ');
        MpeArray(strip,2)=input('38-101: ');
        MpeArray(strip,3)=input('54-153: ');
    elseif congArray(strip)==2
        MpeArray(strip,1)=input('19-52: ');
        MpeArray(strip,2)=input('38-101: ');
    end
end

%Mpe=[0.37200,0.6817664,0.8488143,0]; %data: mass of PRC in
   strip normalized to time 0 value
%site 1: 0.87223686 site 8: 0.88906024

%congener materials properties/PE inputs
log10Kpew=[5.554,6.093,6.633,7.073];
Dpe12=[6.4,2.3,0.81,0.29]; %Dpe*10^12
MW=[291.92,325.88,359.84,393.8]; %molecular weight
log10Kow=[5.84,6.38,6.92,7.36]; %from Hawker and Connell
L=12.5; %half-length of PE
```

```
tau=3; %tortuosity

%process inputs
Dpe=Dpe12.*10^-12;
T=days*24*3600.*Dpe./(L*10^-4)^2; %nondimensionalize time
Kpew=10.^log10Kpew;
%conversion=1./(2.3.*(1-phiArray(strip));

%set-up for iteration %0.433176 0.723544 0.381223 0.694909
   0.958939
nlow=0;
Kdfinal=0;
Mstore=zeros(1,41);
Kdstore=zeros(1,41);
Kdfinalstore=zeros(1,4);

%loop to find Kdfinal by iterating
for strip=numArray
    conversion=1./(2.3.*(1-phiArray(strip)));
for i=1:1:congArray(strip)
    Kdlow=1.5;
for spacing=[0.2,0.02,0.002,0.0002,0.00002]
for n=0:40
    Kd=10^(Kdlow+n*spacing); %choose for expected range
    Kdstore(n+1)=log10(Kd);
    K12=Kpew(i)/Kd;
    Dsed=Deffective(Kd,phiArray(strip),tau,MW(i)); %calls
       function
    Y=Dsed/Dpe(i);
    M=invlap('Mass_out',T(i),0,1e-9,Y,K12);
```

```
    Mstore(n+1)=M;
end
for n=1:41
    if (MpeArray(strip,i)>Mstore(n)) && (MpeArray(strip,i)<
       Mstore(n-1))
    Kdlow=Kdstore(n-1);
    nlow=n-1;
    end
end
end
%post-processing loop
for n=1:41
    if (MpeArray(strip,i)>Mstore(n)) && (MpeArray(strip,i)<
       Mstore(n-1))
    Kdfinal=Kdstore(n-1)+0.00001;
    Kdfinalstore(i)=Kdfinal;
    end
end
end

%fit data to Hawker and Connell
Kdfinalstore_converted=log10(10.^Kdfinalstore.*conversion);
p=polyfit(log10Kow(1:congArray(strip)),Kdfinalstore_converted
   (1:congArray(strip)),1);
Kdfinalstore_converted(4)=p(1)*log10Kow(4)+p(2);
if congArray(strip)==2
    Kdfinalstore_converted(3)=p(1)*log10Kow(3)+p(2);
end
Kdfinalstore=log10(10.^Kdfinalstore_converted./conversion);
```

```
%find mass left of heavy congener
K12=Kpew(4)/Kd;
Dsed=Deffective(Kd,phiArray(strip),tau,MW(4)); %calls
   function
Y=Dsed/Dpe(4);
MpeArray(strip,4)=invlap('Mass_out',T(4),0,1e-9,Y,K12);
if congArray(strip)==2
    K12=Kpew(3)/Kd;
    Dsed=Deffective(Kd,phiArray(strip),tau,MW(3)); %calls
       function
    Y=Dsed/Dpe(3);
    MpeArray(strip,3)=invlap('Mass_out',T(3),0,1e-9,Y,K12);
end

%display mass of heavy congeners to user
disp
   ('*****************************************************************')

if congArray(strip)==2
    disp(['Strip ',num2str(strip),'--Mass left of 54-153: ',
       num2str(MpeArray(strip,3))])
end
disp(['Strip ',num2str(strip),'--Mass left of 72-180: ',
   num2str(MpeArray(strip,4))])
end
disp
   ('*****************************************************************')
```

B.2 runme.m

```
%runMe.m
%Created by Elizabeth Finn (efinn@mit.edu), November 19, 2009
%modified from Loretta Fernandez (2009)
%This script defines the material properties for prc_left,
    target_in, and
%Deffective and runs prc_left and target_in

clear all
global phi Kpew_array Kd_array Dpe_array linespec_array
    MW_array L time;
time=476; % days
foc=0.0116; %site 8: 0.1423; site 1: 0.1369
phi=0.78;
L=12.5*10^-4; %half thickness of polymer (cm)
%volume_array=[]; %LeBas volume
logKow_array=[5.84,6.38,6.92,7.36]; %octanol-water partition
    coefficient
                                        %Hawker and Connell ES&T
                                            1988
Kpew_array=1*10.^logKow_array-0.29; % Kpew for target
    chemical (Lw/Lpew)
Kd_array=50*(1-phi).*2.5.*2.*foc.*10.^(0.74.*logKow_array
    +0.15);
Dpe_array=[6.4,2.3,0.81,0.29].*10^-12; %diffusivity in
    polymer (cm2/s)
linespec_array=['b','g','r','c']; %matlab linespecs
MW_array=[291.92,325.88,359.84,393.8]; %molar mass (g/mol)
```

```
%run scripts to generate transport plots
%target_in
prc_left
```

B.3 prcleft.m

```
% Script used to create plots of fractional PRC loss vs. T
   for various Kd
global phi Kpew_array Kd_array Dpe_array linespec_array Y K12
    MW_array L time;
figure(2)
clf reset
hold on
t=1:1:time; %days
modelarray=zeros(4,5);
%perform transport calculation on all congeners
for n=1:length(Kpew_array)
    K12=Kpew_array(n)/Kd_array(n);
    Dsed=Deffective(Kd_array(n),phi,3,MW_array(n));%cm^2/s
    Y=Dsed/Dpe_array(n);
    T=t*24*3600*Dpe_array(n)/(L^2);
for i=1:time
    M(i)=invlap('Mass_out', T(i),0,1e-9,Y,K12); % invlap.m
        (2,3)
end
%plot for all congeners
plot(t,M,linespec_array(n))
end
%prettify plot
xlabel('Time (days)')
```

```
ylabel('Fractional PRC in Polymer, M(t)/Mo(t)')
title({'Site 1:Fractional PRC Remaining vs. Time';['phi=',
   num2str(phi),' time=',num2str(time) ,'days ','L=',num2str(
   L),'cm']})
```

B.4 massout.m

```
% Laplace-space expression for the mass of PRC transfered
   from
% polymer to porous medium
%   K12 is partitioning coefficient between phase 1 (polymer)
    and phase 2
%   (porous medium)
%   Y is ratio of diffusivities (D(porous medium)/D(polymer))
%   s is the Laplace parameter

function F = Mass_out(s,Y,K12)
F = (1./s)-((sqrt(Y))./(s.^(3/2).*(K12+sqrt(Y).*coth(sqrt(s))
   )));
```

B.5 Data for Robust Linear Fit

```
\begin{figure}[p]
\begin{center}
\includegraphics[width=.5\textwidth]{estcpPW180}
\caption{Map of PCB 180 concentration in pore water (ng/L)
   measured via liquid-liquid extraction}
\end{center}
\label{surferPW}
\end{figure}
```

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