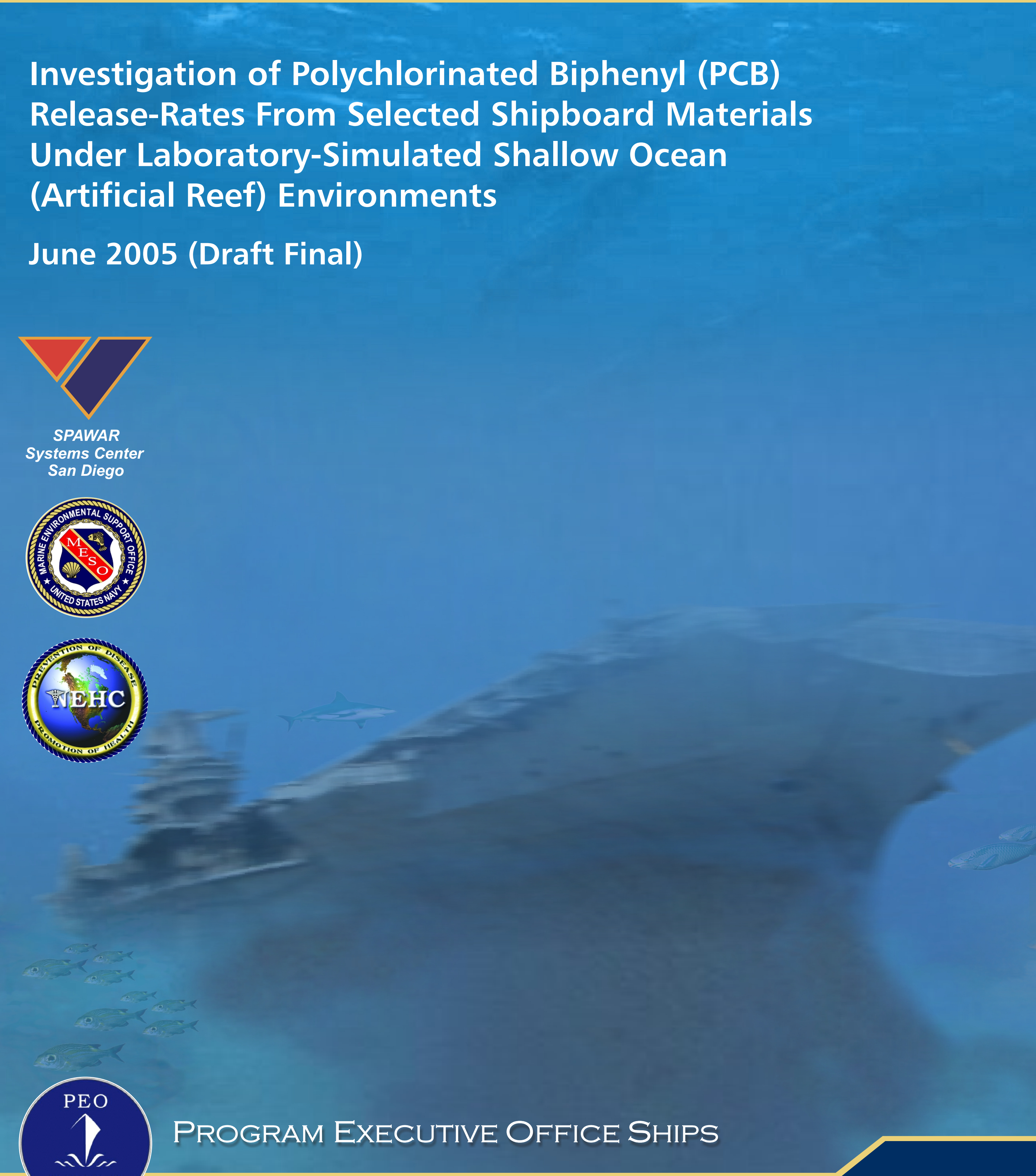
Artificial Reefing

Investigation of Polychlorinated Biphenyl (PCB) Release-Rates From Selected Shipboard Materials Under Laboratory-Simulated Shallow Ocean (Artificial Reef) Environments

June 2005 (Draft Final)



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for the Project Entitled

INVESTIGATION OF POLYCHLORINATED BIPHENYL (PCB) RELEASE-RATES FROM SELECTED SHIPBOARD SOLID MATERIALS UNDER LABORATORY-SIMULATED SHALLOW OCEAN (ARTIFICIAL REEF) ENVIRONMENTS.

Abbreviated Title:

SHALLOW-WATER PCB LEACH RATE STUDY (SW-PCB-LRS)

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ABSTRACT

Release behaviors of polychlorinated biphenyls in solid materials (PCBs-ISM) have been investigated under laboratory-simulated shallow water leaching conditions for a series of intact representative shipboard solids found onboard vessels being considered for use as Artificial Reefs. Solids containing high levels of PCBs (>500 ppm) were targeted and collected from a variety of decommissioned US Navy vessels to represent the highest range of PCBs that could potentially be found onboard ships to be used for artificial reefs.. The following broad classes of shipboard solids were the focus of this effort: Electrical Cable, Felt Gasket, Bulkhead Insulation, Foam Rubber, Black Rubber, and Paint. Pure Aroclor 1254 and 1268 were also evaluated under conditions identical to shipboard solids and serve as positive analytical controls. These Aroclors were selected because one or both of these Aroclors were identified as a primary component in each of the shipboard solids in this study and the leaching behaviors from these Aroclors could be used as proxies for mobile matrices/materials containing Aroclor 1254 or 1268, that were not tested during this investigation (*e.g.* oils and greases). Leaching experiments for all of materials were performed at 25 degrees Celcius to approximate warmer sea-surface temperatures found in United States coastal areas (typical shallow/reef conditions). Leach rates were determined by continuously exposing the solids to seawater under dynamic laboratory-simulated reef conditions for an extended period of time, generally 14-16 months. The PCB mass released from each solid was determined from the PCB mass present in the entire seawater leachate volume surrounding the solid at sequential time intervals over the course of the total exposure or leaching time. In general, the results of these leaching experiments indicate that PCB release from shipboard solid matrices is attenuated to varying degrees as a function of solid matrix type and the release rates are all very slow relative to observed dissolution rates of Aroclor analytical controls. Shipboard solids exhibited strong binding of PCBs (inhibited PCB release), as compared with “free” PCBs, or PCBs unassociated with a shipboard solid material. The shipboard-solid-specific leaching behaviors were also evaluated as a function of time to quantify leach rates to include any temporal effects expected as a result of shipboard solid conditioning dynamics and PCB depletion. None of the shipboard solids exhibited a constant PCB leach rate, nor did the Aroclor controls exhibit constant PCB dissolution rates; rather, the leach rates and dissolutions rates were variable and changed as a function of exposure time. This type of behavior is observed as a rate increase, followed by a rate maximum, beyond which the rate decreases monotonically over a significantly longer timeframe. In all cases, during the leaching exposure period for each solid and Aroclor control, a maximum rate was observed. The required exposure time to reach a maximum rate was variable for each solid, from immediate (days) to gradual (months), suggesting differing degrees of conditioning upon seawater exposure. Leach rates observed over the course of each leaching experiment for any material spanned several orders of magnitude, as presented in the material-specific leaching curves included in this report. Upon comparing the leach rates observed for different shipboard solids, these differences also spanned several orders of magnitude, indicating that PCB release is affected to varying degrees by different solid matrices. The statistical mean (and final values/endpoints in parentheses) of material-specific tPCB leach rates determined in this study over the experimental timeframes were: bulkhead insulation, 91 (24) ng tPCBs/g shipboard solid-day; black rubber, 18 (0.66) ng tPCBs/g shipboard solid-day; foam rubber, 6.1 (1.9) ng tPCBs/g shipboard solid-day; two types of felt gasket, 5.1 (0.93) and 3.9 (1.3) ng tPCBs/g shipboard solid-day, respectively; paint, 0.95 (0.062) ng tPCBs/g shipboard solid-day; and electrical cable, 0.13 (0.044) ng tPCBs/g shipboard solid-day, whereas the mean dissolution rates for Aroclor 1254 and 1268 analytical controls over the experimental timeframes were significantly higher (note the units): 12 (3.5) µg tPCBs/g Aroclor-day and 24 (0.84) µg tPCBs/g Aroclor-day, respectively. As expected, these positive analytical control results represent the maximum concentrations observed in seawater samples collected over the entire study. Although the warm temperature leach rates were the primary focus of the effort

reported here, these studies were complemented by a set of experiments performed at a substantially lower leaching temperature (4 degrees Celcius), to investigate thermodynamic effects for lower temperatures expected at greater ocean depths. The cold temperature leach rate and Aroclor dissolution rate behaviors and relative rankings were similar to the warmer leaching and dissolution rate results detailed in this report. However, leach rate and dissolution rate magnitudes at low temperature were significantly suppressed. Slower initial kinetics was also observed during the conditioning period at low temperature. The observed temperature dependence associated with PCB release is supported by the corresponding Aroclor dissolution rate results and has significant implications for the sinking of vessels as artificial reefs in cold shallow water, in addition to the sinking of vessels in deeper ocean environments. In this report, complete shipboard solid PCB leach rate results and data treatments for ambient pressure (~1 bar) and 25 degrees Celcius are provided, with particular emphasis on using these empirical leach rate data in a risk assessment framework concerned with the re-use of ex-Navy vessels in constructing artificial reefs in U.S. coastal waters. Leach rate behaviors as a function of time were evaluated for both short- and long-term mass loading impacts, with particular emphasis on how one might best utilize these observed empirical leach rate behaviors for sunken vessel ecological and/or human health risk assessment scenarios. In such assessments, it is strongly recommended that shipboard-solid-specific empirical leach rates and regression analyses of specific PCB congeners and homologues described in this investigation be used to characterize the temporal variability of the PCB release behavior and to support the choice of long term leach rate values with sufficient conservatism at an appropriate confidence level.

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We dedicate this report to the memory of Mark Goodrich (1957 - 2005), biologist, modeler extraordinaire, friend, and colleague to those who knew him. Though not here physically, he remains with us in spirit.

An electronic version of this final report, leach rate data plots, Technical Working Group (TWG) minutes and briefing materials, and supporting data/documents can be requested from the authors at the following mailto address: pcb-lrs@spawar.navy.mil.

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ABREVIATIONS AND ACRONYMS

µg	micrograms (10^{-6} grams)
%D	Percent Difference
%RSD	Percent Relative Standard Deviation
A1254	Aroclor 1254
A1268	Aroclor 1268
ACS	American Chemical Society
ADL	Arthur D. Little, Inc.
ANOVA	Analysis of Variance
Aq	Aqueous
AP	Aluminized Paint
ASTM	American Society for Testing and Materials
ASW	Artificial Seawater
AvgLR	Average Leach Rate
BHI	Bulkhead Insulation
BS	Blank Spike
BSD	Blank Spike Duplicate
BRPHL	Black Rubber Pipe Hanger Liner
BZ	Ballschmiter-Zell
CAS	Chemical Abstracts Service (ACS)
Cl	Chlorine
CLP	Contract Laboratory Program
CNO	Chief of Naval Operations
CRQL	Contract Required Quantitation Limit
DBOFB	4,4'-Dibromo-octafluoro-biphenyl
DL	Detection Limit
DQO	Data Quality Objectives
EC	Electrical Cable
ECD	Electron Capture Detection
EPA	Environmental Protection Agency
ERA	Ecological Risk Assessment
EHM	Estimated Homologue Minimum
FGI	Felt Gasket (Inner)
FGO	Felt Gasket (Outer)
FRE	Foam Rubber (Ensolite$^{\text{TM}}$)
GC/ECD	Gas Chromatography/Electron Capture Detection
GCMS-SIM	Gas Chromatography Mass Spectrometry-Selected Ion Monitoring
HHRA	Human Health Risk Assessment
HVAC	Heating, Ventilation, and Air Conditioning
ICAL	Initial Calibration
IRM	Independent Reference Material
IUPAC	International Union of Pure and Applied Chemistry
KD	Kuderna-Danish
L	Liter
LCI	Lower Confidence Interval
LPI	Lower Prediction Interval
LR	Leach Rate

MDL	(Sample-specific) Minimum or Method Detection Limit
MESO	Marine Environmental Support Office, SSC-SD
mg	milligrams (10^{-3} grams)
mL	milliliter
MRL	Method Reporting Limit
ND	Non-Detect
NEHC	Naval Environmental Health Center
ng	nanograms (10^{-9} grams)
ng/L	nanograms per Liter
NIST	National Institute of Standards and Technology
NAVINACTFLT	Naval Inactive Fleet
NAVSEA	Naval Sea Systems Command
NISMF	Naval Inactive Ship Maintenance Facility
OPPTS	Office of Pollution Prevention and Toxic Substances (EPA)
OW	Office of Water (EPA)
PB	Procedural Blank
PCBs	polychlorinated biphenyls
PCBs-ISM	PCBs in Solid Material
PCB-LRS	PCB Leach Rate Study
PCoC	Potential Contaminant of Concern
PEO-Ships	Program Executive Office Ships
pg	picoograms (10^{-12} grams)
PQL	Practical Quantitation Limit
ppb	parts per billion (ng/g, ug/L in water)
ppm	parts per million (μg/g, mg/L in water)
pptr	parts per trillion (pg/g, ng/L in water)
PRAM	Prospective Risk Assessment Model
PSNS	Puget Sound Naval Shipyard
PFTBA	perfluoro-tributyl-amine, $(n\text{- }C_4F_9)_3N$
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
QA	Quality Assurance
QC	Quality Control
REEFEX	Reefing Exercise
RHV	Residual Homologue Value
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SASA	Solvent Accessible Surface Area
SCDNR	South Carolina Department of Natural Resources
SINKEX	Sinking Exercise
SSC-SD	Space and Naval Warfare Systems Center, San Diego
SIM	Selected Ion Monitoring
SOP	Standard Operating Procedure
SRM	Standard Reference Material
SW	Seawater
SW-PCB-LRS	Shallow-Water PCB-LRS
SS	Stainless Steel
TCMX	Tetrachloro-m-xylene
tPCBs	Total PCBs

UCI	Upper Confidence Interval
UPI	Upper Prediction Interval
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

EXECUTIVE SUMMARY

Background

Sinking decommissioned naval and reserve fleet vessels as artificial reefs in the past was a common practice. During the late-1980's, it became clear that the environmental issues surrounding the use of such vessels for reef-building were not sufficiently understood. As a result, the sinking of vessels as artificial reefs was halted, with few exceptions, until the issues of concern could be explored. Various investigative approaches directed at potential contaminants of concern (PCoC) have included monitoring and evaluating existing artificial reefs associated with previously sunken vessels, such as monitoring performed by the South Carolina Department of Natural Resources (SCDNR)[1], and shipyard evaluations of materials found onboard candidate reefing vessels[2], vessels being scrapped, and vessels slated for title-transfer/resale. In addition, the Navy has recently completed screening level ecological and human health risk assessments[3, 4] directly related to this effort. Those assessments evaluated the possible ecological or human health risk of a representative artificial reef created by a previously sunken Navy vessel. The vessel, ex-Vermillion, was an ex-amphibious cargo vessel used to create an artificial reef in 1987 as part of the SCDNR Artificial Reef program off the coast of South Carolina. The overall results of those studies indicated no unacceptable ecological or human health risks associated with the sinking of the ex-Vermillion, prepared using the less stringent cleaning standards and methodologies compared with standards today[5] that are based on knowledge of PCBs in solid materials (PCBs-ISM) onboard such vessels. Additionally, in the mid-1990's, the US Navy initiated a study[6] to assess possible environmental risk(s) associated with sinking ex-warships as targets or testing platforms in operational SINKing EXercises (termed SINKEX). Within the context of the proposed screening risk assessment model, it was determined that a SINKEX did not pose an unacceptable risk ecologically. In the next phase of that investigation, this hypothesis was tested by locating a sunken ship, followed by field sampling, chemical analysis, and a toxicological study as part of a site-specific risk assessment with both ecological and human health endpoints. While the very deep ocean is a much different environment from shallow or estuarine systems, many of the shipboard component materials and PCoC are common to both scenarios. In all of the aforementioned studies, the most common PCoC are a class of compounds, the polychlorinated biphenyls (PCBs), which have been found in a variety of shipboard solids, as either an integral component or, in some cases, as a contaminant. These PCB-ISM are the focus of the technical effort reported here, which seeks to understand the baseline leaching behavior of these types of materials under shallow/estuarine conditions, and how that leaching behavior could ultimately impact a reef ecosystem. A companion study is concerned specifically with evaluating baseline leaching behaviors of PCBs-ISM under laboratory-simulated deep-ocean scenarios, and will complement this shallow-water study in a separate technical report[7].

Methodology

Leaching data were collected for solid materials commonly found to contain PCBs onboard older, out of service surface vessels and submarines. Solids with known high levels of PCBs were purposely chosen for this study because they represented the highest concentrations of PCBs expected for PCBs-ISM that could potentially be present on current and future vessels to be reefed. These PCBs in solid materials (PCBs-ISM) have been shown to leach very slowly at very low levels over time under laboratory-simulated conditions expected in typical coastal environments. These shallow water tests were performed under constant representative conditions of pH 8.1, salinity of 34^{o}%, ambient hydrostatic pressure (~1 bar), 25^{o}C temperature, and dynamic agitation to simulate flow. As a conservative approach, leaching experiments were designed to simulate an open system with sufficient transport of PCBs away from the solid to preclude PCB saturation in seawater to effectively characterize free or uninhibited leaching as the inherent leaching process. Other processes found in natural environments were also precluded to minimize potential effects on observable PCB concentrations resulting from this uninhibited leaching process, including organic particulate sorptive processes, biological processes such as biofouling, biodegradation, uptake/metabolism, or bioaccumulation of PCBs. The shipboard solids were tested intact, with the exception of paint, to simulate what would actually occur onboard a sunken vessel inside a compartment containing PCBs-ISM. The PCBs-ISM PCB signatures were found to be consistent with Aroclor 1254 (A1254), Aroclor 1268 (A1268), or a mixture of both A1268 and A1254. The solids included Black Rubber Pipe Hanger Liner (BRPHL), Electrical Cable (EC), Foam Rubber/Ensolite^{TM} (FRE), Bulkhead Insulation (BHI), Felt Gasket/Inner (FGI), Felt Gasket/Outer (FGO), and Aluminized Paint (AP). Neat Aroclor 1254 and 1268 reference materials were used as positive controls for the shipboard solid leaching experiments. A total of 31 PCB congeners and all 10 PCB homologue groups were measured in seawater leachate as a function of exposure time. These PCB analytes represent the most environmentally significant (toxicologically persistent) PCBs needed to assess both ecological and human health. Total PCBs (tPCBs) were empirically determined by summing each level of PCB chlorination (summing the measured homologue groups). All of the PCB analytes measured in this study are identical to the PCBs evaluated in the ecological risk assessment (ERAs) and human health risk assessments (HHRAs) conducted for using decommissioned Navy vessels as artificial reefs[3, 4] and as targets for sinking exercises (SINKEX)[6]. In general, the leaching data reported in this study are focused on the former, shallow/reef scenario. However data from leach rate studies concerned with evaluating these same shipboard solids as a function of time and temperature are included in this study for comparison.

Results

Leach rate curves were generated for all leach rate experiments across the entire leaching experiment timeframe or leaching series to show the *change in <u>leach rate</u> with time.* This was necessary because most of the shipboard solid leaching behaviors exhibited a temporal dependence over the course of the leaching experiments. Many of the leach rate curves exhibited a pre-maximum period of “conditioning”, during which unstable release behaviors were observed. However, in all cases, leach rate curves eventually achieved a maximum leach rate, followed by a slow, monotonic decrease in the stabilized leach rate with time. This latter, decreasing portion of leach rate curves could be extrapolated out to very long leaching times to determine when the solids might be depleted of PCBs, by assuming that all PCBs in the solid are available for leaching, even though it is reasonable to expect that some of the PCBs are likely irreversibly bound to the source material matrix. The relative leach rates for the materials tested in this study are summarized in Figure 1 below. As indicated above, the observed leach rate behaviors for all materials each exhibited a slow steady decrease with time. The leach rate values plotted in Figure 1 a) are plotted from lowest to highest and correspond to the final empirical leach rates determined in each leaching experiment for each material and the leach rate values in Figure 1 b) correspond to the simple mean of all leach rate values observed over the course of the entire experiment, including the pre-maximum, maximum, and post-maximum leach rates. This figure demonstrates that each of the shipboard solids leach and stabilize at different rates.

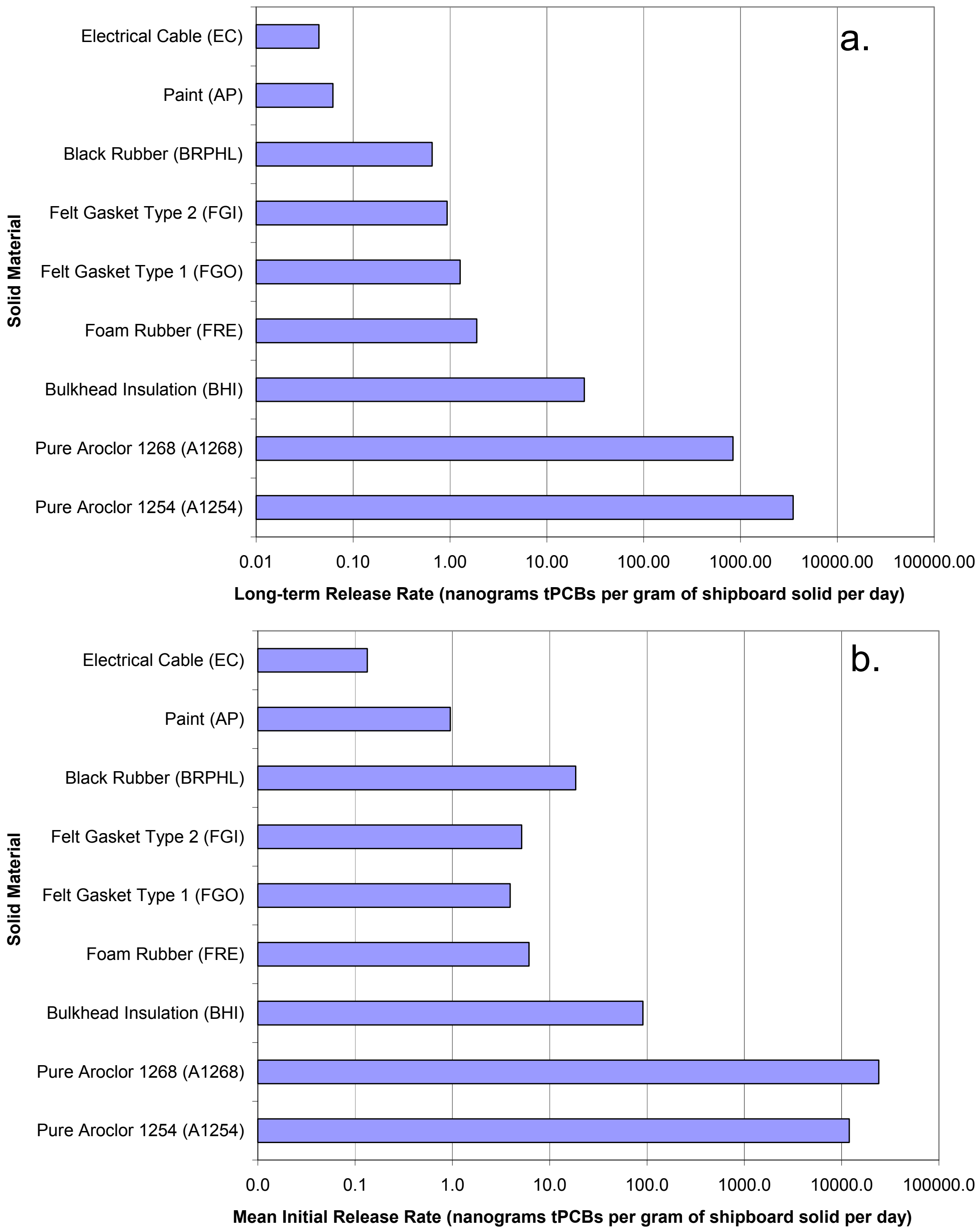


Figure 1 (a & b). Experimental tPCB leach rate differences determined for shipboard solids compared with Aroclor dissolution rates (analytical controls). The leach rates in a) are the long term stabilized leaching values observed at the end of each experiment (final empirical leach rate value), generally after 14 - 16 months of leaching for each material in seawater. Leach rates in b) are higher than a) because these values are the statistical means calculated using all of the empirically observed leach rate values (pre-maximum, maximum, and post-maximum releases) determined over the course of each leaching experiment for each material.

In general, Aroclor dissolution rates and shipboard solid leach rates at low temperatures were also observed to decrease with time, and the magnitudes of rates were lower, as would be expected from purely thermodynamic (solubility) considerations. Initial kinetics appeared to be somewhat suppressed at lower temperature, as indicated by less rapid dissolution and leach rate increases. Post-maximum rate decreases also appeared slower at low temperature, and leach rates for shipboard solids appear to be more affected by temperature than dissolution rates for the neat solid Aroclor controls.

Conclusions and Recommendations

The leach rate data presented here are useful for accurately characterizing the time-dependent leaching behaviors of PCBs from different solid material matrices under physical and chemical conditions specific to a shallow water artificial reef environment. The acceptable leach rate source term in the context of a release and exposure model for risk assessment depends upon what assumptions are considered reasonable within the risk assessment framework being used. Shipboard solid-specific leach rate data can be incorporated to varying degrees of complexity, depending upon the assumptions one is willing to accept. The extremes range from a) assuming a single, mean leach rate over the entire period of time to b) using the leaching curves for the empirical release, followed by a long-term leach rate; either as an extrapolated (changing) rate based on the leaching curve, or an assumed constant rate as an upper limit (conservative case). The latter approach is being considered for use in a Prospective Risk Assessment Model (PRAM), initiated as part of the human health risk assessment (HHRA) in the Navy's REEFEX program.[4] The former approach, using only the final empirical leach rate for each shipboard solid over the entire risk assessment timeframe, was evaluated in the REEFEX ecological risk assessment[3], with PCB mass loading estimates based on the the ex-Agerholm as a surrogate reef-vessel. The constant leach rates for such an approach are included in this report as the "Long-term" (b) column of values (Table 14A). These rates were used in as an example of a loading analysis for the ex-Lawe, a vessel with known PCBs-ISM loadings (Table 14B). The regression analysis and extrapolated curves in APPENDIX A support this choice of long-term conservative leach rate, by demonstrating that the leach rates continue to decrease with time. Table 14A also summarizes data for the empirical leach rates where (a) would apply over the shipboard solid specific-experimental leaching timeframe, and the long-term leach rate (b) would apply over the remaining timeframe of interest. Both of these approaches are compared in the time to depletion example for ex-Lawe in Table 14B.. It is important to note that the leaching amounts and times to depletion in Table 10 for each solid are very different, leading to a complex mixture of PCB source terms at any point in time. The maximum timeframe is dictated by the longest depletion time calculated for that particular scenario, at which point PCB leaching would cease. This calculation scenario assumes that the PCB signatures in the solids found onboard the vessel all leach, *i.e.* the shipboard solids principally contain only leachable PCBs so that all of the PCBs leach in their entirety. This is an unlikely condition, as some PCBs in the solid are likely bound permanently to the solid matrix. Ideally, this is why one would expect to see leach rates for PCBs decrease with time and/or not leach at all in some cases. Neat Aroclor dissolution rates can be used as surrogates for shipboard mobile material matrices not included in the leaching study (e.g. oils and greases) in addition to positive analytical controls for shipboard solid leach rates. The rates of PCB release in Table 10A are applicable as source terms for risk assessments, with appropriate assumptions, and can be applied to potential artificial reef vessels, such as is presented for the ex-Lawe as an example, in Table 10B. A variation of this approach was incorporated into Appendix 8 of the REEFEX ecological risk assessment[3], which evaluated a range of shipboard solid loading estimate scenarios for the ex-Vermillion.

Regression analyses of leach rate curves described in the **CONCLUSIONS AND RECOMMENDATIONS** section of this report and included as APPENDIX A can be employed to validate the use of a constant long-term leach rate value as a conservative estimate of future release. Alternatively, the regression analysis itself can be used as a source term function to predict a continued decreasing release. In general, the PCBs-ISM leach rate behaviors in this study could be fit to a power function (Equation 10), and extrapolated on a log-log basis (Equation 11). It is suggested that the empirical leaching results be used to characterize the early release as in Table 14A, "(a) Empirical", beyond which, the regression functions found in APPENDIX A can be used for estimating a long-term source parameter or to support using a conservative constant leach rate. It is suggested that the use of regression functions be caveated as having been produced from a relatively small amount of data, leading to low confidence in predicted values at long term extrapolation endpoints (times). It is recommended that the upper prediction interval curve/data be used at such endpoints if this approach is chosen. In many cases, the prediction interval is nearly equivalent to the final empirical data value, but is still useful in providing confidence in using the final empirical leach rate value as a long-term conservative leach rate.

INTRODUCTION

Polychlorinated biphenyls are classified as persistent pollutants, environmental health hazards, and as suspected carcinogens. They comprise a class of environmental pollutants that are ubiquitous and can be found in nearly every natural environment tested, including food, animal tissues, soils/sediments, oceans, and fresh-water systems. One of the more important driving forces for this observed persistence in natural environments is the molecular stability of PCBs, reinforced by their tendency to associate strongly with organic materials and partition into those materials from aqueous phases. This stabilization feature leads to bioaccumulation within ecosystems, and ultimately to possible human health consequences. Additionally, this stability and resulting bioaccumulation also aids in the long-term biochemical decomposition of PCBs (sequestration and biodegradation). Fundamentally, PCBs possess low aqueous solubilities, which, in effect, force PCBs to seek out the most desirable molecular environment, the organic phase. This partitioning behavior is a fundamental component of many scientific study designs that have sought to evaluate transport, transport mechanisms, fate, and effects of PCBs in natural environments. Within such studies, an issue not often addressed is that molecular transport of PCBs from a source material into the surrounding environment is also governed by a similar partitioning effect. Differences in partitioning are dictated by characteristics and properties of the source materials themselves; materials such as polymers that contain PCBs as part of their chemical composition, or as contamination within those matrices. Fortunately, from a partitioning standpoint the underlying stabilization force remains: PCBs generally tend to reside more in organic phases [13, 16] and materials similar to shipboard solids[33], rather than in the aqueous phase. This acts to slow or suppress leaching processes, and a large portion of PCBs that do leach at a low level into the aqueous phase tend to be degraded forthright[11, 12] or are sequestered into natural organic materials[41] via absorptive/adsorptive partitioning processes.

PCB Chemistry

The PCB molecular structure is based on the biphenyl structure shown in Figure 2 below, and consists of two covalently linked phenyl rings.

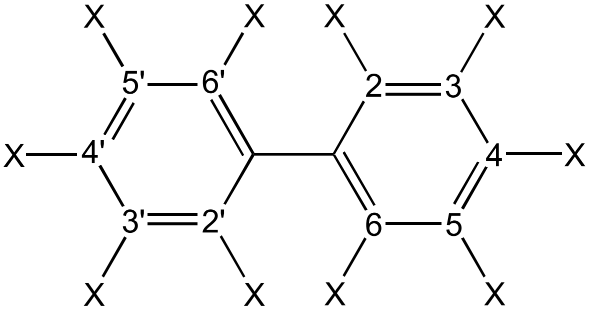


Figure 2. Polychlorinated Biphenyl molecular structure, where X at each numbered carbon can either be a hydrogen (H) or chloro- (Cl) substituent. Each phenyl ring can rotate independent of the other around the covalent bond linking them together (*i.e.* the phenyl rings can be but are not forced to be coplanar). The total number of possible isomers is 209.

The biphenyl rings are substituted at X with either hydrogen (H) or chloro- (Cl) substituents on the numbered carbon positions above in various combinations, with a generic formula of $C_{12}H_aCl_b$ (where a+b=10). The prefix "poly" in polychlorinated biphenyl does not follow the standard chemical naming conventions indicating a "polymer". PCBs are not polymers; rather "poly" simply represents multiple chloro-substituents on the biphenyl ring. The total number of possible combinations of hydrogen and chloro-substituents on a biphenyl ring yields 209 unique molecules or positional isomers, commonly referred to as congeners, excluding the unchlorinated, or fully H-substituted molecule, biphenyl. By convention, these 209 congeners are assigned unique numbers (termed BZ numbers [8]) assigned to them (BZ1-BZ209), which correspond to the same numbers adopted by the International Union of Pure and Applied Chemistry (IUPAC) and the American Chemical Society (ACS) Chemical Abstract Service (CAS), although it should be noted that there have been slight differences in numbers and molecular naming conventions between IUPAC and BZ[9] that should be considered when looking at historical PCB congener data. Additionally, all 209 PCB congeners can be grouped according to chlorination level. These are referred to as homologue groups (Cl1, Cl2, Cl3…Cl10). Within each homologue group are positional isomers that possess the same number of chloro-substituents and resulting molecular weight. The summation of all ten homologue groups corresponds to total PCBs (tPCBs), equivalent to the sum of all 209 congeners. Commercial PCBs were originally marketed under the trade name Aroclor. These were the most common commercial PCBs used in the United Sates and are complex mixtures produced by bulk chlorination. Aroclors are generally described by a 4-digit numerical notation, in which the last two digits indicate the weight percent chlorine (e.g., Aroclor 1254 is 54% chlorinated, at a distribution of sites on the biphenyl rings dictated by the ease of chlorination). Aroclor (trade name) products were manufactured by bulk chlorination in the United States through the mid-late 1970’s, forming mixtures with differing distributions of individual congeners, resulting in oils (Aroclor 1016, 1221, 1232, 1248), viscous liquids (Aroclor 1254), sticky resins (Aroclor 1260 and 1262) and white powders (Aroclor 1268, 1270). The type of Aroclor is typically identified by the percentage of chlorine in a mixture of congeners. For example, Aroclors 1254 and 1268 are manufactured by chlorinating biphenyl to a final chlorine content of 54 and 68 percent, respectively[10]. A notable exception to this is Aroclor 1016, which is 41.5 percent chlorine In practice, all 209 congeners are very difficult to separate, which has lead to analyses of PCBs reported as individual congeners, tPCBs estimated from select congeners, Aroclor (or Aroclor equivalents), and in some instances, homologues, and tPCBs as the sum of homologues.

Although PCBs in natural environments can exist as 1 or more of the 209 distinct molecular isomers described above, only some of these congeners are found at significant levels in the environment. This is due, in part, to availability and use of only certain industrial PCB mixtures (Aroclors with different, but distinct chlorination levels and congener distributions). Selectivity in the natural environment is also partly responsible for this residual or weathered PCB signature, by aqueous-organic phase partitioning and by PCB degradation processes[11]. The least persistent of the PCBs are those that have less than five chlorines per molecule. More heavily chlorinated PCBs persist to a much greater extent in the environment due to their resistance to biodegradation. These PCBs adsorb or bind to sediments or other seawater particulates, exhibit suppressed or decreased aqueous solubilities relative to their lower molecular weight counterparts, and have more of a tendency to accumulate in lipid tissues.[12] Additionally, some PCB congeners, exhibiting coplanarity of the two phenyl rings, with chloro-groups only in one or more of the outer non-ortho positions (carbon numbers 3,3’,4’4’,5, or 5’) or in some cases at one ortho position (carbon number 2), are also considered more toxic than their non-planar counterparts, due to their specificity towards important biochemical receptors which are responsible for toxic and other biological effects.[13, 14] The more toxic coplanar congeners are also generally less soluble in seawater than other PCB congeners.[13, 15, 16] However, even with transport limited by low aqueous solubilities, and because of their environmental stability and persistence, PCBs can readily bioaccumulate in the lipid-rich tissues of marine and other organisms (i.e., they are lipophilic). Fate and transport properties are further exacerbated by the temporal variability in any given exposure scenario.

PCB Partitioning

The rate at which PCBs leach into a seawater environment is controlled by the physical and chemical characteristics of that environment, the molecular solubilities and distribution of the 209 possible unique PCB isomers (congeners) initially residing in the source material, and as mentioned previously, the physico-chemical nature of that source material. The combination of these factors sets up the primary leaching pathway illustrated in Figure 3.

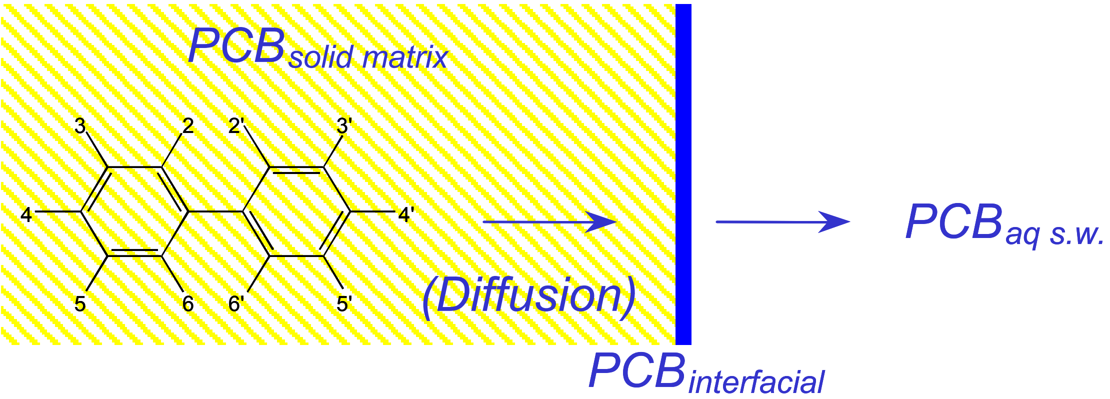


Figure 3. Primary PCB leaching process illustrated for an open system such as is simulated in this study. PCB transport occurs within a PCB containing material primarily by diffusive processes ($\text{PCB}_{\text{solid matrix}}$) and through the material-seawater interface ($\text{PCB}_{\text{interfacial}}$), prior to becoming available to the surrounding seawater environment ($\text{PCB}_{\text{aq s.w.}}$) for subsequent advective transport and sorption onto sediments, particulate matter, and biological materials in the natural ocean environment. In a closed system in the absence of advective processes, similar to conditions in many natural environments, transport out of the solid matrix is suppressed, and is dependent on partitioning between the solid surface and the seawater. Release under these conditions would eventually stop and become static until solvated PCBs are removed from the system by external processes or external partitioning equilibria (see **Figure 4**).

In a closed system, the leaching pathway indicated above (Figure 3) becomes an equilibrium partitioning process between the solid and the seawater leachate. However, equilibrium may not be reached in a natural environment because a variety of mechanisms exist to reduce the effective concentration of PCBs in the leachate (solvent) such as transport of PCBs away from the source material-leachate interface (mixing and dilution), sorption onto natural particulates, and other processes that act to reduce the PCB concentration in the seawater leachate (Figure 4). In the presence of these additional processes, PCB saturation is not likely to occur (except under static, isolated conditions such as might be found in a closed system), and PCB solvation occurs freely or is unsuppressed in the vicinity of the solid surface interface with seawater. As a result, leaching continues unimpeded until PCB depletion of the source material is (theoretically) attained, although, in most organic-based solid materials, it is likely that that many PCBs would be irreversibly bound. In the absence of specific leaching information, fate and transport models generally assume that the source terms characterized by leaching provides a constant concentration of infinite duration and quantity. As a consequence the scientific focus can be directed on the fate and transport of PCBs and on what effect(s) they might have on environmental endpoint(s). This far-reaching assumption does not hold for PCBs in all source matrices because of attenuation processes related to solvent/fluid properties, properties inherent to the source material, and spatial and temporal dependencies of leaching processes that do not allow the PCBs to leach in their entirety or at a rate commensurate with the timescale required for an effect to be observed on environmental endpoints. More specifically, differences in PCB molecular properties, the source matrix physical and chemical properties, source surface interfacial properties, and aqueous phase characteristics will define the leaching scenario and subsequent PCB leach rate for that scenario. Most importantly, these properties will result in a unique leaching behavior for any PCBs-ISM as a function of time. Accordingly, we have attempted to evaluate specific baseline leaching behaviors as a function of time for different representative solid matrices of interest, under laboratory conditions designed to simulate the leaching of

PCBs into natural seawater environments. Our approach includes controlling or removing the additional processes, illustrated in Figure 4 from the laboratory simulation, so that the experimental focus is on determining the rate of leaching corresponding to unsuppressed leaching pathway illustrated in Figure 3 In our approach, transport away from the solid surface and other processes that would reduce the PCB concentration in the seawater in the vicinity of the solid surface is *simulated* by means of a dynamic leaching and sampling design, to be described herein.

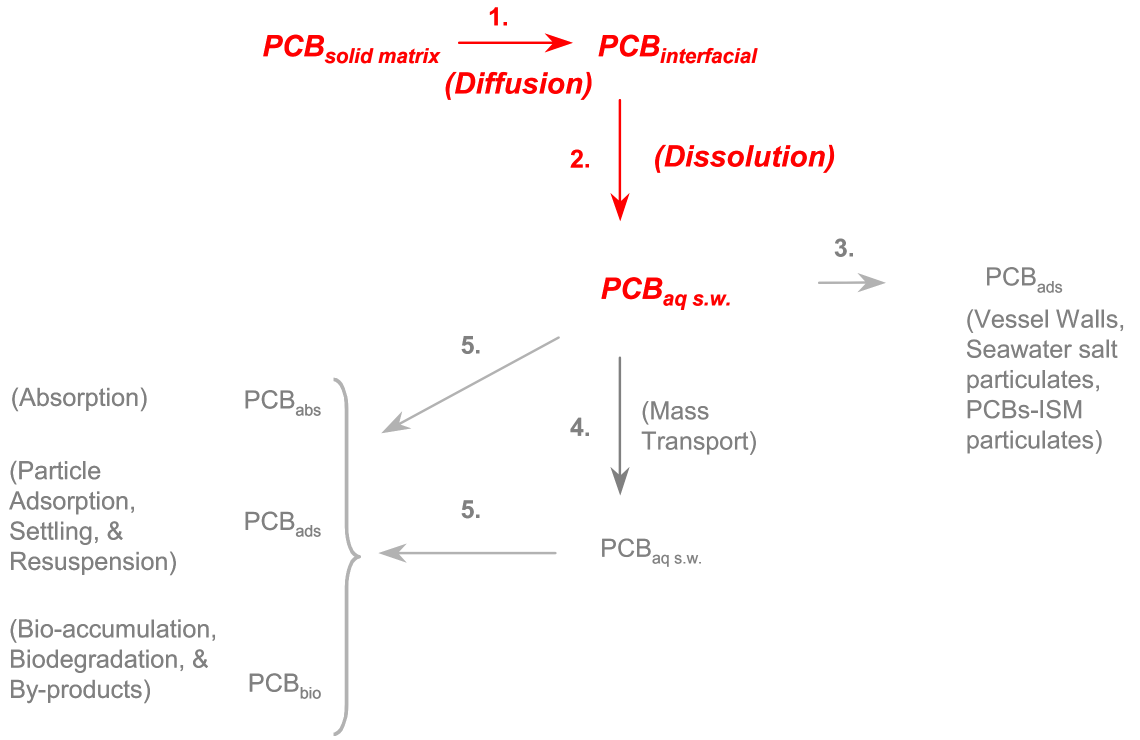
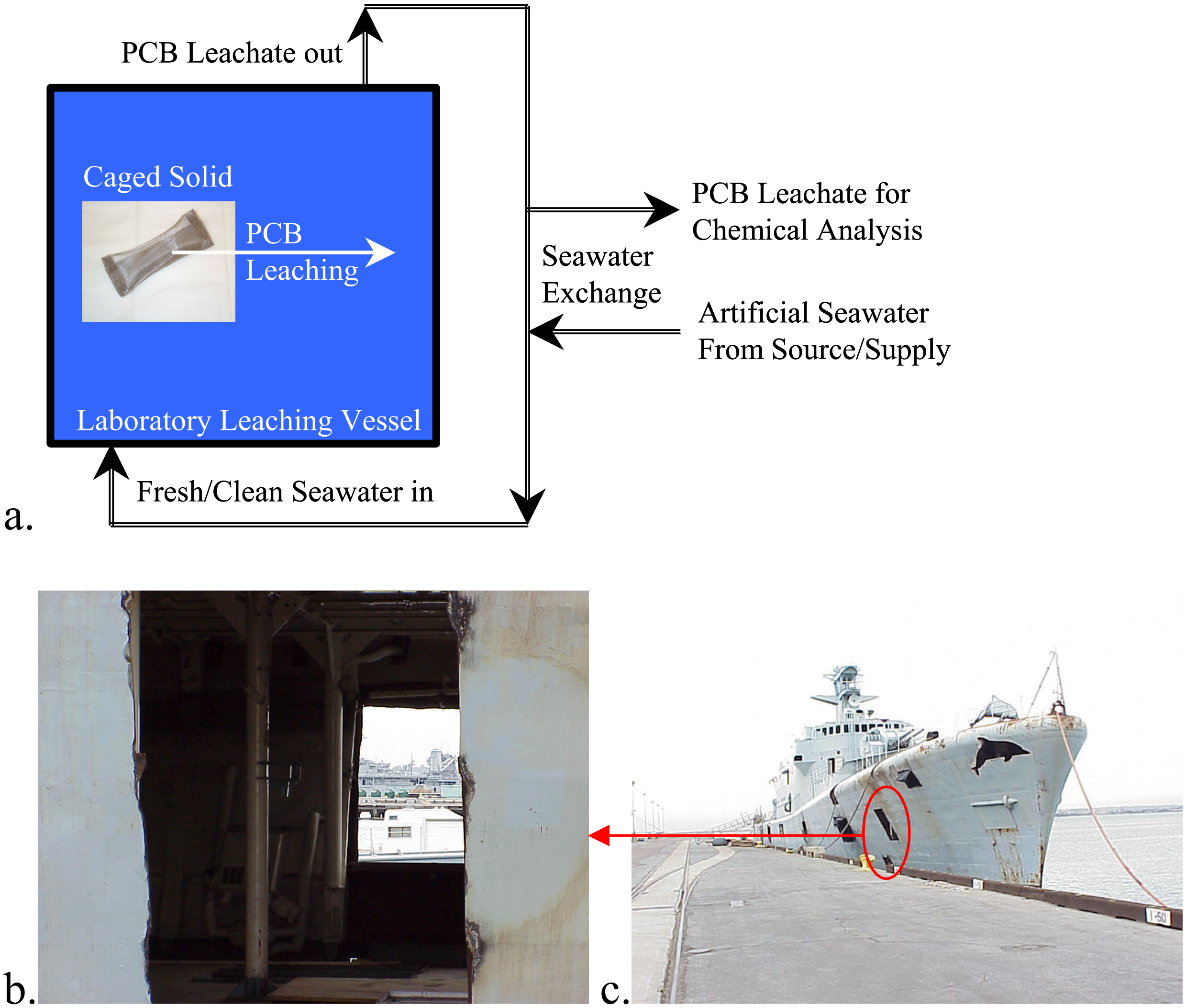


Figure 4. Primary PCB leaching process in red bold italics, (1) and (2), as described in **Figure 3**, are illustrated here with subsequent transport/depletion mechanisms for PCBs in seawater, PCB(aq s.w.). The experimental design minimizes or removes the potential processes represented by (3), whereas processes represented by (4) are simulated by seawater exchange and a dynamic mixing approach. The processes represented by (5) are completely removed by the experimental design. In a closed system, many of these processes are related to equilibrium partitioning and/or PCB uptake/metabolism into biological organisms.

A leaching experiment must take into account parameters which reflect the types of dependencies described above and may include such variables as leachate temperature, hydrostatic pressure, pH, time-induced effects (e.g. PCBs-ISM matrix degradation), surface coatings (if any) on the material, surface area/contact area of leaching surface to seawater leachate, termed the solvent accessible surface area (SASA), molecular structure of PCB congener(s), and PCB congener solubility in the PCBS-ISM matrix versus seawater. For example, an industrial grade PCB mixture, Aroclor 1254, occasionally found in felt sound dampening material is principally composed of molecules with 4-6 chloro-substituents, or up to 116 different congeners.[17, 18] Some of these different congeners will behave in essentially the same manner, whereas others will exhibit leaching behavior differences related to variation in properties such as solubility, differential interactions with the felt matrix, the dynamic surface area of the felt, PCB solid-liquid phase transition temperature, etc. Any one or more of these properties can potentially impact PCB transport, either within the material (diffusion) or subsequently through the PCBs-ISM/seawater interface (solubility-driven behavior), and must be evaluated/quantified for appropriate inclusion prior to the collection and interpretation of empirical leaching data. Once key parameters have been identified and incorporated into the experimental design, well-defined empirical leaching data can be collected, and leach-rates can be calculated for different PCBs-ISM leached under established, designed, and controlled or /systematically-varied chemical/physical leaching conditions.

Conceptual Model for Shipboard PCB Leaching

It is the goal of this study to evaluate the leaching of PCBs from solid matrices, inclusive of inherent material properties that control the process, by simulating the leaching conditions in the laboratory, as they are likely to exist onboard a sunken vessel. This is illustrated schematically in Figure 5 below where the focus is to evaluate PCBs-ISM onboard a vessel that would be contained within a shipboard compartment as it is exposed to seawater as a function of time.



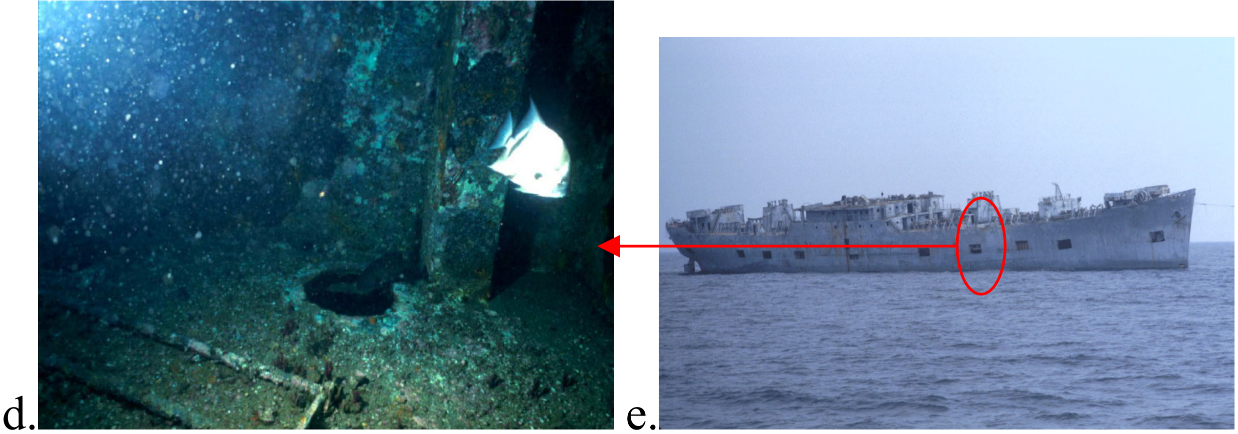


Figure 5. Conceptual schematic (a) for simulating the PCB leaching process expected to occur for a PCB-containing solid inside of a compartment onboard vessels prepared as shown in (c) and (e) and sunk in shallow water as an artificial reef. The PCB release is considered in this study for seawater flowing through open compartment(s) such as shown in (b) and (d) under relatively mild flow conditions that are sufficient to avoid saturation in the leachate above the surface of the shipboard solid inside the compartment. Solvated PCBs in a sealed compartment would be expected to saturate and remain trapped unless the compartment becomes breached. For a closed, but unsealed compartment, saturation would also be expected, but would be subject to PCBs-in-seawater diffusion/transport out of the compartment into adjacent compartments and/or the surrounding environment. Photos (b) and (c) are of the ex-Yukon, a Canadian vessel, while being prepared for use as an Artificial Reef in San Diego coastal waters. Photo (d) is an underwater compartment the ex-Vermillion, a US Navy vessel sunk off the coast of South Carolina in 1988 as an Artificial Reef, and (e) is the ex-Vermillion after being prepared and towed to the site. Photos b) and c) are MESO photos and photos (d) and (e) are courtesy of SCDNR.

In a natural leaching scenario, it is possible that some materials will lose their structural integrity upon exposure to seawater over an extended period of time. It is expected that such smaller individual particles of PCBs-ISM will continue to leach PCBs is the same manner as the intact solid, however, such effects would be spread out over very long periods of time and result in only a slight influence if any, on long term rates because, though release is proportional to surface area, the total surface area increase would not be instantaneous, rather it would occur very minimally as a function of time. This effectively means that natural surface area increases cannot keep up with the PCB release rate, as these two processes are on significantly different timescales. In the laboratory, the solid matrix must still be allowed to undergo any physical or chemical degradation due to its exposure to seawater so that such effects can be captured and included as an inherent component of the leaching mechanism and leach rate value. However, the solid must also be constrained experimentally to remain localized but not isolated from seawater in a single location during leaching to a) simulate a shipboard solid remaining in the relatively protected environment inside a vessel compartment and only evaluate solvated PCB transport, b) avoid artificially degrading or compromising the shipboard solid structural/physical integrity by agitation that is necessary for simulating seawater current flow, and c) minimize the deleterious effects of very small, PCB-containing shipboard solid particulates during the PCB analytical extraction of seawater leachate. The localization of initially intact shipboard solids can be accomplished by "caging" the solid in a small pore-size mesh as described in the Leaching Experimental Approach subsection of the **EXPERIMENTAL DETAILS** section, that freely allows seawater (and solvated PCBs) transport through the pores, but does not allow the transport of solid particulate matter (structurally degraded shipboard solid). This is a key component of the experimental design that results in a true baseline evaluation of the release for only solvated PCBs from the shipboard solid matrix. Caging the shipboard solid simulates the real leaching scenario because a) the material remains localized except for natural structural degradation due to seawater exposure, b) the naturally occurring surface area available for leaching is incorporated, and c) leaching artifacts that might occur by disturbing this natural structural degradation and particle production and release are minimized. As an added benefit to this approach, the surface area associated with the cage/mesh and minimal adsorptive processes that may take place on that clean surface, are considered a suitable proxy for simulating solvated PCB adsorption that could take place on the inorganic surfaces inside a vessel compartment. Once the cage/mesh surfaces are initially passivated through adsorptive processes, the PCBs measured in the leachate are a true measure of the leaching process taking place at the leaching surface of the shipboard solid itself. It should be noted that adsorption on inorganic surfaces is considered insignificant relative to the magnitude of sorptive processes and partitioning likely to occur with the organic surfaces inside a vessel compartment. Such organic surfaces are outside the scope of this effort and are excluded by the experimental design. A more detailed description of this conceptual model as it is applied in the laboratory can be found in the Leaching Experimental Approach subsection of the **EXPERIMENTAL DETAILS** section of this report.

PCBs in Solid Materials (PCBs-ISM) Onboard Vessels

In this report, details of PCB-seawater leaching studies are presented for selected PCBs-ISM commonly found on-board retired military vessels. The majority of vessels that have been found to contain PCBs-ISM were built and/or refurbished prior to the ban of PCB use/production or the subsequent phase-out of PCB-containing materials in the mid-1980's. It is the intent of this effort to simulate and evaluate the leaching of PCBs as it applies to the activity of sinking out-of-service ship hulks in shallow-ocean environments for purposes of building artificial reefs. Leaching results corresponding to this shallow water scenario will be described along with preliminary results of complementary experimental efforts designed to demonstrate the dependence of leaching upon temperature. The relationship between laboratory-scale leaching behaviors of different PCBs-ISM and ship-scale leaching behaviors for prospective vessels will be considered within the likely reef-building scenarios, with the goal of evaluating vessel preparation prior to sinking.

EXPERIMENTAL DETAILS

The experimental effort was undertaken in several phases as described below, each of which contributed towards the ultimate goal of performing leaching experiments for different classes of PCBs-ISM found onboard decommissioned vessels. These classes of PCBs-ISM are considered representative of shipboard solid materials commonly found onboard both surface vessels and submarines. For purposes of this study, the PCBs-ISM tested contained the highest PCB concentrations available on inactive vessels at the time of the study. It is acknowledged that vessels decommissioned after our sampling effort might have PCBs-ISM with higher PCB concentrations or lower PCB concentration. However, in general, the PCB concentrations in the materials located and collected from inactive vessels during our sampling effort will reflect a worst-case PCB concentration. The shipboard solid materials investigated here include felt gaskets, electrical cable, paint, foam rubber (insulation), black rubber (shock mounts), and bulkhead insulation (inorganic). Oils and greases are a class of shipboard solids that have been found to contain PCBs, but these were not a focus in this study because PCB-containing oils and greases are routinely removed along with other liquid materials during remedial actions (performed as part of the process of decommissioning vessels to the inactive fleet). As a result, oils and grease contaminated with PCB quantities needed for performing leaching experiments were not found. These and other field sampling issues will be discussed in further detail below.

Before describing the details of each experimental phase, it is particularly useful to summarize and describe the (possible) experimental parameters and variables of concern, focusing on the potential impact those parameters would have upon planned leaching experiments. These parameters of concern are tabulated in Table 1 and follows an approach similar to the evaluation performed for development of Toxicity Characteristic Leaching Procedure (TCLP)[19] protocols and methodologies.[20] Also indicated is the manner in which experimental parameters were subsequently classified and addressed for the PCB Leach Rate Study (PCB-LRS).

Table 1. Experimental Parameters of Possible Concern for Leaching Studies. Variables indicated as “N/A” are not applicable to this study because it was excluded by the experimental design. Variables indicated as “not controlled” are considered part of the leaching mechanism under the specific conditions set up in this study, defined by the “Controlled” parameters that were the same for each of the solids tested.

Phase or Process	***Property or Parameter***	***Effect(s)***	***Classification***	***How Treated or Controlled***
Solid Matrix	Chemical Composition	Leaching mechanism (PCB binding)	Experimental Variable	Not Controlled
Solid Matrix	Morphology	Solvent Access	Experimental Variable	Not Controlled
Solid Matrix	Surface Area (solvent accessible)	Defines interface with solvent; leaching efficiency	Experimental Variable	Not Controlled
Solid Matrix	Suface Physics/Electrostatics	Solvent Access and Flow Control	Experimental Variable	Not Controlled
Solid Matrix	Matrix Heterogeneity	Localized morphological/chemical differences	Experimental Variable	Not Controlled
Solid Matrix	Pore Structure/Volume/Composition	Solvent Flow; Gas retention; Leachate volume/composition	Experimental Variable	Not Controlled
Solid Matrix	Leachant Permeability/Saturation/ Retention	Solvent Flow; Residence Time	Experimental Variable	Not Controlled
Solid Matrix	Photo/Biodegradability	Solid Matrix Changes	CONSTANT-Controlled	No Biologics Present, Dark Experimental Conditions
Solid Matrix	Toxicity	Solid Matrix Changes; Biodegradability	N/A	N/A
Solid Matrix	Buffering Ability	Solvent chemical properties; degradation; leachability	Experimental Variable	Not Controlled
Analyte (PCB)	Chemical Composition & Phase	Leachability differences	Experimental Variable	Not Controlled
Analyte (PCB)	Concentration	Leachability differences (rates/equilibria)	Experimental Variable	Not Controlled
Analyte (PCB)	Toxicity/Biodegradability	Natural removal efficiency; PCB loss	N/A	N/A
Analyte (PCB)	Heterogeneity	PCB Leachate Availability	Experimental Variable	Not Controlled
Analyte (PCB)	Diffusivity	Transport by diffusion through solvent matrix	CONSTANT-Controlled	Homogeneous Mixing
Analyte (PCB)	Solubility	Transport in and though matrix-solvent interface	Experimental Variable	Not Controlled
Analyte (PCB)	Volatility	PCB Loss at Air-Solvent interface	CONSTANT-Controlled	Closed System, Head Space Minimized above Solvent
Analyte (PCB)	Adsorption Tendency/Lipophilicity	PCB Loss at Solid Surfaces (Solid-Solvent interfaces)	Constant-Controlled	Adsorption Minimized, No Organics, Leaching Vessel Materials with Solvent Contact Pre-cleaned Glass and Stainless Steel Only
Solvent	Chemical Composition	PCB transport and leachability; matrix wetting	CONSTANT-Controlled	ASTM Artificial Seawater
Solvent	Ionic Concentration (Salinity)	PCB transport and leachability; matrix	CONSTANT-Controlled	ASTM Artificial Seawater

Phase or Process	***Property or Parameter***	***Effect(s)***	***Classification***	***How Treated or Controlled***
		wetting		
Solvent	Lipophilicity/Contaminants	Leachability Enhancement	CONSTANT-Controlled	ASTM Artificial Seawater
Solvent	pH/Buffering Capacity	PCB transport and leachability; matrix wetting	CONSTANT-Controlled	ASTM Artificial Seawater
Solvent	Gas Composition (dissolved)	pH; PCB transport and leachability; matrix wetting	CONSTANT-Controlled	ASTM Artificial Seawater
Solvent	Density	Flow; Hydraulic Conductivity	CONSTANT-Controlled	ASTM Artificial Seawater
Solvent	Viscosity	Flow; Hydraulic Conductivity; Saturation	CONSTANT-Controlled	ASTM Artificial Seawater
Solvent	Temperature Dependence	PCB transport and leachability; matrix wetting; PCB solubility	CONSTANT-Controlled	Temperature Maintained as Constant During Leaching
Solvent Dynamics	Flow Gradient	Transport (dispersion/convection/advection)	CONSTANT-Controlled	Closed System Homogeneous Mixing, Seawater Exchange to Simulate Transport, Constant Flow
Solvent Dynamics	Flow Type (laminar or turbulent regime)	Flow Gradient	CONSTANT-Controlled	Closed System Homogeneous Mixing, Constant Flow
Solvent Dynamics	Flow Pattern (continuity)	Matrix integrity; PCB transport/Concentration Gradient	CONSTANT-Controlled	Closed System Homogeneous Mixing, Constant Flow
Temporal/Spatial	Aging Dynamics	Chemical/Physical Property changes with time; matrix integrity	Experimental Variable	Not Controlled
Temporal/Spatial	Weathering	Matrix integrity	CONSTANT -Controlled	Solid Protected/Caged, Aging/Matrix Degradation due to Seawater Exposure Only
Temporal/Spatial	Pressure Dependence	Matrix integrity; PCB solubility	Experimental Variable	Not Controlled, Minor in Ambient Pressure Fluctuations Only
Monitoring/Analytical	Sampling Time	Skew Results of Analysis (leach-rate)	Experimental Variable	Sample Collection and Seawater Exchange Events Selected *in situ* to Characterize Leaching while Avoiding Saturation Effects
Monitoring/Analytical	General Accuracy/Precision/Reproducibility	Skew Results of Analysis (leach-rate)	CONSTANT-Controlled	QA/QC, Data Quality Objectives
Monitoring/Analytical	Leaching Process	Skew Results of Analysis (leach-rate)	Experimental Variable	Sample Collection and Seawater Exchange Events Selected *in situ* to Characterize Leaching while Avoiding Saturation Effects
Monitoring/Analytical	Leachant Sample Storage/Preservation	Skew Results of Analysis (leach-rate)	CONSTANT-Controlled	SOPs using EPA Protocols
Monitoring/Analytical	Sample Prep./Test Methodology	Skew Results of Analysis (leach-rate)	CONSTANT-Controlled	SOPs using EPA Protocols

It is important to note that the primary parameters relevant to ocean depth in leaching studies are temperature and pressure. The temperature variable was evaluated and is reported here, whereas the pressure variable is being evaluated in a separate effort[7]. All other parameters were measured, controlled, or considered an integral element of the solid specific leaching mechanism. As shown in Table 1 above, in some cases a parameter was not present or its contribution was minimized by the experimental design altogether.

Field Sampling of PCBs in Solid Materials (PCBs-ISM)

Three field-sampling events occurred between June and December 1999, to collect PCBs-ISM from components on decommissioned vessels and submarines present at that time in the inactive fleet. The goal of the field-sampling effort was to locate and collect sufficient quantities of PCBs-ISM within each class of shipboard solid to allow for sub-sampling in the laboratory and subsequent leaching of those subsamples under prescribed experimental conditions. It was the intent of the PCB-LRS sampling effort to use the most current results listing of PCBs-ISM from NAVSEA's PCBs-ISM survey program[23] to identify and locate materials for the leach rate study. Types of materials found to consistently contain PCBs onboard Navy vessels are summarized in Table 2. These common material types were selected as representative solids for the leach rate study partially based on analysis of concentration data collected as part of the NAVSEA ship survey program, and partially based on probaty of PCBs being present as a functional component (imparting some specific beneficial property to the solid matrix). Materials that consistently contain high PCB concentrations across multiple vessels age and types were the focus of this effort. Materials that were likely to have acquired PCBs as contamination were not a focus of this study. Note that these historical concentration data, like many other historical PCB data, were typically reported as total Aroclor rather than by individual Aroclor, congeners, or homologues. This made it difficult to quantify Aroclor distribution, even though the type of Aroclor was at times qualitatively identified as being present in the material.

Table 2. Summary Statistics compiled from the NAVSEA Inactive Fleet PCB Survey Program, February 2001[21]. Some Aroclors had been individually quantified in more recent analyses, and are included, but the majority of historical data available at the time of the Leach Rate Study (1999-2002) were reported as total Aroclor. It was also common to find the identity of Aroclors reported only qualitatively. The construction date of vessels, for which these data represent, range from the late 1940's through early 1990's, with PCB sampling performed from the late 1980's through the late 1990's.

Material Type	PCBs Reported As:	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268	tAroclor	
Electrical Cable (EC)	Detections		22		8		108	53	5	17	1649	(all Aroclors noted)
	Mean		102		38.7		174.9	5370.2	848.2	8713.8	397	
	St Dev		424		55.3		642.4	38449.1	1818.2	31353.4	3454.1	
	Median		8		17		19.5	27	24	19	24	
Bulkhead Insulation (BHI)	Detections		12		1		36	4	8	3	254	(1254/1260/ 1262/1268 noted)
	Mean		12.7		1000		5581.4	422.8	131.5	337.1	1168.3	
	St Dev		21.6				7429.8	470.3	351	574.1	6059.5	
	Median		8		1000		2450	345.5	6.5	9	25	
Rubber (BRPHL)	Detections	2	15		3		45	13	2	14	910	(all Aroclors noted)
	Mean	1.7	7.5		14.5		34.2	2787.9	80	6351.4	649.7	
	St Dev	0.4	1.9		17.3		70.6	7390.3	0	14970.5	4994.7	
	Median	1.7	8		8.6		14	22	80	140	28	
Paint (AP)	Detections		8				7	8	4	3	764	(1221/1254/ 1260/1262/ 1268 noted)
	Mean		21.3				14.4	110.1	11.2	867.7	822	
	St Dev		26.2				11.9	167.1	12.4	1,500.2	3,727.8	

Material Type	PCBs Reported As:	Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268	tAroclor	
	Median		8				9.2	48.5	6.7	2	80	
Foam Rubber/Ensolite (FRE)	Detections										642	(only 1254 noted)
	Mean										1523.9	
	St Dev										3336.3	
	Median										260	
Felt (FGO/FGI)	Detections					1		7		2	310	(1242/1254/1260/1262/1268 noted)
	Mean					44.6		171,190		37,900	32920.2	
	St Dev							247531.5		46810.5	69300.1	
	Median					44.6		69000		37900	140	

Prior to a given field-sampling event, the most recent shipyard PCBs-ISM survey was obtained for each inactive vessel at the shipyard. It was found that in most cases, the more recent the report, the more likely (but not certain) it would still have PCBs-ISM available, meaning the remedial action22 had not yet occurred or was not yet complete. PCBs-ISM samples were needed at or above 500ppm PCBs in the solid to realistically expect a detectable level of leached PCBs as a function of time at the scale required by the laboratory leaching experimental design. Finding and sampling PCB-ISM with such high concentrations presented a unique challenge for the field-sampling effort – resulting in a "race" to collect such field samples prior to an imminent remedial action. Much of the success of a field sampling trip hinged on the vessel's state of preparation and planned use, which affected how well marked (by shipyard personnel) the prior sampling location on a vessel might be. For example, onboard ships slated for a fleet training exercises (to be used as a target in a SINKing EXercise or SINKEX), it was a common occurrence to find that a potential target sampling area (shipboard compartment) had already been surveyed for PCBs, remediated, cleaned of debris and all floatable materials, including most notably, any previous PCBs-ISM sampling tags. When a target sample of PCBs-ISM was found, it was considered viable (for leaching studies) if it contained PCB concentrations reported at ≥ 500ppm. Sample naming conventions typically followed shipyard sample-naming conventions, which reflected where a sample was located onboard a vessel, using such information as deck level, frame number, compartment name, and/or physical 3-dimensional location/description within a given compartment.

Sample collection methodologies were dependent upon the type of shipboard solid sample and how much was available for collection. If an intact PCBs-ISM vessel component could be collected, it was removed and placed in clean plastic sample collection bags for later sub-sampling in the laboratory. If it was too difficult to remove an intact component, sampling of the PCBs-ISM portion of that component was performed to the maximum extent possible using NAVSEA's PCBs-ISM survey program methodologies[23]. This included the use of precleaned glass sample vials/containers for the sample, and sample-dedicated utility blades, precleaned with hexane prior to collection. Table 3 provides a summary and description of the shipboard solid samples collected and used in the leach rate study, with a specific brief description of the sample collection described for each class of shipboard solid in the sections that follow. As indicated, one sample of each shipboard solid was selected and subsampled for leaching studies.

Table 3. Descriptive Summary of Shipboard Solids (PCBs-ISM) Samples Used in the Leach Rate Studies.

PCSs-ISM Description	PCB-LRS Abbreviation	PCB-LRS Sample ID	Reported Shipyard Analysis	Representative Solid Analysis (PCB-LRS)	Leached Solid Pre-leaching Concentration	Comments
				by Best-fit of PCB Congener Fingerprint	by Sum of Homologues	
Electrical Cable	EC	01-18-6-L-3B	1,800 ppm A1254	1,800 ppm A1254, 160 ppm A1260	1200 ppm	Intact, No Metal Shielding, Partially Painted
Felt Gasket (inner)	FGI	1-123-1-Q-3B	Not analyzed by shipyard	140,000 ppm A1268	230,300 ppm	Intact - Between Flange Heads, Not Painted
Felt Gasket (outer)	FGO	1-123-1-Q-3D	150000 ppm A1268	100,000 ppm A1268	11,7400 ppm	Intact - Protruding from Between Flange Heads, Painted
Foam Rubber (Ensolite)	FRE	PSNS-647-165-9A	5,100 ppm A1254	7,100 ppm Aroclor 1254, 550 ppm A1260	8,900 ppm	Intact, Partially Painted
Aluminized Paint	AP	5-110-0-E-4B	570 ppm A1260	470 ppm A1254, 540 ppm A1268	430 ppm	Not Intact, Scraped from Solid Substrate Creating Particles
Bulkhead Insulation	BHI	1-51-0-E-5A	2,000 ppm A1254	160 ppm A1254, 94 ppm A1260	440 ppm	Intact, Insulation Only, No Pressboard Backing (Support)
Black Rubber (Pipe Hanger Liner)	BRPHL	PSNS-636-62-4A	500 ppm A1254	2,100 ppm Aroclor 1254, 72 ppm A1260	1,600 ppm	Intact, Not Painted
Neat Aroclor 1254 Standard Reference Material	A1254	212-147A-S			100% by Weight	PCBs Influenced by Aroclor Matrix Only, No Shipboard Solid Matrix
Neat Aroclor 1268 Standard Reference Material	A1268	214-59B-S1			100% by Weight	PCBs Influenced by Aroclor Matrix Only, No Shipboard Solid Matrix

Felt Gaskets. Sampling Location: Norfolk Naval Shipyard, 15 June 1999, ex-Dixon (AS-37)[24].Two types of felt gasket samples were collected, one corresponding to the outer approximate 1/8 inch of gasket protruding from the junction between heating-ventilation-air-conditioning (HVAC) flanges. (This type of sampled gasket is referred to throughout this report as an "outer" felt gasket.) This type of felt gasket was typically painted and the target sampling included the paint as part of the intact sample. The collected sample protruding from the flange was the lowermost (most accessible) piece of gasket, which is also where mobile PCBs would be expected to accumulate by gravity/flow over time. The shipyard analysis of the targeted outer felt gasket indicated 150000 ppm, a suitably high concentration for leaching. The second type of felt gasket field sample was collected as the intact flange from which the "outer" felt gasket sample above was collected, with the intent of subsequent disassembly in the laboratory. The felt gasket found between the flange heads is referred to as "inner" felt gasket throughout this report. It was expected to have a PCB concentration similar to the outer felt gasket, even though the shipyard had not analyzed this "inner" gasket between the flanges. The flange was disassembled in the laboratory and the felt material sandwiched between the flange heads was subsampled using methods described in the Laboratory Sub-sampling of Shipboard Solid Materials section of this report. Both of these (inner and outer) felt gasket samples were tested intact in leaching experiments.

Electrical Cable. Sampling Location: Norfolk Naval Shipyard, 15 June 1999, ex-Dixon (AS-37)[24] and an ex-Barracks Ship (APL-34)[25]. Attempts to sample intact electrical cable were unsuccessful on ex-Dixon, because cross-cutting of electrical cables was not allowed (for electrical safety or potential vessel sale/re-use). However, a vessel was located in the shipyard with cables that could be cross-cut, and entire lengths of cable could be collected intact, including any outer armored shielding and with internal copper center conductor. A cable sample of this type was located and collected from the ex-Barracks vessel (APL-34), with 1800 ppm, as indicated by the shipyard analysis. This intact cable sample was subsampled in the laboratory at a later time, after removing the outer armored shielding. Subsamples of this intact cable were tested in leaching experiments.

Aluminized Paint. Sampling Location: Norfolk Naval Shipyard, 15 June 1999, ex-Dixon (AS-37)[24]. An aluminized paint sample was collected, but not as an intact coated surface (painted substrate). This sample was located and collected from heating/cooling pipes in an engine compartment, for which shipyard surveys indicated 570 ppm as Aroclor 1260. The paint sample was collected by scraping the paint with a new, dedicated, precleaned utility knife and capturing the paint chips into a clean glass container as the paint flaked off of the underlying substrate. This process resulted in paint particles as field samples, and subsequent homogenized laboratory subsamples for leaching experiments, unlike an intact paint on a substrate surface.

Bulkhead Insulation. Sampling Location: Norfolk Naval Shipyard, 15 June 1999, ex-Dixon (AS-37)[24]. A sample was collected into solvent precleaned sample containers using a dedicated solvent pre-cleaned utility knife similar to shipyard survey methods [23]. This yellow fiberglass insulation sample was located in a workspace partition, sandwiched behind a pressboard cover. The pressboard was also collected, as a physically separate sample, distinct from the underlying fiberglass insulation. Shipyard surveys had found the insulation sample to contain 2000 ppm Aroclor1254. The insulation sample (not the pressboard backing/lagging) was subsampled for leaching per protocols described in the Laboratory Sub-sampling of Shipboard Solid Materials section.

Black Rubber. Sampling Location: Puget Sound Naval Shipyard, 29 July 1999, ex-Nathaniel Greene (SSBN-636)[26]. This PCBS-ISM was collected as a nearly intact shock mount on an equipment bracket. The sample is an unpainted, soft, rubbery polymer material with no apparent oil or grease present. Shipyard survey analysis indicated it contained 500 ppm. It was subsampled for leaching studies in the laboratory per protocols described in the Laboratory Sub-sampling of Shipboard Solid Materials section.

Foam Rubber. Sampling Location: Puget Sound Naval Shipyard, 29 July 1999, ex-Pogy (SSN-647), a Sturgeon Class Attack Submarine[27] and ex-Nathaniel Greene (SSBN-636)[26]. Several samples of a foam rubber, also referred to as Ensolite®, were collected. These samples are likely PVC/Nitrile-based, assuming they were the original components installed onboard the vessels and had not been replaced with reformulated materials. Most samples were attached to the hull with an adhesive backing that upon removal, contained rust particulates. In addition, many of these samples were partially or entirely painted. The sample used for leaching was a painted sample from ex-Pogy, collected from a bracket in an engine room, and was likely present for head protection and to provide anti-sweat properties. The shipyard survey analysis indicated 5100 ppm for this material, which was later subsampled for leaching studies in the laboratory per the protocols described in the Laboratory Sub-sampling of Shipboard Solid Materials section.

Neat Aroclor Controls. Two neat Aroclor mixtures were also “collected” by purchasing them as National Institute of Standards and Technology (NIST) traceable PCB analytical standards. These pure PCBs, Aroclor 1254 and Aroclor 1268 were subsequently treated as shipboard solid samples to serve as analytical controls to measure seawater Aroclor dissolution capacity under conditions identical to the leaching of shipboard solids throughout the leaching studies. Their respective concentrations are 100% by weight, being pure materials. These Aroclors represent a PCB-ISM sample not influenced by a shipboard solid matrix. The pure PCB matrix does act as a matrix itself for the many different PCB congeners it contains. From the perspective of a single PCB congener in the material, the other PCB congeners in the mixture are analogous to a shipboard solid matrix, albeit with a maximum cohesive-type (PCB-PCB) interaction, rather than the minimal cohesive interaction expected due to low PCB concentrations in the shipboard solids. The most distinctive differences between neat Aroclors and shipboard solids are related to matrix characteristics, i.e. Aroclor 1254 and 1268 are mobile, dynamaic matrices that can themselves dissolve away, very much unlike a shipboard solid matrix. This distinction is significant and, for purposes of rationalizing leaching mechanism, it is only valid to use Aroclor results to understand dissolution properties that may contribute toward observed leaching behaviors. Aroclor 1254 and 1268 samples can perhaps be used as reasonable proxies for Aroclor 1254- or 1268-containing oil films and semi-solid greases.

Laboratory Sub-sampling of Shipboard Solid Materials

Field samples were subsampled using a protocol developed in this work that focused on minimizing the possibility of any cross-contamination between classes of PCBs-ISM. Representative subsamples of each field sample were collected for a) leaching under different laboratory-simulated shallow/estuarine or deep-ocean conditions and b) chemical analysis of the solid to confirm that the PCB concentration was similar to that reported in the shipyard survey analysis. These “nominal” representative solid concentrations will be described and discussed in detail later in this report (see the PCBs-ISM Characterization section); however, it should be noted that in most cases, shipyard concentration values were confirmed within an order of magnitude. PCB concentrations that differed significantly from shipyard analyses are indicative of the sometimes-extreme variation found in shipboard PCBs-ISM concentrations or in some cases may reflect changes in analytical technologies over time. The following details describe how solid samples collected from vessels were routinely subsampled in the laboratory, independent of the type of shipboard solid sample, or if the sample had been collected intact or not.

In three cases, the collected shipboard solid sample was comprised of an assembly or composite that first required disassembly prior to subsampling the PCBs-ISM portion of it. Inner felt gasket subsamples were collected from between flange-heads, originally bolted together to connect HVAC ducts. Intact electrical cable, originally collected with painted armored shielding, was subsampled for leaching without the armored shielding. However, for the entire EC sample, in areas where the paint had bled through the armored shielding onto the cable itself, small amounts of residual paint were present. The third composite sample was a bulkhead insulation sample, collected with the pressboard backing described previously. For this shipboard solid, only the insulation was subsampled for laboratory testing.

For all materials except for paint particles and analytical Aroclor controls, each subsample was prepared on a tray that had been twice-cleaned with HPLC-grade methanol and lined with a large sample-specific laboratory wiper (low-lint or cleanroom Kimwipe). The cutting of PCBs-ISM was performed each time with a new, stainless steel dissection blade twice-cleaned with HPLC-grade methanol prior to use. For subsamples of electrical cable, the final operation required the use of wire cutters to sever the inner copper core once the dissection blade cut through the outer layers of material. The wire cutters were precleaned with HPLC-grade methanol prior to use and the cable was bent ~150° to expose the copper core and minimize physical contact with the inner resin and outer shell of the cable during cutting.

Subsamples were photo-documented and a unique sample ID was assigned to each subsample by appending a capital letter alphabetically to the field ID, e.g for a sample named "FieldID1", subsamples would be assigned the names "FieldID1A", "FieldID1B", "FieldID1C", etc. A similar naming convention was also adopted for control samples such as PCB standards and procedural blanks, for which subsamples were treated in an experimentally identical manner to shipboard solid subsamples.

Leaching Experimental Approach

The approach that was taken to assess the leaching behavior for the baseline leaching process in Figure 3 requires an experimental design that will control the contributions from the additional processes shown in Figure 4, and remains consistent with the conceptual model illustrated in Figure 5. The transport PCBs away from the solid surface of the shipboard solid (i.e. seawater advection) was approximated experimentally by gentle mixing. This is particularly important for purposes of avoiding saturation at the shipboard solid-leachate interface, which would result in suppression of the primary leaching process, i.e. solvation of PCBs at that interface. In the presence of such a saturation effect, the PCB concentration in the leachate would dictate the leaching behavior, rather than allowing the physico-chemical properties of the solid sample and solid-leachate interface to dictate the leaching behavior. In light of this, a primary goal of the experimental design was to avoid such a saturation condition. This was accomplished through seawater-leachate exchange well below the saturation point. The seawater exchange effectively simulated advective transport of PCBs in the leachate away from the solid surface (see Figure 5a). When an exchange was performed, the known total amount of leachate was replaced with a known amount of fresh, clean seawater, and the leaching continued until the next exchange, and so on, until the end of the leaching experiment was reached. In this manner, the leaching was restarted at zero PCB concentration in the seawater leachate after each sampling event.

A second issue of concern centered on the possibility that natural degradation of the shipboard solid might be artificially enhanced due to stirring in the leaching vessel. Disintegration during the leaching experiment would produce particulates of PCBs-ISM material, which could then contribute towards a false positive (PCBs in solid particulate vice solvated PCBs) in the leachate sample analysis. Previous solubility studies performed on felt samples at SSCSD[28], produced results confounded by this type of behavior, where it was reported that the presence of PCB-rich particulates significantly skewed the analytical chemical results. In that work, it was also noted that the mixing process used during leaching significantly altered the physical integrity of the samples tested. Stirring felt samples freely in seawater is unlike what would be expected onboard a sunken vessel in the natural environment and clearly encouraged/hastened felt gasket disintegration and dispersal over the course of the experiments, resulting in PCB extraction and chemical analysis difficulties. In our study, steps were taken to ensure that any similar effects would be minimized. The experimental design incorporated a barrier system to minimize physical damage to the sample over the course of the experiment and to localize any particulates that might exist within that barrier. As is shown in Figure 6 below, the outer barrier consisted of a stainless steel (SS) "cage", nominally 1/8 inch mesh size, precleaned with hexane and dried prior to use. Within that cage, a small pore size (nominally 1-micron), binder-free, precleaned glass-fiber filter was included to minimize the transport of any PCBs-ISM particulate matter into the leachate, while at the same time, allowing the free flow of seawater leachate to and from the shipboard solid surface. When a leaching experiment was initiated, the shipboard solid subsample was wrapped in a filter, pre-wet with doubly-distilled deionized water, caged in the stainless steel mesh, and immediately placed in a leaching vessel to begin leaching as described in the General Leaching Experiment Design and Methodology section below. The increased leaching vessel surface area introduced by these materials was considered to be a portion of the total leaching experimental surface area. It is expected that this surface area would likely adsorb a small amount of PCBs until its surfaces were passivated (saturated or inert to further adsorption). This is a reasonable approximation for the inorganic surface area susceptible to similar sorptive processes near a shipboard solid in a compartment onboard a sunken vessel. In effect, after an exposure period, when PCBs saturate all surfaces in a leaching experiment, the resulting laboratory leaching simulation reflects the scenario where a shipboard solid in the compartment of a ship is surrounded by surfaces that have been PCB-passivated (are inert to PCBs in the leachate), though it is acknowledged that some sorption on organic solid surfaces in a compartment would likely contribute to PCB removal from seawater via partitioning processes. In the laboratory, the stainless steel cage and glass fiber filter remain with and become an integral part of the shipboard solid sample under test; which approximates a vessel compartment containing PCBs in equilibrium with its surrounding compartment surfaces. Natural degradation processes of shipboard solids in seawater under a given leaching scenario are still allowed to occur, but particulates are localized within the cage, and the observed PCB concentration in the leachate reflects increases or decreases in surface area and/or PCB dissolution due to such processes. These effects, if they exist, are considered part of the shipboard-solid-specific leaching behavior.

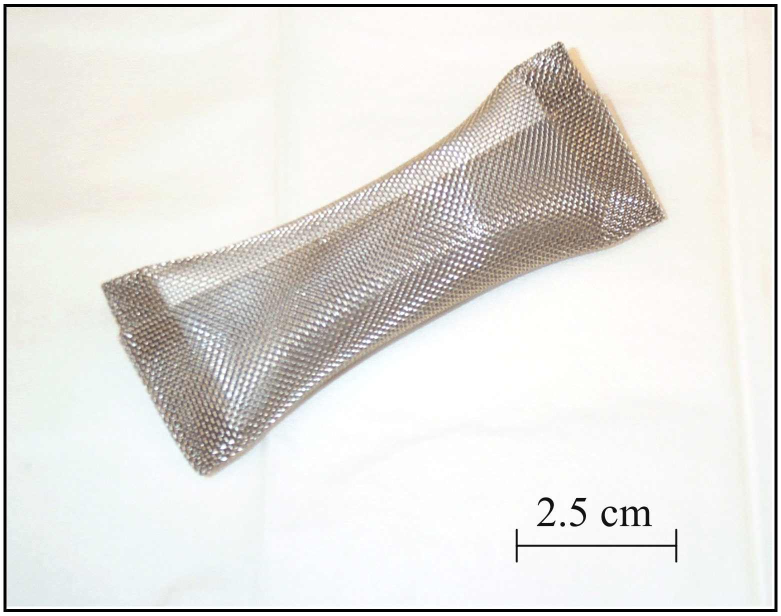


Figure 6. Photo of a shipboard solid sample cage used in this study to localize shipboard solid particulates in the leaching vessel, as described in the text above. The primary reason for caging samples is for shipboard solids, such as felt gasket, that might lose physical integrity, would produce unrecoverable particulates of shipboard solid belonging in the leaching experiment as source rather than with the leachate as loss during filtration and separation. The filter around the solid sample allows for this conservation of shipboard solid mass throughout the entire experiment by acting as an in situ particulate filter. Because the fragile glass fiber filter contained no organic binder (a potential PCB sorber), the SS mesh provided a rigid support, protecting both the solid and glass mesh from physical perturbation during leachate mixing, sampling events, and seawater exchange operations. A cage identical to the one shown here was used during the study as one of the negative controls (procedural blanks without shipboard solid). This type of cage was also used for the positive analytical controls (neat Aroclor compounds).

Samples consisting solely of the SS cage and glass fiber filter barrier described above were prepared and leached under each of the different leaching experimental conditions to control for system contamination. These samples, referred to as leaching procedural blanks, were prepared and treated identically to experiments performed with shipboard solids and with Aroclor analytical controls.

Insomuch as Aroclor dissolution experiments are considered to be positive analytical controls for A1254 & A1268 solvation capacity, leaching procedural blanks are considered to be negative analytical controls. The former represents the maximum PCB concentration expected and the latter represents the minimum (zero) PCB concentration expected under any given experimental condition for leaching of shipboard solids.

Artificial Seawater Leachate Preparation

Leaching of PCBs-ISM was performed in artificial seawater (ASW) for consistent exposure conditions rather than fresh or reconstituted natural seawater. This ASW leachate was prepared from an American Society for Testing and Materials (ASTM) standard[29] per the standard operating procedure (SOP) included in APPENDIX B. This ASW is prepared from pure ACS reagent-grade inorganic salts in accordance with a recipe designed to provide a constitutional equivalent to typical seawater, with a salinity value of 34±0.5 ^{o}%, and a pH of 8.0±0.2. Natural and reconstituted seawater can contain organic particulate matter, which is present at levels significant enough to remove trace amounts of PCBs through sorptive processes. The use of ASTM ASW avoided these possible processes that would interfere in the leaching process and assured that all materials were leached under the same exposure conditions. Additionally, the presence of trace levels of heavy metals in the ASW salts inhibits biological growth, and removes biological pathways to PCB/leachate loss in the experiment. ASW was prepared in 20L batch sizes as needed and consistency from batch-to-batch was determined through pH and salinity measurements. Throughout the leaching studies, at least one sample of each batch was used for negative controls and in this way, evaluated for possible PCB contamination via laboratory operations during ASW preparation. When a new ASW preparation (batch) was completed, it was crudely filtered through a coarse glass frit to remove any gross particulate matter (occasional salt precipitates). This filtered ASW was used to initiate and/or replenish leaching experiments during leachate sampling operations until nearly consumed, at which time another seawater batch was prepared. New seawater batches were prepared approximately every 4-6 weeks throughout the leaching study timeframe. In this manner, the ASW being used at any point in time remained relatively fresh, with less possibility of degradation effects, such as salt precipitation or losses in buffering capacity (pH instability).

General Leaching Experiment Design and Methodology

The approach to performing the leaching experiments in this study is described here with emphasis on maintaining a simulated shallow-water leaching condition/scenario, while at the same time performing analytical sampling of PCB leachate as a function of time. The sampling design is critical with respect to avoiding saturation effects, as previously described. Throughout a given PCB leaching experiment (time-series), the primary focus was on ensuring that leachate samples were collected for conventional PCB chemical analyses (described in the Analytical Chemistry of PCBs section), while at the same time not allowing PCB concentrations to approach saturation in the ASW leachate. Finally, the sampling design ensures that the solid and filter/cage remain wetted with ASW leachate, so that the leaching process is not halted, even during sampling, and so that the ASW in the filter/cage does not begin dehydrating and precipitating salts. Such salts could act to remove PCBs (by occlusion or sorption) from the ASW leachate, thus artificially decreasing the PCB concentration in the leachate. Salt precipitates could also adhere to or become trapped on the PCBs-ISM filter/cage, effectively blocking the leaching pathway, and contribute toward an artificially decreased leachate PCB concentration.

A hypothetical leaching behavior is generally expected to consist of an initial pulse or fast short-term release of PCBs followed by a slower long-term release, with the maximum leach rate observed somewhere in between or perhaps even as the initially observed rate itself, particularly if the leaching kinetics are too rapid to observe experimentally. Rapid PCB release makes it necessary to sample more often (short sampling interval) earlier in a leaching experiment, and perhaps less often (longer sampling interval) as leaching begins to slow down later in the experiment. The sampling interval is thus a key variable that must be considered in the sampling design. Our routine sampling approach for a leaching series included collecting a sample immediately after submerging the shipboard solid to characterize any rapid PCB release, then continued sampling on a progressive escalating sampling interval at 1 hr, 2 hrs, 4 hrs, 8 hrs throughout the first day, once on day 2, once on day 4, and again on 7 during the first week, then on day 14, and then day 28 during the first month. This was followed by a longer sampling interval, approximately once every 6-8 weeks over many months until the experiment was terminated and a final sample was collected. All samples collected for conventional chemical analysis, required that the entire leaching volume be collected from the leaching vessel and then replenished with clean ASW, effectively restarting the leaching at zero PCB concentration in the leaching vessel. Additionally, to avoid time-dependent adsorption issues[30] on the glass surfaces of the leaching vessel, leaching vessels were replaced once weekly with new/fresh, precleaned amber glass leaching vessels.

Simulated leaching at different ocean depths is primarily dictated by temperature and hydrostatic pressure as experimental variables. Shallow, coast-like leaching conditions were simulated in this work by immersing caged shipboard solids in seawater, inside of 950mL precleaned amber glass leaching-vessels with Teflon®-lined caps, and placing the leaching vessels in a 25°C constant temperature bath, shown in Figure 7(a), to maintain a constant shallow-water leaching temperature. The temperature of the water bath was chosen to represent the average seasonal maximum shallow water temperature along United States coastal regions.[31] The leaching vessels were labeled and weighed prior to placing the caged sample in them and prior to filling with a known mass of ASW leachate. Pressure effects, compared to temperature effects, were expected to contribute minimally to leaching, thus ambient pressure (~1 bar) was chosen for experimental simplicity as a low-pressure extreme, although hydrostatic pressures in "shallow" water might actually approach 5 bar at 100 ft depths. Preliminary results in a concurrent study indicate that a 20°C temperature decrease (see preliminary low temperature leaching results at 4°C, summarized in APPENDIX E) has a much more significant effect than observed for a hydrostatic pressure of ~325 bar (a two-three order of magnitude pressure increase).[32] Leachate mixing to simulate dynamic flow around the sample was achieved using a laboratory benchtop shaker operating at a rate of 45 rpm, above which the water bath became unstable. The temperature of the shaker water bath was maintained at a constant 25°C, stabilized by recirculation in series with an external water bath, for which the chilling element was purposely cycled in feedback mode against the heater. The low temperature studies summarized in APPENDIX E were collected as shown in Figure 7(b), for which leaching experiments were performed identically, but in a refrigerated forced air cabinet, to maintain a constant 4°C temperature.

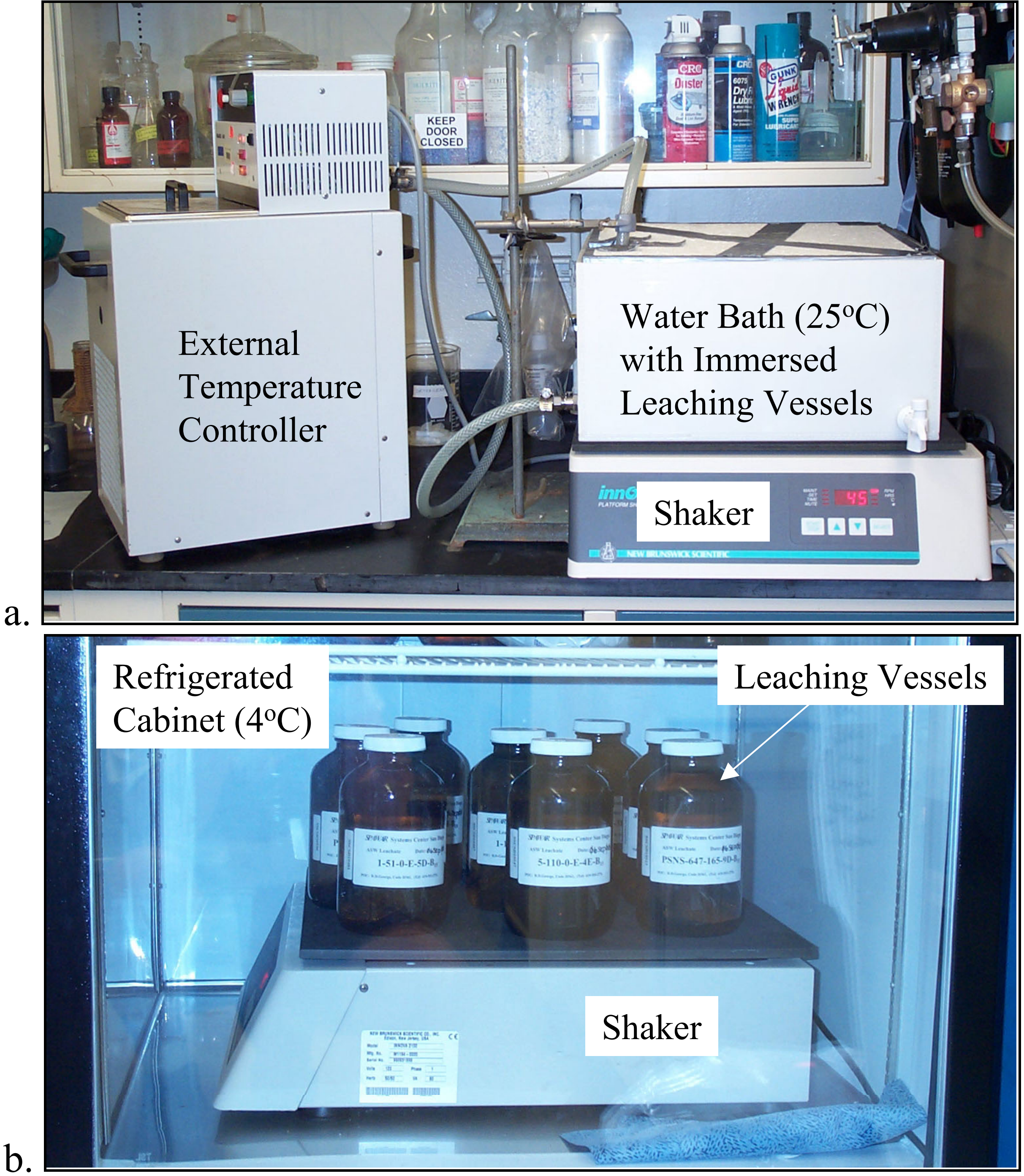


Figure 7 The constant temperature apparatus for ambient pressure leaching at 25°C is shown in photo (a) and that for 4°C is shown in photo (b). Both systems used gentle mixing via a benchtop shaker table, operated at 45 rpm to simulate dynamic flow around the shipboard solids under test, and maintained a constant temperature throughout the course of the leaching experiments (1-2 years).

To achieve some degree of comparability between leaching results for different PCBs-ISM, all leaching experiments for a given leaching scenario were performed identically. All leaching variables were controlled or maintained at constant values chosen to represent that scenario, (*e.g.* pressure, temperature, pH, salinity, etc.) Other, sample-specific variables were measured (e.g. shipboard solid mass, sample size, leachate volumes, etc.) to use for leaching data reduction and analysis. Care was taken to ensure that Environmental Protection Agency (EPA)-accepted methodologies and protocols were followed in general throughout the study, especially during standard laboratory operations such as sample handling, leachate sampling, sample storage, and analytical chemistry-related methodologies. Only pre-cleaned glass, stainless steel, or PTFE (Teflon®) in that order of preference, was allowed to come into contact with seawater leachate containing PCBs, based on published literature concerning PCB loss and degree of reversibility for common laboratory polymers/plastics.[33] Precleaned glass containers containing PCB leachate were considered part of the ASW leachate sample due to the possible adsorption issues. Thus, glass sample containers were extracted along with the leachate when the analytical chemistry commenced for that sample.

Analytical Chemistry of PCBs

Whenever possible, screening-level PCB analyses were performed using commercial immunoassay techniques (measured as Aroclor 1254, modification of EPA Method 4020 [34]). Commercially available immunoassay kits and methodologies were modified and validated for seawater as presented in an ACS Environmental Chemistry Symposium as part of this work.[35] These screening analyses were performed on aliquots of small volume (2 mL) seawater leachate samples, collected to aid in defining primary sampling intervals in real time as described in a companion paper at that symposium.[36] Subsequent conventional high throughput analyses were performed under a performance-based contract with Arthur D. Little, Inc. (ADL). PCBs were quantified in seawater and in leached solids using GC-Mass Spectrometry in Selected Ion Monitoring mode (EPA Method 680[37]) entitled "Test Methods for Determination of Pesticides and PCBs in Water and Soils/Sediment by Gas Chromatography-Mass Spectroscopy"). GC-MS/SIM analyses were performed using SOP ADL-2845, a modification of Method 680, entitled "PCB Congeners, Homologues, and Aroclors by Gas Chromatography/Mass Spectrometry in the Selected Ion Monitoring Mode". This method uses a DB5 Column, under the following conditions, excerpted from the Arthur D. Little (ADL) Sample Preparation and Analysis Method Summaries section and the detailed SOP ADL-2845 included in APPENDIX B.

The GC/MS was operated in SIM mode to obtain the desired sensitivity that is comparable to that of a GC equipped with an ECD. The GC/MS was first tuned with perfluoro-tributyl-amine, (PFTBA = n- $C_4F_9)_3N$), a common mass calibration standard for mass spectrometry, to verify accurate mass assignment and to maximize the sensitivity of the instrument in the mass range of interest (100 to 300 atomic mass units). After tuning, an initial calibration was performed which consisted of five calibration standards, at different concentration levels, spanning the concentration range of interest. Average response factors for each target compound and surrogate are calculated from the initial calibration standards relative to the internal standard compounds added to the sample extracts just prior to instrumental analysis. Continuing calibration standards, at a mid-range concentration level, were analyzed at the beginning of each analytuical sequence and every 18 hours or after every 10 sample analyses to monitor sensitivity and linearity of the GC/MS. Sample analyses were performed *only* after acceptable calibration analyses were obtained. The average response factors generated from the initial calibration were used to calculate the concentrations of target compounds and surrogates in the experimental and quality control samples. The recoveries of the surrogate compounds spiked into the sample prior to extraction were used to assess sample-specific extraction efficiency. The target compound concentrations were adjusted based on sample-specific surrogate recoveries to correct for differences in extraction efficiency.

In general, the sample-specific detection limits were at the sub-part per trillion levels for congener GC-MS/SIM analyses. Method 680 was most useful for empirical determinations of tPCBs as the sum of measured homologues. The conventional method for estimating tPCBs uses an algorithm, derived from specific congener data (measured using GC-ECD Methods 8081M or 8082[38]), similar to how Aroclors are measured. Representative subsamples of shipboard solids were initially analyzed for Aroclor content (tPCBs as Aroclor) using EPA Method 8082 to compare with reported shipyard analyses and to confirm that there would be sufficient PCB levels present for analytical detection in seawater leachate. Method 8082 was not used for any other samples. One batch of Aroclor analyses, performed for a subsample of electrical cable as a comparison with Method 680, utilized GC-ECD Methods per SOP ADL-2818 "Determination of Chlorinated Pesticides and PCB Congeners by Gas Chromatography-Electron Capture Detection (GC/ECD)", a modified version of EPA's Method 8081M using dual, dissimilar columns and dual detectors. The following is taken from SOP ADL-2818 and included in the Arthur D. Little (ADL) Sample Preparation and Analysis Method Summaries section of APPENDIX B. A Restek RTX-5 column (or equivalent) was used as the primary column and a DB-17 column (or equivalent) was used as the confirmation column. Prior to sample analysis, an initial calibration was performed which consisted of five calibration standards, at different concentration levels ranging from 1 to 200 ng/mL. Average calibration factors for each target compound and surrogate are calculated from the initial calibration standards (external standardization). Continuing calibration standards, at a mid-range concentration level, were analyzed at the end of each analytical sequence and every 16 hours or after every 10 sample analyses, which ever was more frequent, to monitor sensitivity, retention time stability, and linearity of the GC/ECD. Sample analyses were performed *only* after acceptable calibration analyses were obtained. The average calibration factors generated from the initial calibration were used to calculate the concentrations of target compounds and surrogates in the environmental and quality control samples. When coelution occurred between one or more target compounds or when interference occurred on the primary column, the results were reported from the confirmation column for the affected compounds. Compound identification was based on 1) detecting a peak within the established retention time window for a specific compound on both the primary and confirmation columns and 2) the analyst's judgment. The recoveries of the surrogate compounds spiked into the sample prior to extraction were used to assess sample-specific extraction efficiency. The target compound concentrations were adjusted based on sample-specific surrogate recoveries to correct for differences in extraction efficiency.

EPA Method 8081M was used in a comparability study with results from Method 680, described above, for the representative electrical cable subsample only. Method 680 (GC-MS/SIM) was used as the conventional analytical method of choice for all seawater leachate and leached solid analyses, based on a detection limit evaluation performed at the beginning of the leach rate study for a selection of common congeners of interest (Figure 8). A more detailed description of sample-specific method detection limits (sometimes referred to as "minimum detection limits") can be found in the Definition of Method Detection Limits section of this report.

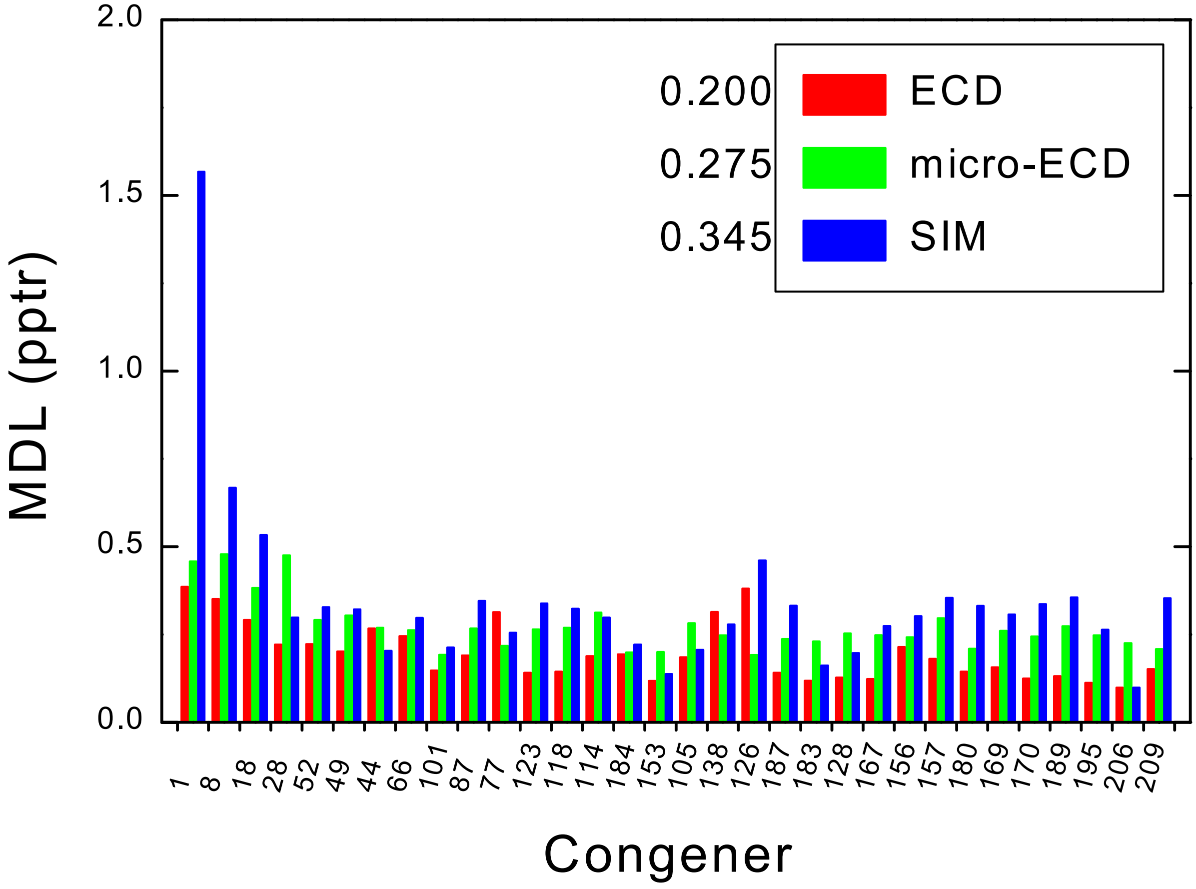


Figure 8. Minimum Detection Limit (MDL) study values for PCB target congeners in representative PCB-LRS water samples using three different methods, GC-ECD (EPA Method 8081M), Micro-GC-ECD (modified EPA Method 8081M), and GC-MS/SIM (EPA Method 680). Micro-GC-ECD is shown for comparison purpose only and was not used in this study. The average congener MDL using each method is shown next to the legend.

The PCBs shown in the list of target analytes in Table 4 and Table 5 represent the analytes of interest in this work and are the same congeners of concern in the companion SINKEX and REEFEX studies[3, 6]. The measurement of homologue groups allows one to empirically account for all PCBs in the sample without separately/individually quantifying each of the 209 PCB congeners. Summation of the homologue groups also allows for an empirical determination of tPCBs, as mentioned previously. The congener target analytes correspond to PCB congeners considered to be of importance in both ecological and in human health risk assessments. These include PCB congeners that are thought to interact with biological receptors in a manner similar to dioxins, and are thus referred to as dioxin-like PCBs. The 13 dioxin-like PCBs in Table 4 (annotated in red), correspond to non-ortho and mono-ortho PCBs that, at the inception of this study, were considered dioxin-like by both Environmental Protection Agency (EPA) [39] and World Health Organization (WHO), and the di-ortho PCBs (170 & 180) considered at that time to be dioxin-like by the WHO. It is acknowledged that PCB 170 and PCB 180 are PCB analytes included in this study and PCB81 (3,4,4',5-tetrachlorobiphenyl) is not a PCB analyte included in this study, as a result of compiling dioxin-like listings at the time of this study's inception. WHO 1997 TEF reevaluation studies have since resulted in adding this congener and removing PCB170 and PCB180. The EPA dioxin reassessment [40] has 14 dioxin-like PCBs listed, including PCBs 81, 170 & 180.

Table 4. Congener Analytes of interest in the PCB leach rate study. Those shown in red and noted with an asterisk (*) are considered to be dioxin-like and were compiled at this study's inception from EPA and WHO lists of "dioxin-like" PCB congeners . Subsequent to this, PCB81 (3,4,4',5-tetrachlorobiphenyl) was listed as dioxin-like in WHO TEF reevaluation studies, which also resulted in PCB 170 and PCB 180 being removed from WHO dioxin-like congener list, whereas the EPA dioxin reassessment document [40] lists 14 dioxin-like PCBs, including congeners 81, 170, and 180. Dioxin-like PCBs that are considered to be coplanar are indicated with CP0 (non-ortho) and CP1 (mono-ortho), following the convention in reference [39].

IUPAC Number	IUPAC Name
8	2,4'-Dichlorobiphenyl
18	2,2',5-Trichlorobiphenyl
28	2,4,4'-Trichlorobiphenyl
44	2,2',3,5'-Tetrachlorobiphenyl
49	2,2',4,5'-Tetrachlorobiphenyl
52	2,2',5,5'-Tetrachlorobiphenyl
66	2,3',4,4'-Tetrachlorobiphenyl
77* (CP0)	3,3',4,4'-Tetrachlorobiphenyl
87	2,2',3,4,5'-Pentachlorobiphenyl
101	2,2',4,5,5'-Pentachlorobiphenyl
105* (CP1)	2,3,3',4,4'-Pentachlorobiphenyl
114* (CP1)	2,3,4,4',5-Pentachlorobiphenyl
118* (CP1)	2,3',4,4',5-Pentachlorobiphenyl
123* (CP1)	2',3,4,4',5'-Pentachlorobiphenyl
126* (CP0)	3,3',4,4',5-Pentachlorobiphenyl
128	2,2',3,3',4,4'-Hexachlorobiphenyl
138	2,2',3,4,4',5'-Hexachlorobiphenyl
153	2,2',4,4',5,5'-Hexachlorobiphenyl
156* (CP1)	2,3,3',4,4',5-Hexachlorobiphenyl
157* (CP1)	2,3,3',4,4',5'-Hexachlorobiphenyl
167* (CP1)	2,3',4,4',5,5'-Hexachlorobiphenyl
169* (CP0)	3,3',4,4',5,5'-Hexachlorobiphenyl
170*	2,2',3,3',4,4',5-Heptachlorobiphenyl
180*	2,2',3,4,4',5,5'-Heptachlorobiphenyl
183	2,2',3,4,4',5',6-Heptachlorobiphenyl
184	2,2',3,4,4',6,6'-Heptachlorobiphenyl
187	2,2',3,4',5,5',6-Heptachlorobiphenyl
189* (CP1)	2,3,3',4,4',5,5'-Heptachlorobiphenyl
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
209	Decachlorobiphenyl

Table 5. Homologue Group Analytes of interest in the PCB leach rate study.

HOMOLOGUE GROUPS
Monochlorobiphenyl (Cl1)
Dichlorobiphenyl (Cl2)
Trichlorobiphenyl (Cl3)
Tetrachlorobiphenyl (Cl4)
Pentachlorobiphenyl (Cl5)
Hexachlorobiphenyl (Cl6)
Heptachlorobiphenyl (Cl7)

Octachlorobiphenyl (Cl8)
Nonachlorobiphenyl (Cl9)
Decachlorobiphenyl (Cl10)

Table 6. Aroclor analytes of interest in the PCB leach rate study.

AROCLOR TYPES
Aroclor 1221
Aroclor 1232
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
Aroclor 1262
Aroclor 1268

The list of congeners analyzed in PCB-LRS samples compares reasonably well to congeners commonly reported in studies of natural environmental samples. The 36 congeners commonly found in the environment are shown in Table 7, which is reproduced from McFarland and Clarke.[41]

Table 7. PCB congeners of concern found in the environment. Details are described in the text. Congeners listed in McFarland and Clarke[41], but not analyzed in PCB-LRS samples are shaded.

IUPAC NUMBER				
Group 1A	Group 1B	Group 2	Group 3	Group 4
77	105	87	18	37
126	118	99	44	81
169	128	101	49	114
	138	153	52	119
	156	180	70	123
	170	183	74	157
		194	151	158
			177	167
			187	168
			201	189

McFarland and Clarke[41] described their list of 36 congeners by enzyme-induction type. Induction of some enzyme types may be linked to metabolic carcinogenic processes. Group 1A-B congeners are most likely to contribute to adverse biological effects in environmental samples. Group 1A congeners are aryl hydroxylase enzyme inducers. Group 1B congeners are mixed type inducers (mixed function oxidase enzyme -type) frequently reported in environmental samples. The toxicity potential of congeners is inferred by this property (mixed function oxidase enzyme induction). Group 2 congeners are Phenobarbital type mixed function oxidase enzyme inducers prevalent in the environment, and most are relatively abundant in tissues. Group 3 congeners are weak or non-mixed function oxidase inducers, but are frequently found in environmental tissue samples (fish and invertebrates). Group 4 congeners are mixed type inducers that are relatively scarce in environmental samples.

Sample Extraction Details

Shipboard solid sample extraction was performed using ADLs SOP ADL-2819.04, "Extraction of Polychlorinated Biphenyls and Chlorinated Pesticides from Sediment or Shoreline Soil Samples." The solids were thoroughly cut or ground up into small pieces and returned to the original sample container for chemical analysis. Approximately 75 grams of sodium sulfate was mixed into each sample, followed by the addition of 100 mL of 50:50 dichloromethane/acetone. Each environmental and quality control sample was spiked with PCB surrogate solution prior to the first addition of the extraction solvent. The sample surrogates are listed in Table 8. The QC samples that were processed along with the samples included one procedural blank (PB), one blank spike (BS), and one blank spike duplicate (BSD). The concentration of the surrogate compounds spiked into the samples was determined based on the expected contamination level in the samples. For this project, all surrogates were spiked at high levels in the shipboard solid samples. In addition to the surrogate solution, the BS, BSD, quality control samples were spiked with a subset of the target PCB compounds.

Organic compounds were extracted from the sediment samples using a 50:50 mixture of the organic solvents dichloromethane and acetone. For each sample, a 100-mL aliquot of solvent was added to the original sample container and placed on an orbital shaker for 12 hours. The samples were centrifuged and the organic solvent layer was decanted into a flask. This extraction procedure was repeated two more times with fresh aliquots of solvent and shaking for a shorter period of time. The 3 solvent extracts per sample were combined and water was removed from the combined extract by adding approximately 75 g of sodium sulfate. Alumina column cleanups were performed on the sample extracts to remove potential contamination that would interfere with sample analysis. All extracts were concentrated to approximately 1 mL, using KD concentrators and nitrogen evaporation. Extracts were split into archive and working volumes. The working extract volume was then exchanged into hexane for PCB analyses.

PCB-leachate (seawater), procedural (leaching) bottle blanks, or stainless steel/glass caging sample extraction was performed using SOP ADL-2824, "Extraction of Semivolatile Hydrocarbons and PCBs/Pesticides from Water Samples", a modification of EPA Method 3510B, “Separatory Funnel Liquid-Liquid Extraction”[42]. The following description is excerpted from SOP ADL-2824, included in APPENDIX B, and in the Arthur D. Little (ADL) Sample Preparation and Analysis Method Summaries section of APPENDIX B. With every sample preparation batch the following quality control samples were prepared: procedural blank (PB), blank spike (BS), and blank spike duplicate (BSD). Each environmental and quality control sample was transferred to a separatory funnel and spiked with polychlorinated biphenyl (PCB) surrogate solutions prior to the first addition of the extraction solvent. The sample surrogates are listed in Table 8. The concentration of the surrogate compounds spiked into the samples was determined based on the expected contamination level in the samples. For this project, all surrogates were spiked at low levels in the water samples. In addition to the surrogate solution, the BS and BSD quality control samples were spiked with a subset of the target PCB compounds.

Table 8. Internal Standard and Surrogate Compounds used in the PCB leach rate study.

INTERNAL STANDARD
Tetrachloro-m-xylene (TCMX)
SURROGATES
4,4’-Dibromo-octafluoro-biphenyl (DBOFB)
PCB 103
PCB 198

Organic compounds were extracted from the water, procedural (leaching) bottle blanks, or stainless steel/glass caging samples using the organic solvent dichloromethane. For each sample, a 120-mL aliquot of solvent was added to the separatory funnel; the separatory funnel was then sealed and shaken vigorously for 1-2 minutes. The organic layer was allowed to separate from the water phase and then was drained into a flask. This extraction procedure was repeated two more times with fresh aliquots of solvent. The 3 solvent extracts per sample were combined and water was removed from the combined extract by adding approximately 75 g of sodium sulfate. All extracts were concentrated to approximately 1 mL, using Kuderna-Danish (KD) concentrators and nitrogen evaporation. Extracts were split into archive and working volumes. The working extract volume was exchanged into hexane for PCB analyses.

Definition of Method Detection Limits

The U.S. Environmental Protection Agency defines the method detection limit (MDL) to be "the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero."[43] This procedure consists of preparing and analyzing seven aliquots of a standard spiked at three to five times the expected MDL. The MDL is defined as approximately three times the standard deviation of the mean value for the seven analyses. The Arthur D. Little Environmental Monitoring and Analysis laboratory (ADL) calculated sample-specific method detection limits (sometimes referred to as minimum detection limits) by adjusting the MDL for sample-specific preparation factors such as sample mass extracted, percent solid content, and dilution factors. It was the sample-specific MDL that was reported in the electronic data deliverables submitted to the Navy for the organic compound results.

Sample-specific MRLs calculated for each sample were based on the concentration of the lowest level calibration standard adjusted for all sample preparation factors. ADL's MRL was consistent with a practical quantitation limit (PQL). The MRL is considered to be the value at which the results can be accurately quantitated. Results reported at concentrations less than the MRL (and thus less than the lowest calibration standard) were qualified with a "J" by the laboratory to indicate that the result was an estimated value. In general, on a compound-by-compound basis, the MRLs were normally 3 to 10 times greater than the MDL.

The fundamental difference between detection limits and quantitation/reporting limits is that detection limits are considered the lowest concentration that can be accurately detected by the method, whereas, quantitation limit is considered the lowest concentration that can be accurately quantitated by the method. Thus, results reported at concentrations below the quantitation/reporting limit were considered to be estimated values and qualified with a "J". Often, the quantitation limit is set at the concentration equal to the concentration of the lowest level calibration standard. For example, within a Contract Laboratory Program (CLP) type Statement of Work for Organics, the contract required quantitation limit (CRQL) is equal to the lowest level calibration standard adjusted for sample preparation factors.

For the PCB-LRS project, any compound confirmed to be present in the sample (e.g., mass spectrum meets identification criteria) was reported as a positive result regardless of the result concentration. All results detected at concentrations below the sample-specific MRL were qualified with a "J" flag by the laboratory. These results were considered to be estimated values due to uncertainty in quantitation below the calibrated range of the instrument. Occasionally, there were also positive results reported at concentrations below the MDL when the compound identification criteria were met. If a compound was not detected or did not meet the compound identification criteria, the compound was reported as a nondetect (ND). In electronic data deliverables, the nondetect values were reported with a value of zero and a "ND" qualifier. It was left to the judgment of the PCB-LRS Principal Investigator to determine the best value to be used for nondetects based on specific data analysis needs.

Quality Assurance and Quality Control

A number of quality assurance (QA) measures were added to the processing of samples to monitor quality control (QC) and to aid in the assessment of the usability of the data with respect to the project objectives. An important part of this was the evaluation of specific QA/QC samples for accuracy, precision, and potential contamination. The method summaries in the performance-based contract project-specific work plan and reproduced in this report contain details of the quality control samples required for each analytical method. The data quality analyses and Data Quality Objectives (DQO) for the PCB analysis methods are summarized in Table 9.

Each lot of solvent received at the ADL laboratory was tested by the applicable analytical method to determine potential solvent contamination prior to use. Preparation of analytical standards in analytical grade solvents is described in the relevant laboratory SOP. Prior to spiking the samples with surrogate, matrix spike, and/or internal standard solutions, all standard solutions were analyzed to determine accuracy of preparation and potential contamination.

Instruments were calibrated prior to sample analysis by analyzing standard solutions containing the target and surrogate compounds at different concentration levels spanning the concentration range of interest. The linearity of the instrument over the selected concentration range was also checked. A continuing calibration standard was analyzed regularly to check the stability of the instrument response and the compound retention times. If the variability of either the initial calibration or the daily calibration did not meet the criteria set in the project-specific work plan, a new calibration was run and the affected samples reanalyzed.

To assess the accuracy of the calibration standards, an independent reference material (IRM) was analyzed. Instrument calibration was considered acceptable if the reported concentrations of the compounds in the IRMs were within 15 percent of the target concentrations for GC-ECD analysis, and within 20% for GCMS-SIM.

Standard Reference Materials (SRMs) were obtained from National Institute of Standards and Technology (NIST) and are samples that have been repetitively analyzed to determine certified values. SRMs were used to assess the effect of the sample processing procedures and matrix on method accuracy.

A procedural blank was processed and analyzed with each sample preparation batch in order to monitor potential contamination resulting from laboratory solvents, reagents, glassware, and processing procedures. These procedural blanks are for evaluating the analytical laboratory methods. They are different from the leaching experiment procedural blanks described previously (in the subsample preparation section), for which leachate samples were collected and analyzed as typical seawater leachate samples, to determine potential contamination during laboratory leaching operations.

Blank spikes and blank spike duplicates were prepared by spiking representative target compounds into a blank matrix to assess the effect of the sample processing procedure independent of sample matrix effects on method accuracy and precision. Duplicates samples were prepared by extracting and analyzing a second representative aliquot of sample. Comparisons of the original and duplicate sample results were used to assess the effect of the sample processing procedures and sample matrix effects on method precision. A surrogate is a known compound, which is not present in environmental samples, that is added to a sample prior to processing. The chemical properties of the surrogate compounds must be close to the target compounds. The surrogate was measured to assess the sample preparation efficiency and impacts of sample handling. Surrogates may also be used to adjust the target compound concentrations to correct for loss during sample preparation (surrogate correction). Surrogates were added to all samples prior to preparation.

Target compound concentrations, surrogate and matrix spike recoveries, and additional QC sample results were determined. After careful checking and review, analysts transferred data electronically from the instrument data systems to ADLs data management software for further data review, qualification, and edits. All data summary forms were generated from the data management software and were compared with the instrument quantitation reports for accuracy. The data summaries were arranged in spreadsheet format.

The chemistry data for each analysis were reduced and reviewed by ADL laboratory staff and then assembled into the final laboratory data package. The assembled package was reviewed and validated by the facility supervisor or staff responsible for each analysis. The data were checked to ensure that data quality objectives were met, that the analyses met the project objectives, and that the data were traceable and defensible. The Project Manager also reviewed the data for compliance with the documented procedures and quality objectives. Data were also reviewed for internal consistency and against expected or known values. All final laboratory data packages and the associated electronic data deliverables were audited by the Quality Assurance Manager or data review specialists according to the procedures outlined in ADLs data auditing SOP.

As previously mentioned, all results detected at concentrations below the sample-specific minimum reporting limit (MRL) are qualified with a "J" by the laboratory. These results are considered to be estimated values due to uncertainty in quantitation below the calibrated range of the instrument and due to increased variability at concentrations near the method detection limit (MDL).

Table 9. Data quality objectives and criteria for PCB congeners, homologues, and Aroclors by GC/MS SIM, PCB Congeners by GC/ECD.

Element or Sample Type	Minimum Frequency	Data Quality Objective/Acceptance Criteria
Initial Calibration	Prior to every batch sequence.	5-point curve. %RSD <25% for 90% of analytes and <35% for all analytes.
Continuing Calibration	Must end analytical sequence and every 12 samples or 18 hours, whichever is more frequent.	%D <25% for 90% of analytes and <35% for all analytes.
Procedural Blank	Every batch/every 20 field samples.	No more than 2 analytes to exceed 5x PQL unless analyte was not detected in associated sample(s) or associated sample compound concentrations are >10x blank value.
Blank Spike/Blank Spike Duplicate Sample	Every batch/every 20 field samples.	50-150% recovery, RPD <35%.
Duplicate Analysis	One per 40 field samples.	RPD <35% for all analytes that are detected at concentrations >10 times the MDL; mean RPD <35%.
Matrix Spike, Matrix Spike Duplicate Sample	Every batch/every 20 field samples.	45-150% recovery, RPD <35%.
Surrogate Standards	Every sample.	45%-125%: all surrogates, one is allowed out
IRMs (SRM specified per batch)	One set per batch of samples after every ICAL.	Values ≤20% (<15% for GC-ECD) difference of true value for all certified analytes.

Sample Custody Procedures

Sample custody control was maintained at each laboratory through the use of several tracking systems designed to protect sample integrity. The sample custodian initiated laboratory chain of custody documentation when the sample was relinquished by the courier. Samples were inspected to ensure that:

- minimum sample volumes were received,

- appropriate containers and preservatives were used,
- acceptable sample conditions were maintained (e.g., temperature, no breakage), and
- samples were received within allowed shipping time (e.g., next-day air).

Immediately upon receipt by the analytical laboratory, the sample custodian assessed and documented the conditions of the samples and initiated sample login. The contents of each shipping container were checked against the information on the chain of custody forms. Temperature blank samples were checked to verify that samples were maintained within specified temperature ranges. If anomalies were noted in the chain of custody form, the ADL Project Manager was informed. Any samples that were improperly preserved were noted on the chain of custody form and SSC-SD personnel) were notified immediately. The SSC-SD personnel and ADL Project Manager then determined the necessary corrective action. The laboratory assigned an internal unique identifier to each sample, or used the sample identification number assigned in the field with the container number and project name to track individual sample containers so that the sample would not be confused with samples from another project.

The field chain of custody document was completed and maintained in the project file. While within the laboratory, the sample was held in appropriate storage areas to maintain sample integrity. Upon completion of the analysis, any remaining sample was placed into long-term storage. When sample analysis and all quality control checks were completed and a final data report was issued, the unused sample portion and/or extract was stored up to six months or longer if requested by the SSC SD Principal Investigator. Samples were sent to SSC-SD for archiving if requested and were not disposed of without the written permission of the SSC-SD Principal Investigator. Sample disposal was then documented in the project file.

Data Management

A master electronic database was designed, populated, maintained, and compiled on an individual leaching experiment basis at SSC SD throughout the experimental effort. Pertinent PCB-LRS project data, including specific experimental information, screening analysis results, draft results of conventional sample analysis, and final results of conventional sample analysis (including quality control results), were transcribed or imported into the database by SSC-SD personnel. Leaching laboratory data were manually entered into database files directly from laboratory notebooks and/or logbooks. All analytical data reported electronically were archived in their original format (as delivered) prior to input into the SSC database. Any subsequent revisions to the file were archived as the latest version and the original version was archived separately as a draft report and not used except for tracking purposes.

Data Evaluation and Data Reduction

An evaluation of project data was continuously performed by SSC-SD personnel, throughout each leaching experiment. This was used to verify that analysis results were within specified QC allowances and that all sample-associated information was correct. When a questionable issue was identified, the ADL analytical project manager was informed to clarify the issue or correct the data analysis report. In the former case, the clarification was simply noted in the database. In the latter case, a revised analysis report was prepared with corrected data. The revised dataset was then entered or imported into the database as the most recent version and the original data remained archived separately as a draft original file, as previously indicated. Preliminary leach rate calculations were performed as soon as possible to evaluate the leaching progress in as near to real time as possible. This was particularly important for leachate samples that contained tPCB concentrations (as Aroclor 1254) lower than 2 ppb, the practical detection limit for immunochemical screening analyses.

The methodology for calculating leach rates is directly related to the leaching experimental design. Any given leachate sample was an independent evaluation of the leaching behavior of the solid under test in that leachate volume over a specific (partial/incremental) time period, starting from when fresh seawater was introduced to the leaching vessel until when the sample was collected for conventional chemical analysis, the time corresponding to the sampling interval. A complete leaching experiment was comprised of a series of such partial leaching experiments, performed on the same shipboard solid sample (by removing the caged solid from a previous leaching vessel and placing it in a new leaching vessel with new ASW leachate as described in the leaching experiment design), repeated over the entire leaching experimental timeframe. This is illustrated for a hypothetical dataset in Figure 9, where each concentration data point plotted vs. time corresponds to the concentration in each partial leaching evaluation.

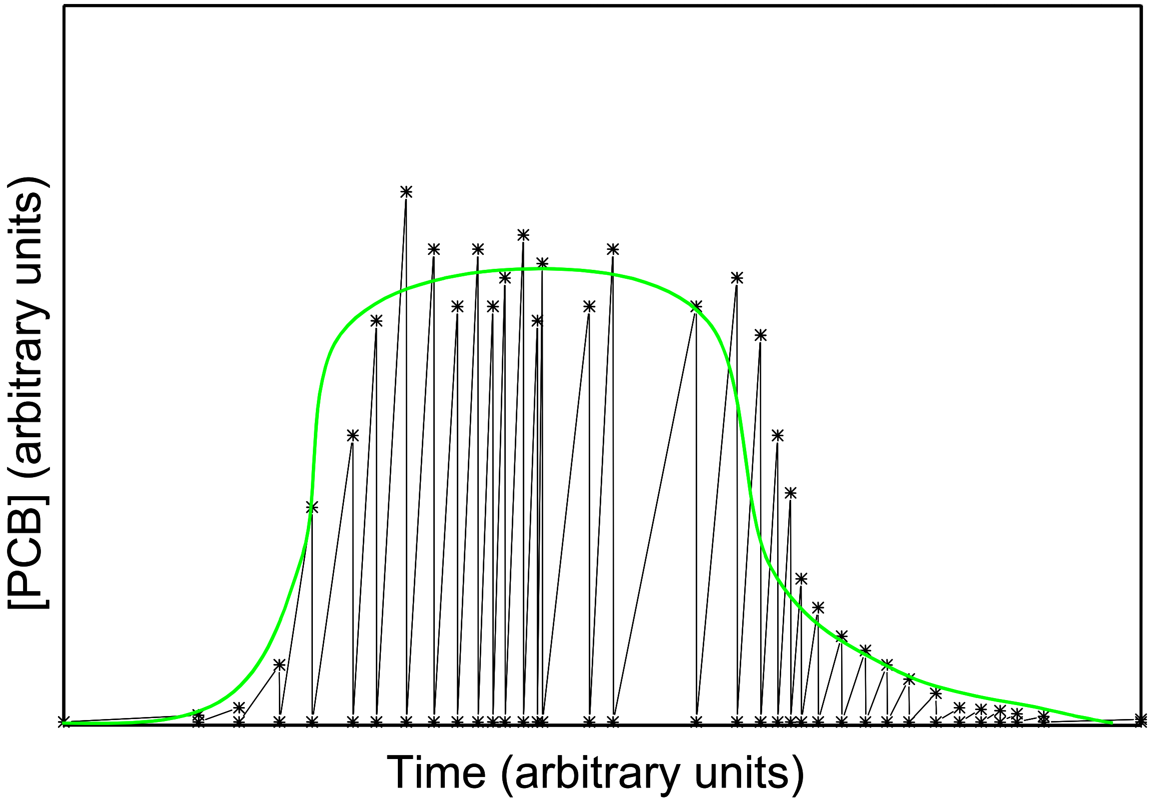


Figure 9. Hypothetical leachate concentration data. Each positive slope (straight line) between *'s is proportional to the average leach rate for that partial or incremental leaching experiment as described in the text. The average leach rates (AvgLR) for these hypothetical data are plotted vs. absolute leaching time below in **Figure 10**.

The average leach rate (AvgLR) for each sampling interval is proportional to the measured change in concentration over the time period for each partial leaching experiment across the leaching series as functionally described in Equation 1. The AvgLR can be calculated by using the exposure volume in each given leaching interval to determine the mass released as a function (F) of time as shown in Equation 2 and illustrated in Figure 10.

Equation 1

$$\text{Average Leach Rate (AvgLR)} = F(d[PCB]/dt)$$

Equation 2

$$F(d[PCB]/dt) = V*\Delta[PCB]/\Delta t = ([PCB]_f - [PCB]_i)*V/(t_f - t_i)$$

where d[PCB] is the differential change in PCB concentration, dt is the corresponding differential change in leaching time, V is the leaching interval (exposure) volume, t_i is the beginning of the leaching interval and t_f is the endpoint of the leaching interval.

By design, the final concentration in a leachate sample is equivalent to the change in concentration, because each partial or incremental leaching experiment starts at a concentration effectively equal to zero (fresh seawater) and leaches with time until it is collected at the end of that incremental leaching experiment. The change in time (Δt) or time that the solid spends in a particular seawater leachate sample volume for a partial/incremental leaching experiment is conveniently equivalent to the sampling interval ($t_f - t_i$). Equation 2 can then be described simply by the following batch reactor equation.

Equation 3

$$\text{AvgLR [ng/day]} = [PCB]_f *V/\ t_f - t_i$$

A leach rate curve describing the rate behavior for the shipboard solid under test is prepared by plotting the average leach rates (AvgLR, Equation 2) for each of the partial/incremental leaching experiments in the complete leaching series vs. the absolute leaching time or total exposure time (not Δt, the partial or sampling interval). The absolute leaching time is indexed or referenced to the date and time that leaching for the shipboard solid was initiated (t_0). This type of curve is shown in Figure 10 for the hypothetical concentration data plotted in Figure 9 by assuming a hypothetical leaching volume of 1 L for each partial/incremental leaching experiment (over each interval, Δt).

Figure 10. Example of a hypothetical Leach Rate (AvgLR), proportional to the change in the hypothetical leached PCB concentration data in **Figure 9**, plotted as a function of time (absolute leaching time).

Leach Rate Analysis

Complete leaching curves for each shipboard solid tested were derived as described in the previous section. Such curves represent the average leaching behavior as a function of absolute leaching time, or seawater exposure time, and reflect the degree to which each shipboard solid matrix suppresses PCB release. It is particularly useful to evaluate these leaching curves to determine leach rate dynamics or stability as a function of time. The leach rate for a given shipboard solid, if leaching occurs, must increase from zero to some value upon exposure to seawater. If leach rate kinetics allow it, *i.e* if the leaching timescale is similar to the experimental timescale, this would be observed as an increasing AvgLR early in the leaching process (early in absolute leaching time). It is possible for the AvgLR to very slowly increase or grow in over time, or perhaps begin leaching from the maximum observable experimental value, indicative of an initially unobservable leaching process because it is occurring on timescales much faster than the experimental timescale. In any case, it is expected that a maximum AvgLR would be reached at some point early in the leaching process, and then either remain constant or begin to decrease over time. How long a leach rate experiment is performed dictates whether sufficient leaching behavior is observed. Both the AvgLR and the amount of mobile PCBs initially present in the shipboard solid control this behavior and define the time to depletion in the solid.

If a decreasing AvgLR was observed over the course of a leaching experiment, with at least 4 decreasing AvgLR data points, they were best-fit to an appropriate curve, and evaluated using analysis of variance (ANOVA)[44]. This curve-fitting approach provided a crude predictive capability subject to statistical validity and confidence, but was most useful to evaluate whether the 95% confidence or prediction limits for such an extrapolated curve would support utilizing the empirical endpoint of the AvgLR curve beyond the 1-2 year experimental timeframe (e.g. as the long-term conservative AvgLR to perform risk assessments over periods of 2-100+ years). The confidence and prediction limits for future

AvgLR values were calculated using standard statistical equations available in most curve-fitting and analysis programs. The latter (prediction) limits were calculated for 20 future predictions and are generally larger than confidence limits because of decreased precision in predicting future specific values as opposed to predicting future average values (confidence limits). In all cases, the fit was performed only on points $\geq$ the observed curve maximum.

Data Quality Analysis

The leachate analytical chemistry data quality met or exceeded data quality objectives. At the conclusion of the leaching experiments, each solid-specific dataset was evaluated to verify analysis of the correct number and type of samples, and to ascertain whether the analytical data from each chemical analysis were internally consistent. The data were also inspected to ensure that all appropriate quality assurance/quality control procedures were followed, and that the data were scientifically or experimentally meaningful, from a practical leaching experiment perspective. If an issue was noted during this evaluation, the data were reanalyzed blindly, i.e. without any information provided to the analyst for the sample/data issue in question. A revised/corrected dataset then replaced the original/incorrect dataset, and was treated like a new dataset, i.e. subjected to the inspection process again. The original dataset was retained as an archived preliminary draft. Using this methodology, a high quality dataset for each leaching experiment was finalized for use in the data reduction and analysis phase. The analytical chemistry QAPP specified in this study used a performance-based QA/QC evaluation with ongoing quality control evaluations using standard reference materials/certified reference materials (SRM/CRM) and other quality checks that required repreping/reanalysis as corrective action if QA/QC criteria were not met. This lessens the need to have 3rd party validation as normally done under CLP because "unuseable" data are not reported (they are rerun instead). Analytical chemistry data and associated analytical QA/QC can be found in APPENDIX C.

In addition to the general data quality evaluation/validation described above, an evaluation of uncertainty or confidence level was performed for each analyte on a congener-specific detection limit basis, i.e. individual congener detection and congener detection within the homologue groups. (The term “detection limit” is used throughout to mean sample-specific method detection limit, unless indicated otherwise.) In cases where a congener was detected above the sample-specific detection limit, but below the sample-specific minimum reporting limit (MRL), the value was marked or J-flagged, indicated less confidence in the value because it was below the lowest calibration standard. Congener analysis results below the detection limit were flagged as ND. Because a process (leaching) was being sampled and evaluated, much different from sampling a distribution (e.g. sampling in the natural environment), all experimentally determined congener and homologue data were considered valid, and used in this study as measured. For similar reasons, non-detected (ND) congeners and homologues were not assigned a value of zero, or estimated, and were thus not treated quantitatively or included as part of an experimental leaching curve.

An important reason for measuring PCB homologue group concentrations with GC-MS/SIM method is to provide an empirical value for tPCBs by summing the measured homologue values. This approach is not as widely used for environmental studies because, historically, many regulatory sampling and analysis programs have required only the measurement of specific congeners of interest and subsequently an estimation of tPCBs from the environmental concentrations of those congeners was performed. Much of the toxicological and risk assessment information available is also centered on congeners and estimated tPCBs. In this effort, we were presented with the opportunity to obtain an empirical value for tPCBs, vice an estimation of tPCBs. Thus, to reduce this type of uncertainty, we measured and summed homologues for tPCBs as this provided a more accurate tPCB value.

The data quality analysis for homologues is performed as with congener analytes (on a congener-specific and sample specific detection limit basis) except this is only for congeners *detected* within each homologue group (mass-selected at the detector). For *undetected* congeners in the homologue group, as a reasonable estimation of the maximum congener concentration (conservative congener limit), it is generally accepted that the amount that could be present at undetectable levels, would be ½ the sample-specific detection limit (DL) for that congener.[45, 46] This is derived by assuming that the likely mean concentration of results is randomly distributed below the detection limit with a normal distribution. For a homologue group, which is comprised of all congeners mass selected and detected at the molecular weight for congeners in that homologue group, the contributing/present congeners in that homologue group need not be isolated chromatographically to quantify the total amount of that homologue group present (can be done if all of those congeners are specifically separated and analyzed for as target congeners). What this means is that non-target (not isolated chromatographically) congeners in a homologue group can be quantified, even for a GC peak with multiple coeluting congeners belonging to a given homologue group, as part of that homologue group, by molecular weight without separation into individual GC peaks. Rarely, if ever, are all of the possible congeners (209) distributed across all homologue groups (10) determined specifically in analyses of environmental samples, due to coelution of difficult-to-separate congeners. Because of this, it is necessary to derive an approach for estimating a *conservative homologue upper* , similar to that described for the conservative congener limit above.

The algorithm developed for calculating conservative homologue limits is based on the average sample-specific congener DL across all (31) target congeners. A homologue DL is calculated by multiplying the number of possible GC peaks corresponding to both the non-detected target congeners and non-target congeners in a given homologue group, by this average sample-specific DL. The number of peaks in each homologue group is initially reduced by the number of co-eluting congeners[47, 48, 49, 50] and reduced further by the number of detected (target) congeners. The algorithm then compares the sum of detected target congeners in a homologue group to the total possible congeners in that homologue group, and calculates the hypothetical concentration possible (conservative limit) for that homologue group. This estimated conservative limit is defined as the concentration where all of the congeners in the homologue group could be present (50% of the time) at just under their detection limit. Of the possible 209 congeners, 31 congeners, spread across the ten homologue groups, were measured specifically in this study. Those detected in a given sample are used as indicated above to first decrease both the measured homologue group value (Equation 4) and the calculated homologue conservative limit value (Equation 5), giving an increased confidence to the hypothetical homologue value. In addition, co-elution of multiple congeners within GC peaks (if peak not detected, multiple congeners in that peak are therefore not detected) was used as indicated above to decrease the hypothetical conservative limit for a homologue group measurement. Finally, after minimizing the conservative limit in this way, it was then compared to the residual homologue value to gain insight into how well the residual measured homologue value represents both the non-target and non-detected target congeners in the homologue group. This algorithm was applied to each sample analyzed in the leach rate dataset, on a sample-specific basis (based on sample specific detection limits) to determine a reasonable conservative limit for all non-detected and detected (below MDL value) homologue groups in all samples analyzed.

Equation 4

$$\mathrm{RHV_h}\ [\mathrm{ng/L}] = \mathrm{DHV_h} - \mathrm{DCV_h}$$

$\mathrm{RHV_h}$ is the residual homologue value for a given homologue group, $\mathrm{DHV_h}$ is the detected homologue value for a given homologue group, and $\mathrm{DCV_h}$ is the detected (target) congener values within a given homologue group.

Equation 5

$$\mathrm{EHM}\ [\mathrm{ng/L}] = \tfrac{1}{2}\,((\#\mathrm{NDC_h} + \#\mathrm{NTC_h})*\mathrm{AvgCDL_h})$$

EHM is the estimated homologue minimum for a given homologue group, $\#NDC_h$ is the number of non-detected (target) congener peaks for a given homologue group, $\#NTC_h$ is the number of non-target congener peaks for a given homologue group, and $AvgCDL_h$ is the average target congener sample specific MDL. The use of $\#NDC_h$ and $\#NTC_h$ takes into account the number of congeners that may co-elute in any given GC peak. (If a peak is not detected, then all co-eluting congeners in that peak are not detected). Results of this homologue uncertainty analysis for all leaching experiment data are included in the Shipboard-Solid-Specific Homologue Data Quality Evaluation and Validation section of APPENDIX C.

EMPIRICAL DATA AND OBSERVATIONS

PCBs-ISM Characterization

Shipboard solid materials and corresponding PCB concentrations were summarized in Table 3 for intact shipboard solids. These chemical analyses of representative PCBs-ISM subsamples were analyzed for Aroclor content by GC-ECD and compared against the initial shipyard analyses. In all cases, the concentration of primary Aroclor (1254, 1260, or 1268) was determined to be greater than 100 μg/g (ppm), and in some cases, the solid was found to contain congeners for which a best-fit analysis indicated the possibility of more than one Aroclor. There were no trends observed for the Aroclor ratio in solids that contained more than one Aroclor. Because solid analyses are destructive to the sample, these representative results were considered an estimate of the nominal pre-leaching concentration in subsamples of that particular solid prior to leaching.

The actual concentrations specific to each leached solid was determined subsequent to leaching by performing a solid analysis for each leached solid, followed by a mass balance for each leaching experiment. This approach provided a means of indirectly determining the starting concentration in the solid at the beginning of the leaching experiment, for each leached subsample and leaching experiment. The mass-balance was performed as in Equation 6 for each leaching experiment by summing the tPCB mass that had leached into seawater leachate throughout the leaching experiment, and then adding that to the tPCB leached solid analysis result.

Equation 6

$$[PCB]_I \text{ [g PCB/g shipboard solid]} = (M_R + M_L)/M_S$$

In this equation, for any given leaching experiment, $[PCB]_I$ is the concentration of PCBs initially in a shipboard solid, M_R is the total mass of PCBs released over the course of the leaching experiment, M_L is the residual PCB mass in the leached solid, and M_S is the mass of solid tested. Because leaching experiment PCB analyses were performed on the basis of empirical tPCBs (sum of the measured homologues) to reduce uncertainties associated with performing Aroclor analyses, it was assumed that the Aroclor signatures (relative amounts of Aroclors) in the solid samples used for leaching were similar to the best-fit Aroclor signatures in these representative solid samples (Table 3).

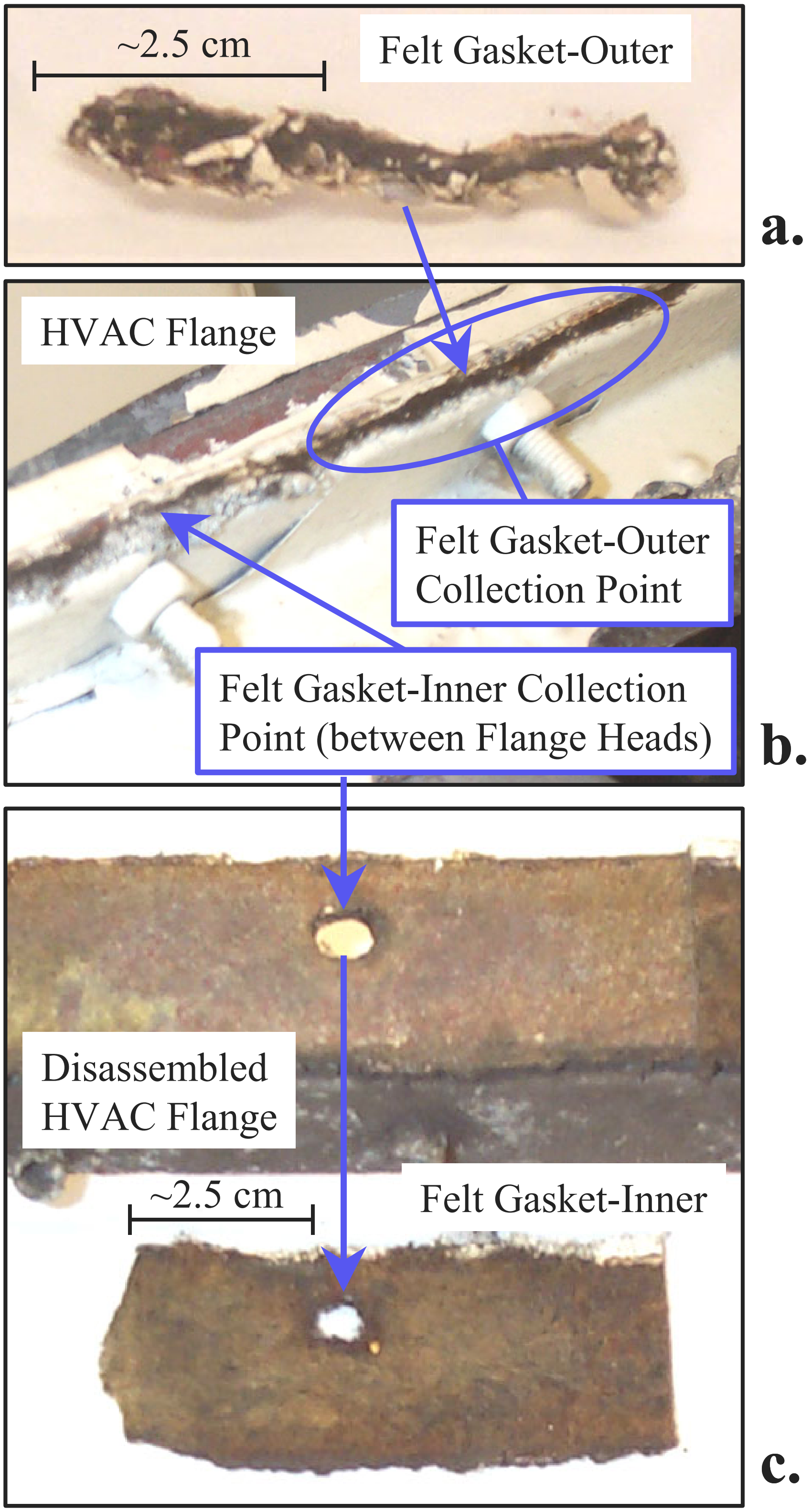
The Aroclor determinations performed in this study are reproduced in Table 10 below, along with three additional Aroclor analyses of the physically separable/dissectible components of electrical cable and foam rubber. Representative photographs and schematics of the electrical cable components and foam rubber samples are presented in Figure 11 with photos of the other shipboard solids. Electrical cable was separated into inner core (resin binder adjacent to outer plastic sheath) and middle (paper/resin insulation adjacent to copper center conductor) components and analyzed in addition to the intact cable (all components including center copper wire). Paint chips were removed from the foam rubber and analyzed in addition to the intact foam rubber with paint analysis. The additional analyses of physically separated/dissected electrical cable and foam rubber were performed to identify, if possible, where the bulk of the PCB source resided in the material. Unfortunately, it is apparent from these results that PCBs are present at quite significant levels in all three components of electrical cable and in both components of foam rubber. Note that for the foam rubber sample, unlike the A1254 signature, the A1260 signature in the intact solid is lower, indicating that it seems to be more closely associated with the paint component rather than the foam rubber itself.

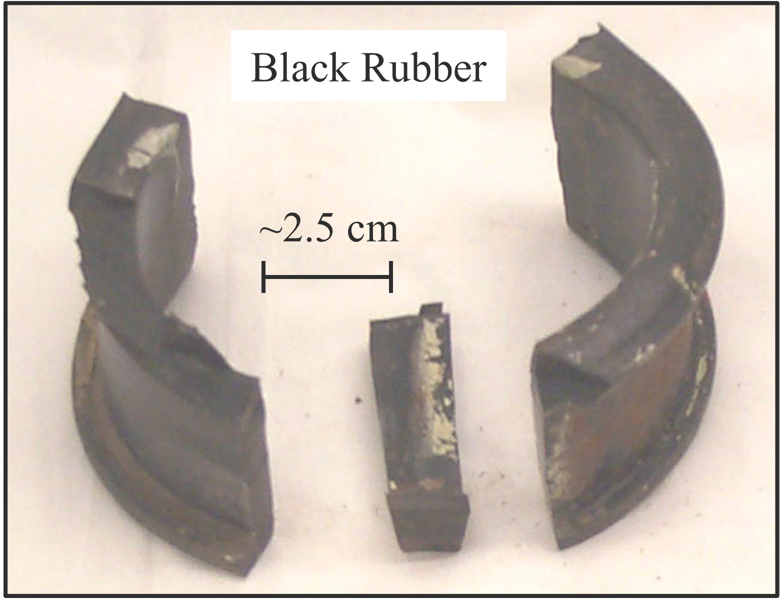
Table 10. Aroclor concentrations in μg/g (ppm) as determined for best-fit analyses of the congener fingerprint for *representative* subsamples of each shipboard solid used in leaching experiments. These materials correspond to the shipboard solids collected during the ship sampling effort for which subsamples were subsequently leached in this study.. Separate determinations were also made for different physical dissections of both electrical cable and foam rubber subsamples in an effort to possibly identify the primary PCB-containing components for these samples. These included the paint-only portion of the foam rubber field sample, the inner component only (resin binder adjacent to outer plastic sheath) of the electrical cable field sample, and the middle component only (paper/resin insulation adjacent to copper center conductor) of the electrical cable field sample.

μg/g (ppm)	**Felt Gasket (outer)**	**Felt Gasket (inner)**	**Black Rubber**	**Bulkhead Insulation**	**Aluminized Paint**
Aroclor 1221					
Aroclor 1232					
Aroclor 1242					
Aroclor 1248					
Aroclor 1254			2,100	160	470
Aroclor 1260			72	94	540
Aroclor 1262					
Aroclor 1268	100,000	140,000		46	120
μg/g (ppm)	**Foam Rubber**	**Foam Rubber Paint Chips**	**Electrical Cable**	**Electrical Cable (middle)**	**Electrical Cable (inner)**
Aroclor 1221					
Aroclor 1232					
Aroclor 1242			8.4	3	2.9
Aroclor 1248					
Aroclor 1254	7,100	3,300	1,800	610	1,200
Aroclor 1260	550	1,100	160	78	100
Aroclor 1262					
Aroclor 1268					

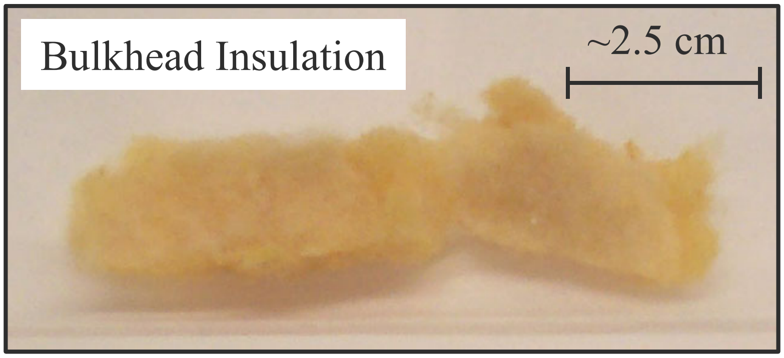
Shipboard Solid Materials

Photos of each representative shipboard solid are shown in Figure 11. These photos represent the actual appearance of each shipboard solid subsample prior to leaching. Except where noted in the subsample-specific report sections below, the appearance of the solids did not differ significantly from these photos after seawater exposure over the experimental (leaching) timeframe. In most cases the length of each solid (as leached) corresponded to ~3 inches, except for those solids shown in Figure 11 (a & d), which were both ~2 inches in length. The Aroclor 1254 and Aroclor 1254 control samples were placed on 1”x 3” pieces of binder free glass fiber filter, similar to the one in the paint sample photo (Figure 11 f). The masses of the shipboard solids were recorded prior to leaching. Shipboard solids were generally described in the **EXPERIMENTAL DETAILS** section of this report.

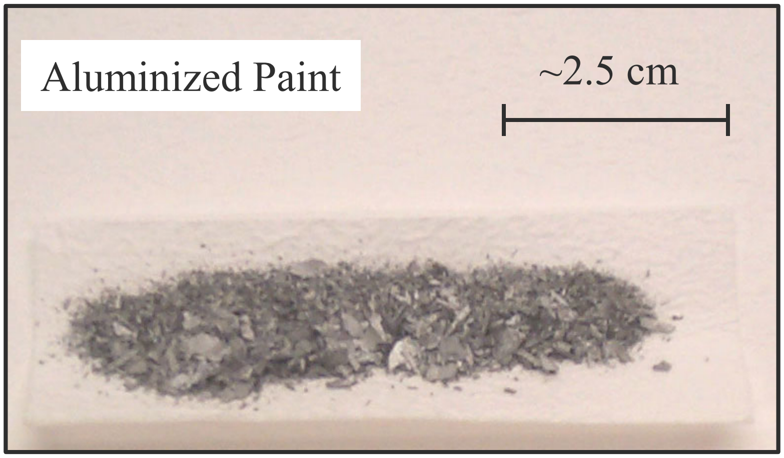



Black Rubber
~2.5 cm

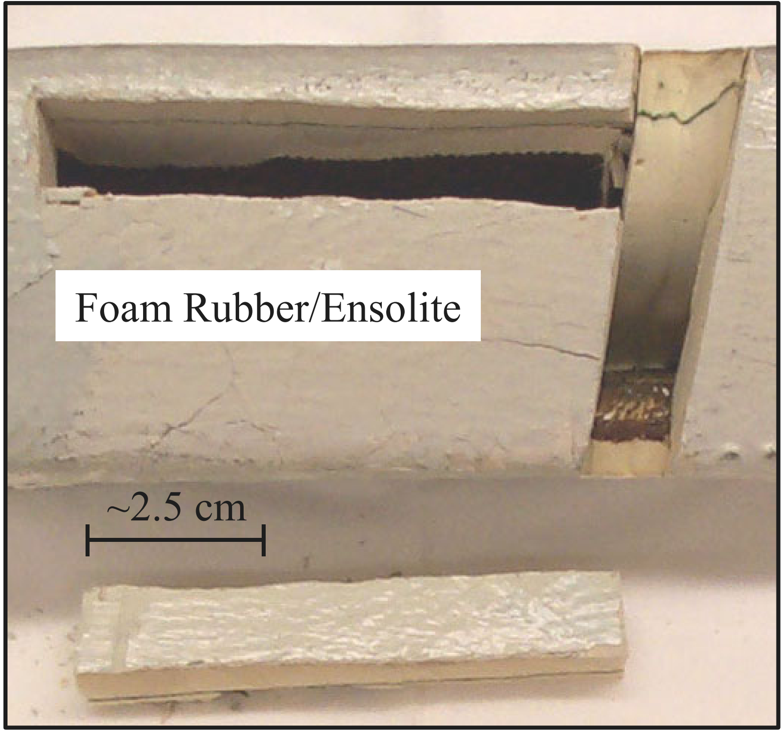
d.


Bulkhead Insulation
~2.5 cm

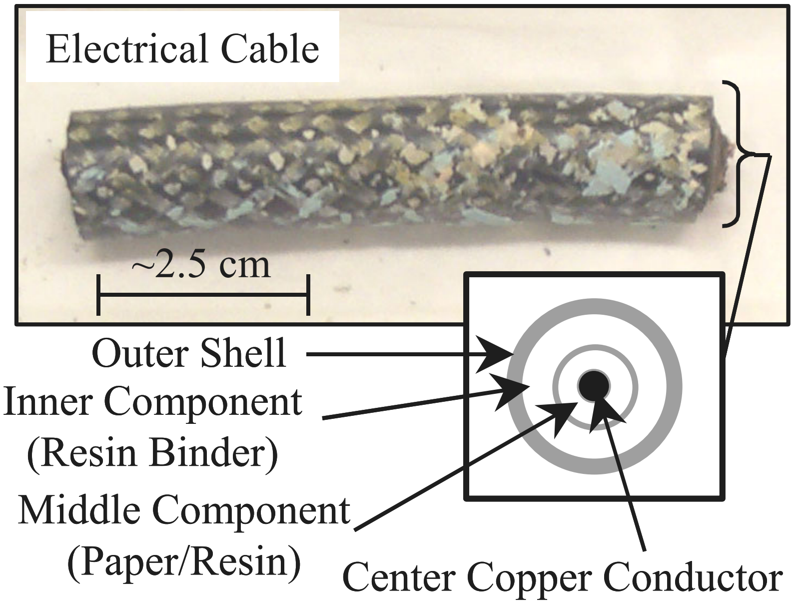
e.


Aluminized Paint
~2.5 cm

f.



g.



h.

Figure 11 (a-h). Representative photos of shipboard solids: a) Felt Gasket-Outer (FGO), b) flange bottom edge where FGO was collected, c) Felt Gasket-Inner (FGI) with flange collection site, d) Black Rubber Pipe Hanger Liner (BRPHL) – subsample is shown in center, with remaining pieces of the ship sample on the left and right, e) Bulkhead Insulation (BHI), f) Aluminized Paint (AP), g) Foam Rubber/Ensolite^{TM} (FRE), and h) Electrical Cable (EC) with a schematic illustrating its internal components. The masses of each leached solid are reported in the respective leaching subsections of the **Shipboard Solid Specific Leaching Data** section.

Leaching Data Description

Ideally, a leaching experiment would be performed by placing the solid into a large enough volume of seawater to avoid saturation with PCBs, and by avoiding dilution effects or other effects related to removal of the required volume of seawater leachate (~1L) for conventional very low-level PCB analysis. Such an ideal approach would result in an experimental concentration versus time plot in a constant volume of water, a prerequisite for evaluating kinetics of leaching behaviors, especially for individual PCB congeners using classical data analysis techniques. Unfortunately, this ideal approach would require *a priori* knowledge of the leach rate for any given solid, which was not available. Indeed, this is the solid-specific property we sought to empirically determine in this work because such leaching data were not available. To work around the experimental difficulties and detrimental effects associated with PCB saturation and dilution issues related to sample (volume) removal, an experimental approach was developed during the preliminary phase of this study using a sample of felt gasket-inner as a representative test solid, prior to the leaching experiments described in this report. This particular solid was, at the time, assumed to represent the experimental extreme (solid expected to be most difficult to contain for mass balance purposes, and was likely to have a worst-case release because of the tendency to break apart with physical stress induced by stirring action), i.e. a fast-leaching solid for leaching experiments based on a typically high PCB concentration and potential for artificially induced high surface area. The preliminary development did not analyze leachate using analytical chemistry. Rather, the benchtop methodologies and standard operating procedures were developed, evaluated, and optimized during this phase, prior to initializing experiments for which analytical results were collected and are ultimately reported here. Additionally, the approach developed and used in the study allowed for analytical data collection as a function of leaching time in known volumes of seawater leachate, while remaining below the saturation limit in the immediate volume of seawater leachate surrounding the solid at any time during the leaching process. The process used to avoid saturation also allowed for a more conservative measure of leaching under completely advective conditions, a condition not likely to be the case within the vessel where PCBs-ISM reside. The practical concentration (saturation) limit for Aroclor was empirically observed using pure standards as positive analytical controls, for dissolution under conditions identical to the leaching conditions for shipboard solids. Because the shipboard solids exhibited leaching at tPCB concentrations below these positive controls, the experimental leaching curves reported here are considered true leach rates, including only the leaching suppression dictated by the shipboard solid matrix itself.

Each leaching experiment was, in effect, performed to simulate the ideal case above through seawater exchange, by sequentially exposing a given shipboard solid to individual ~1L aliquots of clean seawater at time intervals designed to avoid PCB saturation in each seawater leachate aliquot. This approach also allowed for the detection of very small changes in PCB release, on the order of sub-nanogram quantities of congeners, unlike the larger mass release that would have been required by increasing the sampling time periods for a large-scale experiment analyzing 1L aliquots from a very large leaching volume. These intervals or “micro” leaching experiments between seawater exchange points coincided with leachate sampling events and represent the sampling interval, or time between analyses of PCBs in the seawater leachate. The micro-leaching/sampling experiments were continued until such a time that conventional chemical analysis of the seawater leachate indicated that leaching had either stopped or had reached what appeared to be a stable leaching condition subsequent to an empirically observed maximum leach rate. The mass normalized average leach rate ($AvgLR_M$) was then calculated as an extension of Equation 3 for seawater leachate samples that had previously contained the solid of interest, as shown in Equation 7, by analyzing the leachate to determine the PCB concentration and then converting that concentration into the mass PCBs released into that volume, and finally by dividing that value by the leaching time (sampling) interval, *i.e.* the time that the solid had been exposed during the micro-leaching experiment.

Equation 7

$$\text{AvgLR [ng/g-shipboard solid-day]} = ([\text{PCB}]_f * V / (t_f - t_i))/M_S$$

where $AvgLR_M$ is the mass normalized average leach rate over the leaching interval, t_i and t_f are the initial and final time indices, respectively for the leaching interval, [PCB] t_f is the PCB concentration at the endpoint of the partial/incremental leaching interval, V is the leaching volume for the leaching interval, and M_S is the mass of the solid being tested. It should also be noted that for all calculations of mass release using PCB concentration data, the calculated number is generally limited to 2 significant figures by the reported sample analysis volume.

A series of micro-leaching experiments for each solid were plotted as a function of absolute leaching time and used to evaluate the average leach rate behavior as a function of entire seawater exposure or overall/absolute leaching time. At the conclusion of the entire leaching experiment, defined as a complete series of micro-leaching experiments, it was possible to reconstruct the classical experimental concentration behavior versus time curve corresponding to the large scale experiment described above, where a solid would have been placed in a constant large volume of seawater leachate. This constant volume is the sum of all incremental volumes to which the solid was exposed over the course of the experiment, and as an inherent benefit, this analytically validated experimental protocol used an incremental volume that avoided a saturation condition. The classical concentration vs time curves are referred to as cumulative concentration curves and were prepared by calculating concentration using Equation 8 below and plotting (C_i) as a function of leaching (exposure) time.

Equation 8

$$C_i = \frac{\sum_{j=1}^{i}\left(C_j\,V_j\right)}{\sum_{k=1}^{n} V_k}$$

Where where C_i = PCB concentration for the i^th^ data point in the cumulative concentration plot, C_j = PCB concentration for the j^th^ incremental experiment, V_j = volume of artificial sea water for the j^th^ incremental experiment, V_k = incremental volume of artificial seawater in the k^th^ incremental experiment, and n = total number of incremental experiments in the test (total number of incremental solid seawater exposure experiments), which is equal to the number of data points.

Shipboard Solid Specific Leaching Data

The following sections contain data and results specific to leaching experiments performed for each shipboard solid tested (photodocumented in Figure 11) under the physico-chemical leaching conditions of interest, as described in the experimental details section of this report. The leaching results for each solid are illustrated graphically below with plots of cumulative PCB concentration in the total exposure volume versus leaching time (using Equation 8, and reconstructed as described above to represent the classical experimental leaching curve). The average PCB leach rates calculated from concentration vs. time data and plotted versus overall or absolute leaching time are presented in the **RESULTS AND DISCUSSION** section. For both concentration plots and average leach rate plots, the data are plotted according to level of chlorination (homologue groups), resulting in up to ten plots per shipboard solid, depending upon the target homologues detected over the course of a given experiment. It is entirely possible for a target homologue group to be detected, and target congener within that group to not be detected because it was not practical to analyze for all congeners within the homologue groups. However, because a homologue group is the empirical quantitation of *all* congeners present within that chlorination level, non-target congeners still contribute to the homologue group value, even if target congeners were not detected. In the following figures, only the homologue groups detected during each solid leaching experiment are plotted along with the corresponding target congeners detected in each homologue group. Homologues and target congeners not detected over the course of the leaching experiment are not plotted, but appear as a placeholder in the legend to indicate that it was not detected. It is suggested that the list of target analytes in this study be utilized for reference purposes while viewing the plots. These can be found in Table 4 and Table 5 of the **EXPERIMENTAL DETAILS** section. As noted previously, there are no specific Cl1 homologue group congeners targeted in this study.

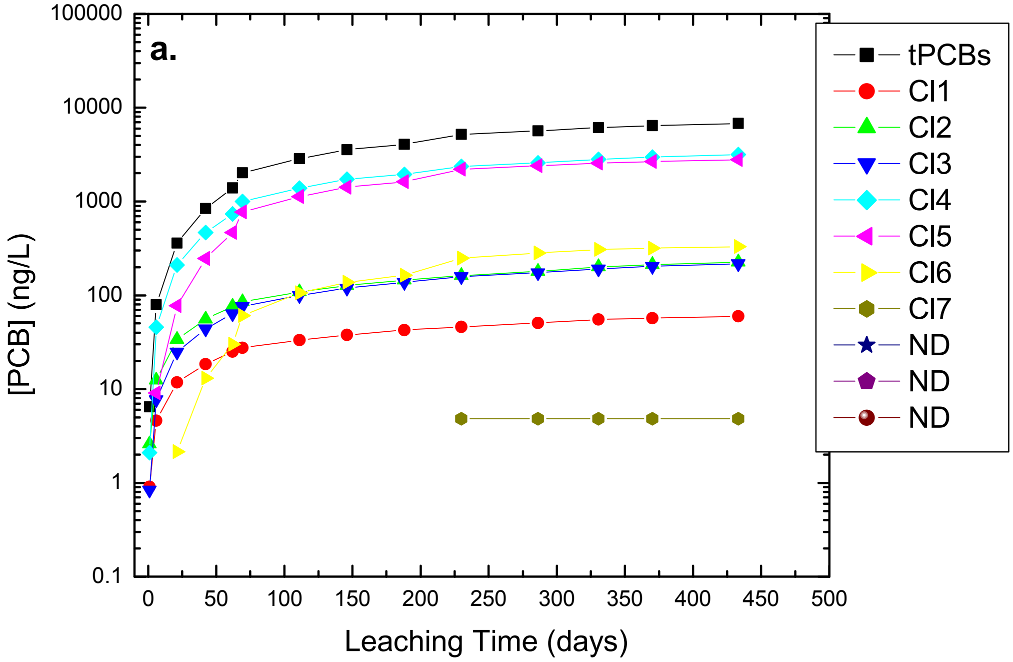
For the concentration vs. time plots below, the slope of a line drawn between any two adjacent points on a curve is equal to the average leach rate (AvgLR) between those points, and corresponds to the calculation in Equation 7. Accumulative concentration curves that continue to increase reflect a leach rate greater than zero and continued leaching with time, whereas truly horizontal portions of curves correspond to a leach rate of zero, indicating a leaching cessation for that particular analyte. In some cases, curves exhibit a mixture of these behaviors, where leaching stops and then begins again, sometimes more than once, as indicated by both increasing and horizontal curve regions (slopes > 0, then = 0, then > 0 again, etc.). Caution is recommended when evaluating plots by visual inspection; what might appear to be a horizontal line in some cases may indeed be a slightly sloped line because the y-axis is plotted as a log scale to facilitate viewing the entire curve. This concern can be evaluated or confirmed by inspecting the corresponding leach rate curve in the Average Leach Rate Calculations section to see if an average leach rate value exists at that concentration point.

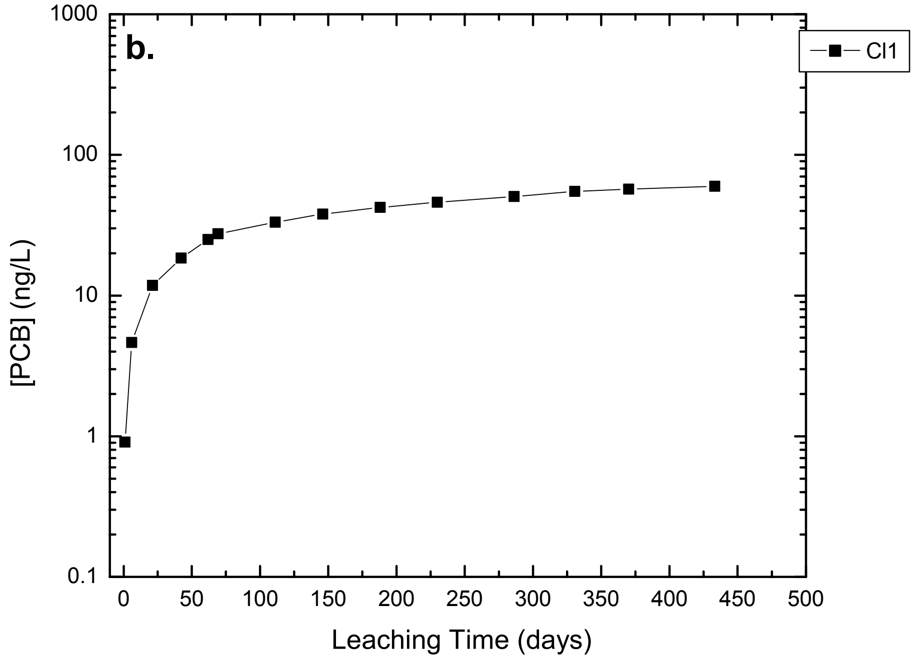
In all cases, the upper limit for any experimental leach rate for a shipboard solid is approximated by a positive analytical control (curve for neat Aroclor dissolution experiment). The lower empirical limit of the leach rate range is bounded by results obtained for a negative control, blank leaching experiments that do not contain PCBs. These negative control (procedural method blank) experiments were performed under conditions identical to shipboard solid leaching conditions, but only with a cage (without a shipboard solid sample matrix). Results from all negative controls analyzed over the course of the leaching experiments are included in the Leaching Procedural Blank Data section of APPENDIX C. The shipboard solids that representative solid analyses indicate contain Aroclor 1254 (A1254), but not Aroclor 1268 (A1268) are the Black Rubber Pipe Hanger Liner (BRPHL), Electrical Cable (EC), and Foam Rubber/Ensolite^{TM} (FRE). These will be described relative to the A1254 positive analytical control curves for maximum comparability. The remaining solids will be described in the context of the A1268 positive analytical control curves as the representative solid analyses of these solids were shown to contain A1268 in some cases also with A1254; these are Bulkhead Insulation (BHI), Felt Gasket-Inner (FGI), Felt Gasket-Outer (FGO), and Aluminized Paint (AP).

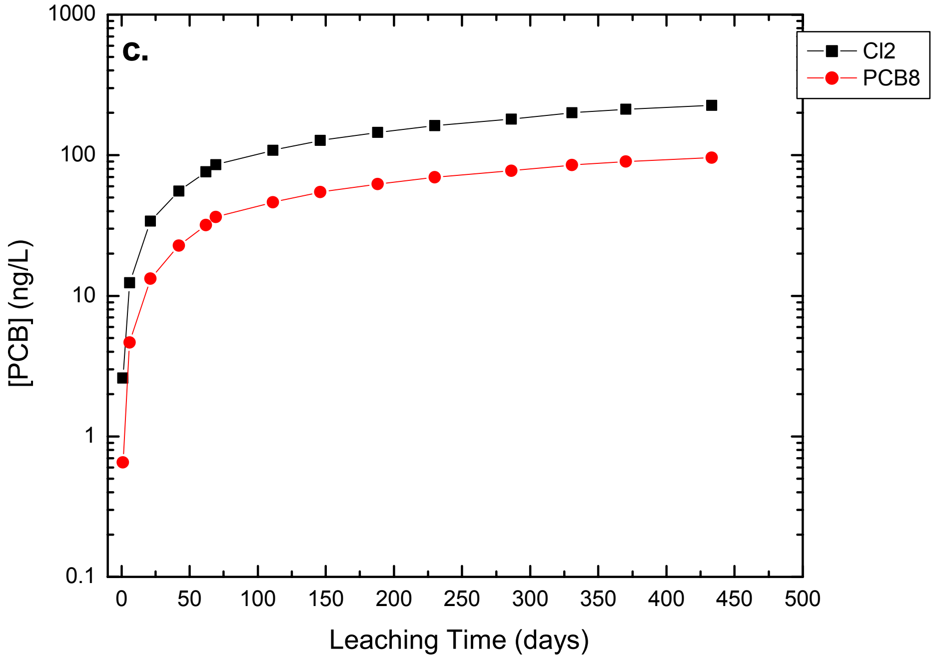
As previously indicated, each congener and homologue group has unique dissolution and leaching characteristics relative to the other congeners or homologues in that solid. Fingerprinting focuses on these individual congeners or homologues that dissolve or leach into a solvent, in this case seawater leachate. In each of the Aroclor dissolution and shipboard solid-specific leaching behavior sections below, fingerprints are calculated and plotted as percent of total, *i.e.* each congener or homologue value is normalized to the total PCBs value detected in that sample. Within each section, homologue and congener fingerprints associated with the solid are compared with the fingerprints associated with the total PCB released into the seawater leachate. In addition to this comparison, the results for four unique leachate samples (resulting in four sets of homologue and corresponding congener fingerprints) are presented across each entire leaching experiment, *i.e.* series of micro-leaching experiments for a solid as described above for the total exposure time. The first leachate PCB fingerprint presented for each tested material corresponds to the maximum observed rate and the final fingerprint corresponds to the final empirical rate (at the end of the entire experiment). Between these two endpoints, two intermediate fingerprints are shown to illustrate obvious changes in the observed fingerprint, related to analyte-specific changes in material-specific leaching behaviors. These were generally chosen to include the broadest or narrowest fingerprint distribution and the most distinct change in fingerprint distribution and/or relative magnitude observed over the course of the experiment.

Aroclor 1254 (A1254) Analytical Control Dissolution Behavior

Concentration behaviors are plotted below for pure A1254 leached at 25^{o}C and ~1 bar as a function of seawater leaching time (exposure time). Homologue groups Cl1-Cl7 were leached from A1254, and Figure 12(a) include these homologue concentration curves (lower curves). Each point on the tPCB concentration curve (upper curve) is calculated as the sum of the homologue concentrations below it. Each homologue group is plotted as the upper curve in subsequent plots Figure 12(b-h). Curves for the target congeners detected in each homologue group are plotted with each corresponding homologue curve. As the tPCB curve shows, the long-term empirical upper limit approaches 10 ppb (10,000 ng/L) over the nearly 450 day experiment, for 21.1 mg of A1254 in a 13.89 L total leachate exposure volume.




b.
Cl1
1000
100
10
1
0.1
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


c.
Cl2
PCB8
1000
100
10
1
0.1
[PCB] (ng/L)
0
50
100
150
200
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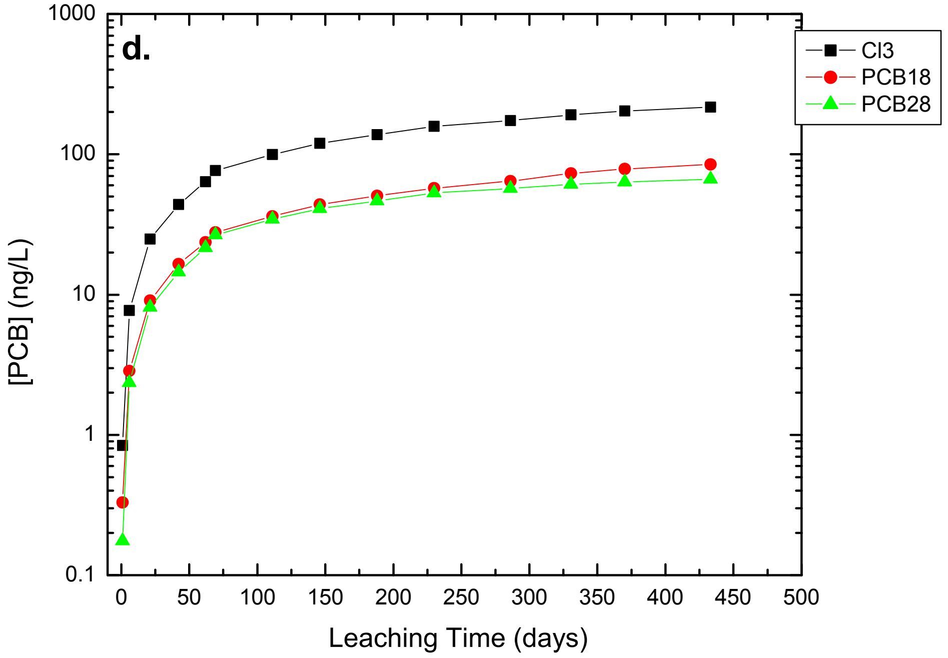
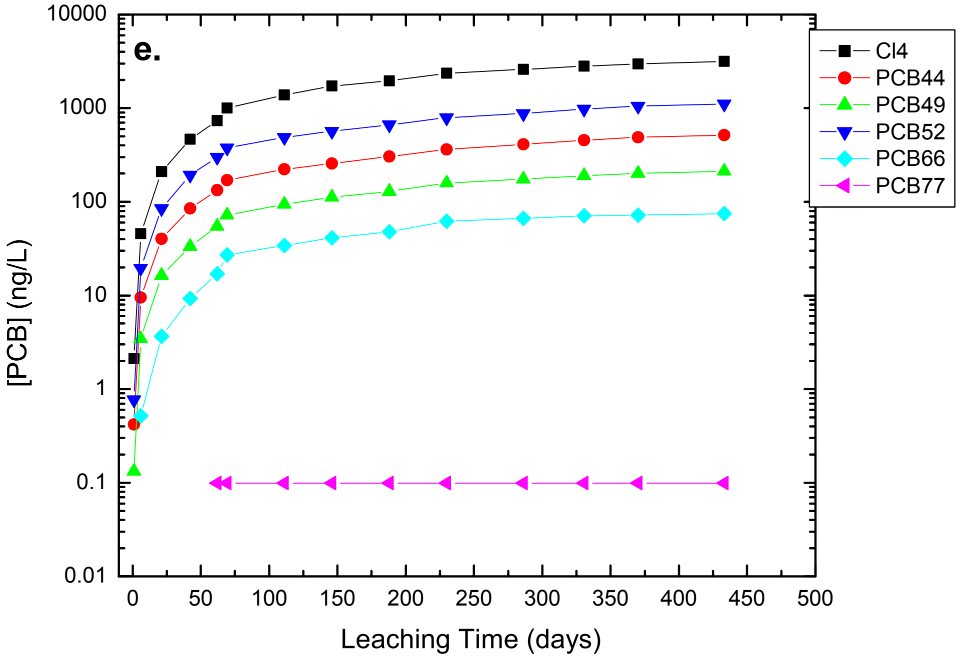
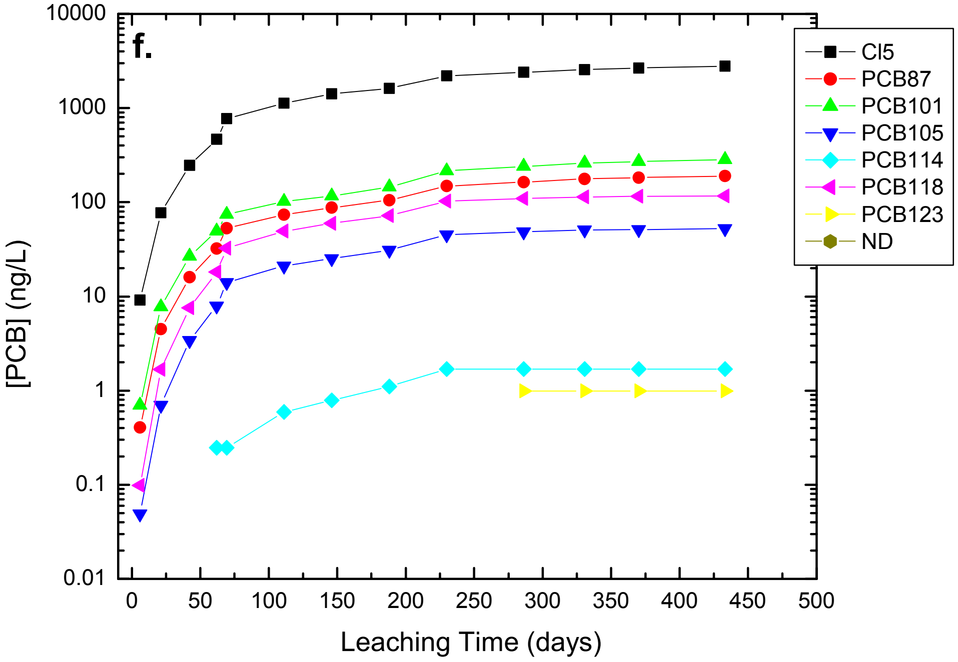
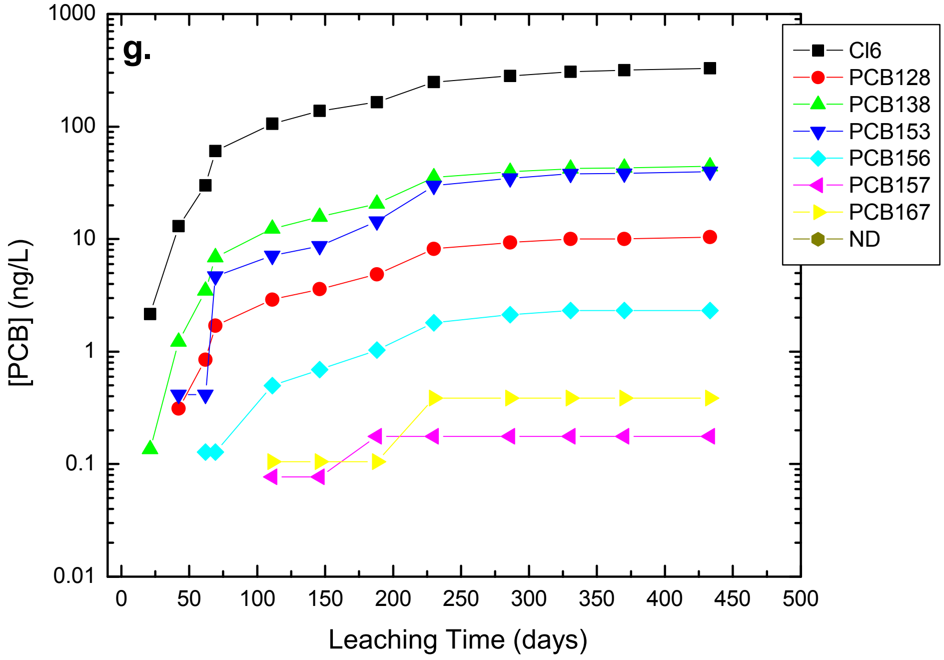
300
350
400
450
500
Leaching Time (days)


d.
1000
100
10
1
0.1
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl3
PCB18
PCB28


e.
10000
1000
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77


f.
10000
1000
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
PCB114
PCB118
PCB123
ND


g.
1000
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl6
PCB128
PCB138
PCB153
PCB156
PCB157
PCB167
ND

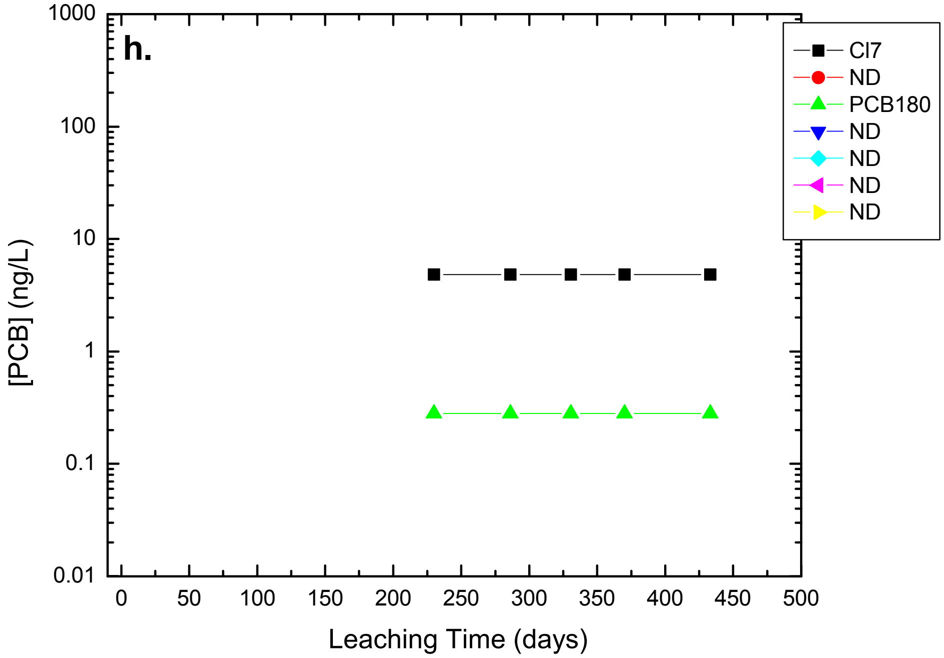


Figure 12 (a-h). Experimental PCB concentration vs. exposure time for 21.1 mg of pure Aroclor 1254 exposed to a total volume of 13.13 L of seawater leachate. Plot a) shows tPCBs concentration and contributing homologue group concentrations vs. exposure time, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-h) are homologue group concentrations and corresponding target congener concentrations within homologue groups Cl1-Cl7 vs. time.

Figure 13 shows the total released homologue and congener distributions or fingerprints, and compares these released PCB signatures to the initial PCB signatures determined for pure A1254. All detected homologues and congeners are normalized and plotted as percent of total PCBs in each matrix, (seawater vs. "solid"), even though in many instances the percent contribution to total PCB level was < 0.1% of the total amount of PCBs present. These levels of homologues and congeners in "solids" can be significant if they release into seawater, as reflected in many of the seawater PCB signatures. The most significant levels of release were from homologue groups Cl1-Cl6 as shown below.

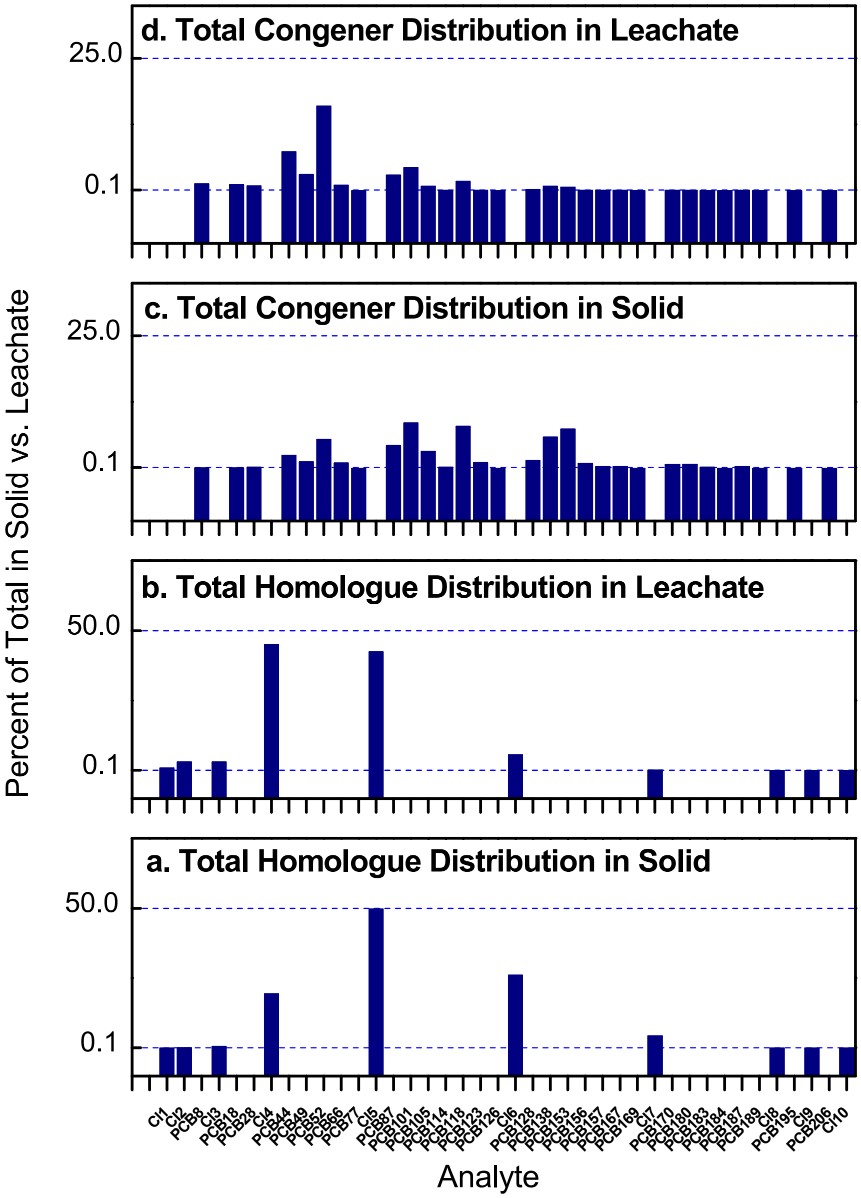


Figure 13 (a-d). Experimental homologue and congener PCB signatures for pure Aroclor 1254 "solid" (a & c) compared with total homologue and congener distributions of PCBs released from A1254 into seawater (b & d). The latter distributions correspond to all PCBs released, also represented by the cumulative concentration endpoint for all analytes plotted in **Figure 12**. The solid distributions correspond to the pre-dissolution PCB content in the pure solid A1254, derived from the mass balance performed at the conclusion of the experiment. Analytes present below 0.1% are indicated using an offset linear scale. Variances at these very low sub-percentage levels are not visible on the scale shown here, but are included in the mass balance tables in APPENDIX C.

PCB fingerprints, normalized as percent of total, for specific A1254 seawater samples are presented below at key intervals across the entire experiment (exposure time). Figure 14homologue group fingerprints correspond to a) the maximum dissolution rate, b) the broadest congener and homologue distributions, c) a decrease in pentachlorobiphenyl with a concurrent increase in tetrachlorobiphenyl homologue groups (primary homologue group inversion), and d) the final empirical dissolution rate. The respective target congener fingerprints in these samples are depicted in Figure 15(a-d).

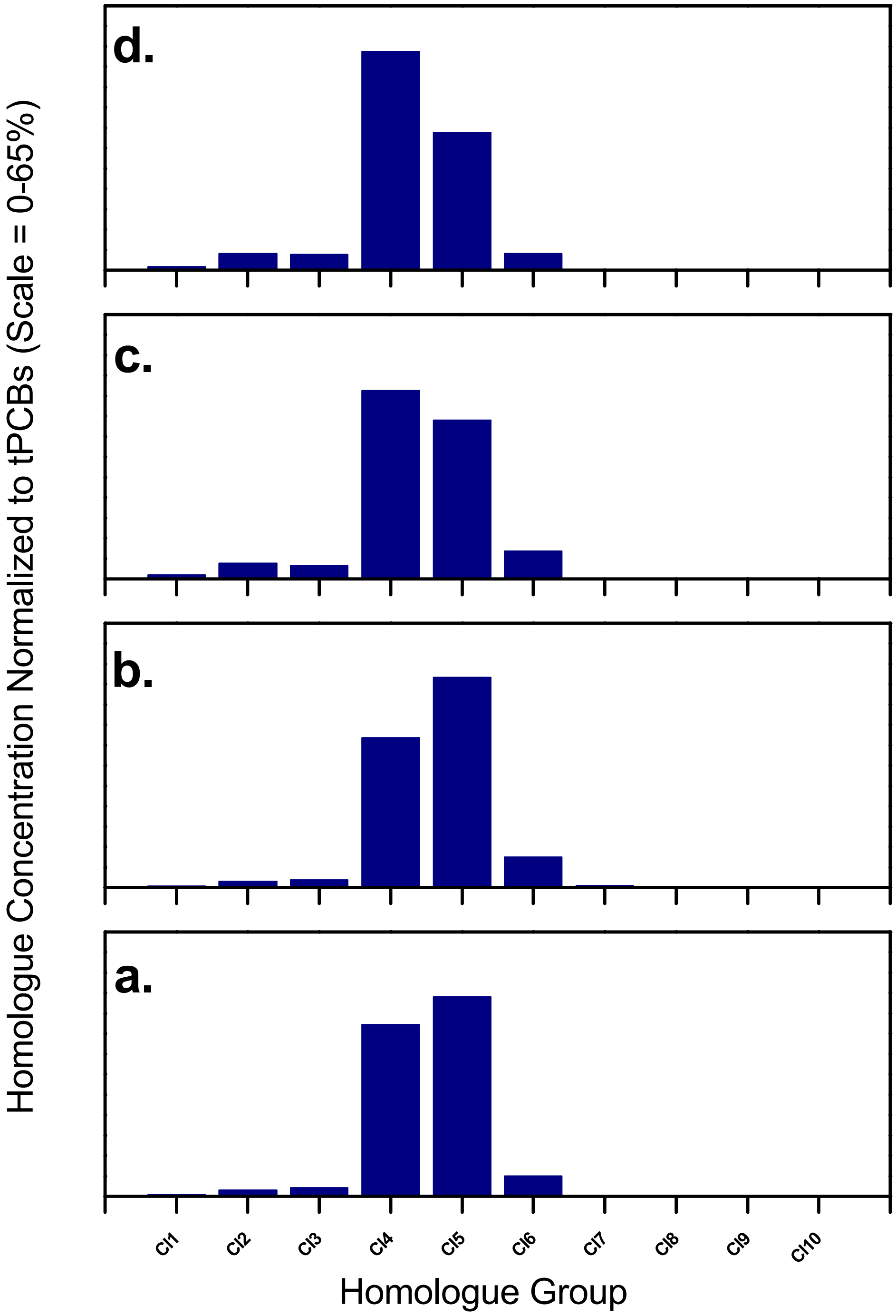


Figure 14 (a-d). Homologue fingerprints during the pure Aroclor 1254 experiment, normalized as percent of total, corresponding to intervals a) 62 to 69 days, b) 188 to 230 days, c) 230 to 286 days, d) 370 to 433 days.

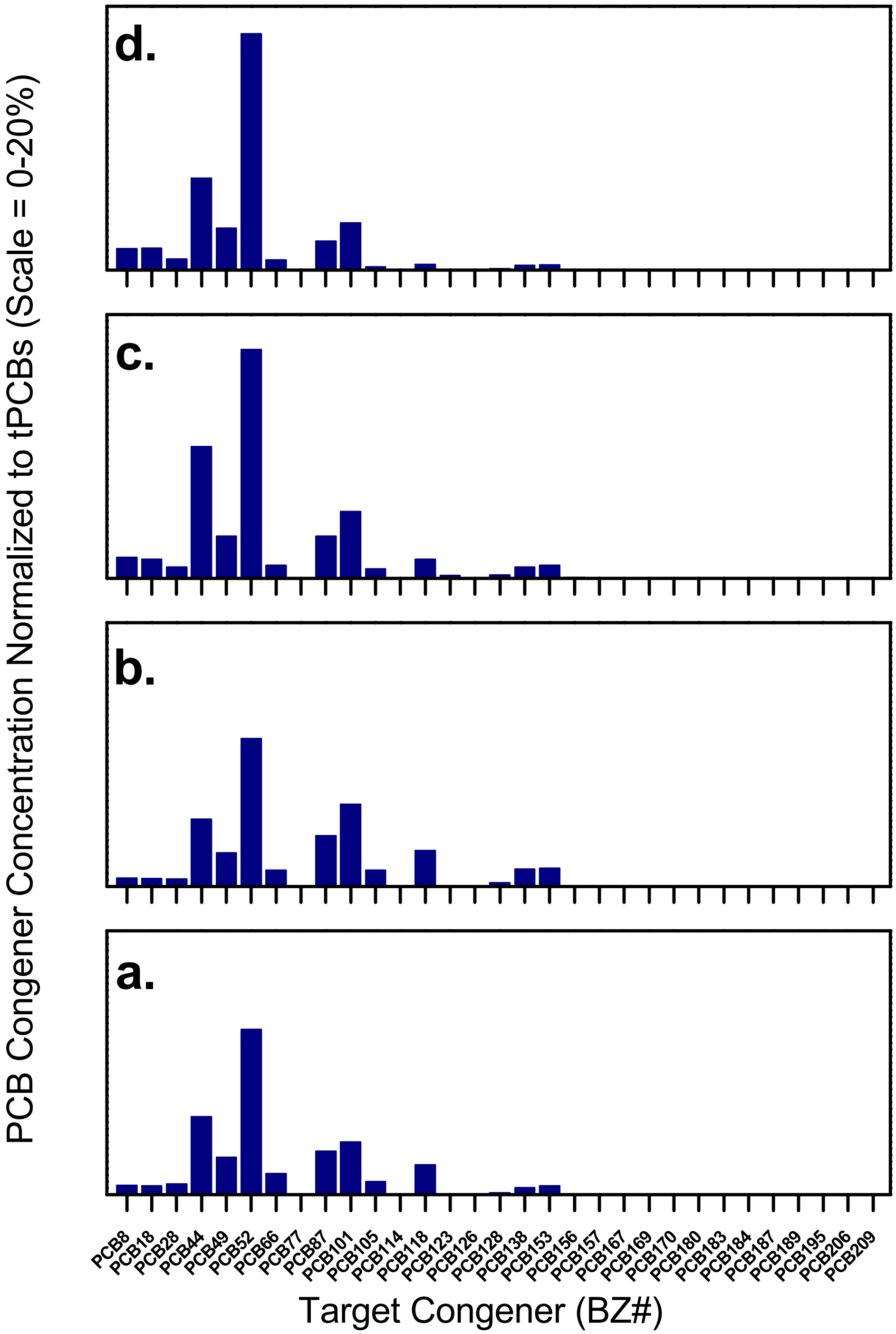


Figure 15 (a-d). Congener fingerprints during the pure Aroclor 1254 experiment, normalized as percent of total, corresponding to different intervals a) 62 to 69 days, b) 188 to 230 days, c) 230 to 286 days, d) 370 to 433 days.

In an effort to establish an effective saturation limit as an upper bound for A1254 PCB analytes leaching from shipboard solids that contain A1254, the most concentrated leachate sample in the experimental series for Aroclor 1254 was evaluated (analytical concentration data are included in APPENDIX C.) This leachate sample (212-147-AS-T36) occurred for the leaching interval from 188 -

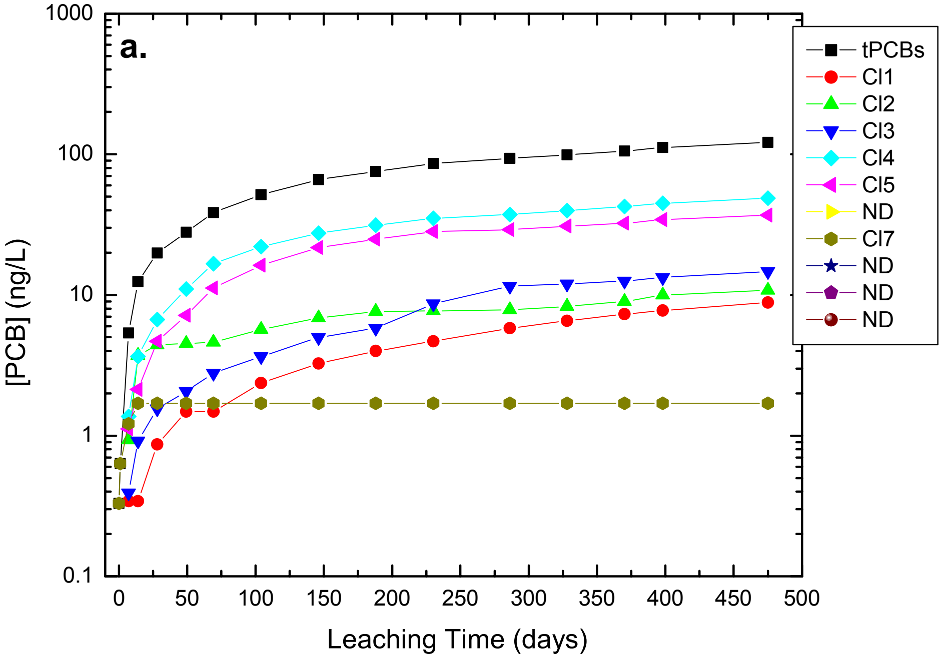
230 days (significantly less than the longest time-interval in the experiment), with a tPCB concentration of 16051 pptr (ng/L), and contributions from homologue groups Cl1-Cl7. However, upon closer inspection, only the Cl4-Cl7 homologue concentrations in this sample (5900, 8300, 1200, and 69 pptr respectively) corresponded to maximum homologue concentrations observed in all A1254 leachate samples collected. As one would expect based solely on solubility considerations, lower molecular weight species were released at higher levels earlier in the leaching process; homologues Cl2 and Cl3 exhibited concentration maxima (330 pptr each) much earlier in the leaching experiment at 111 days, whereas the Cl1 maximum concentration occurred at 21 days (100 pptr). Homologue groups Cl8-Cl10 were never detected in any leachate samples across the entire leaching experiment and cannot contribute to the solubility estimate. The effective A1254 saturation limit is estimated as the sum of all observed maximum homologue group concentrations (16200 pptr) and assumes that the solubility of any given homologue group is not significantly perturbed (suppressed) by the presence of other dissolved homologue groups at their maximum observed concentrations. It must be recognized that the actual solubility for such a complex mixture is likely time-dependent, but should still lie above the highest concentration observed here experimentally (16051 pptr = 0.016051 ppm). In comparison, solubilities reported in the literature and compiled by Mackay, *et al*[51] for A1254 in freshwater is in the range 0.01 - 0.3 mg/L (ppm), providing a reasonable assurance that we are below saturation across the A1254 leaching experiment, except perhaps in this particular sample. However, on a homologue basis, if one takes homologue solubilities also reported in Mackay, *et al*[51]and applies these to the homologue quantities observed in the neat A1254 control in this study, the estimated solubility range is 0.0032 - 0.0182 mg/L (ppm), much lower relative to the literature reported empirical A1254 range above, by a factor of 3 - 16.

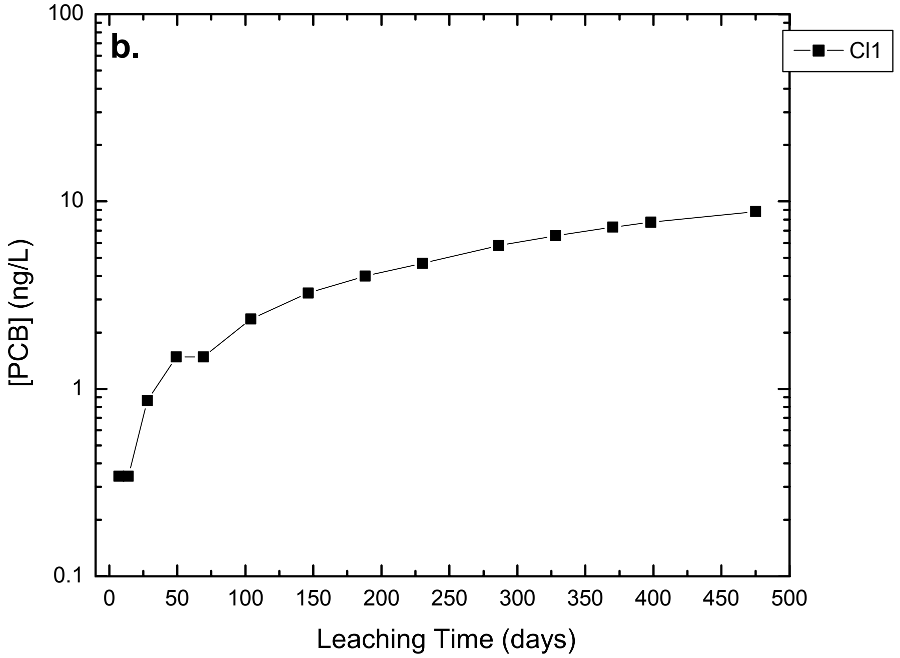
The concentration maxima of target congeners, if detected within each of these homologue groups, were observed to occur in the same leachate samples as their corresponding homologue group maxima, with the following exceptions: Cl2/PCB8 140 pptr (at 42 & 111 days), Cl4/PCB77 1.4 pptr (at 62 days, only detection), and Cl5/PCB123 (at 286 days, only detection). These exceptions indicate that solubility of individual congeners in seawater leachate may not be the only factor contributing to the dissolution, i.e. it is likely that the presence of insoluble PCBs in the Aroclor matrix are retarding the fundamental congener solvation. It should also be noted that in some cases, it is possible that the occurrence of different maxima in different (sequential) leachate samples over time is related to uncertainty in the analytical data rather than other factors contributing to the leaching mechanism, particularly for concentrations that are very similar to the apparent maximum. For example, the concentrations for PCB8 for day-17, day-43, day-62, day-69, day-111, day-146, day-188 are 120 ng/l, 140 ng/l, 130 ng/l, 63 ng/l, 140 ng/l, 120 ng/l, 110 ng/l ng/l respectively (Appendix C). All of these concentrations, with the possible exception of the 63 ng/L value, are within expected analytical precision of each other. (The Relative Standard Deviation (RSD) for the six similar values is 10% whereas the RSD for the first six corresponding PCB8 blank spike sample results and PCB 8 blank spike duplicate sample results is 13% and 15% respectively. Similar concentrations are also observed for the Cl2 group in all six of these samples and the RSD is 25%, for which the concentration could have contributions from as many as 12 congeners.) Clearly the variability in PCB8 leachate sample results for these six leaching time periods is comparable to that from analysis of standard materials, and if one assumes that all of the contributing dichloro- congeners in the Cl2 homologue group behave similarly, then a Cl2 group analysis of standard materials would yield results similar to that observed for PCB8 in the BS and BSD samples. What this means is, in some cases, simply for analytical reasons, it may not be possible to determine for all analytes what the exact maximum concentration is from these empirical studies, but we can determine the range.

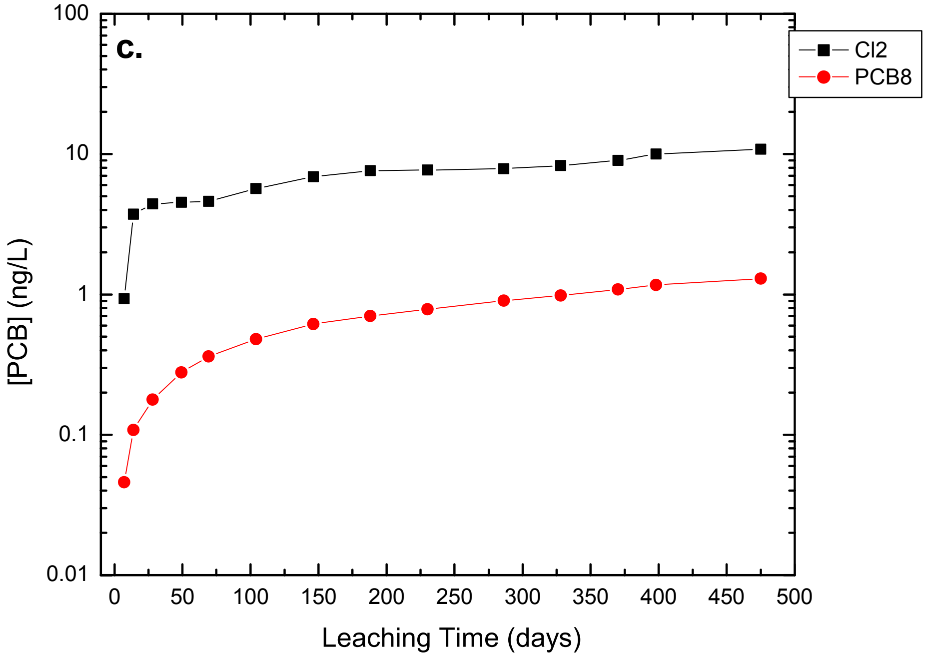
Finally, if one considers that the maximum concentration observed was 16051 pptr (meaning all other A1254 leachate concentrations lie below this value), the effective A1254 saturation limit was estimated at 16200 pptr, and the concentration in the total experimental leaching volume was 6797 pptr (as indicated by the final concentration value in Figure 12a and in the cumulative concentration table in APPENDIX D, Aroclor 1254 (A1254) Results), then the observed dissolution behavior must indeed be limited by the pure Aroclor 1254 solid matrix itself. If this Aroclor solid could have released more PCBs, then it would have been reflected in an increased cumulative leachate concentration, at least up to the value experimentally shown to be possible in a leaching sample, i.e. 16051 pptr, and likely up to the estimated saturation limit of 16200 pptr. These combined observations demonstrate that this leaching experiment defines an upper limit for Aroclor1254 PCB release from the most closely related solid matrix possible: itself, in the form of a mixture of solid PCBs.

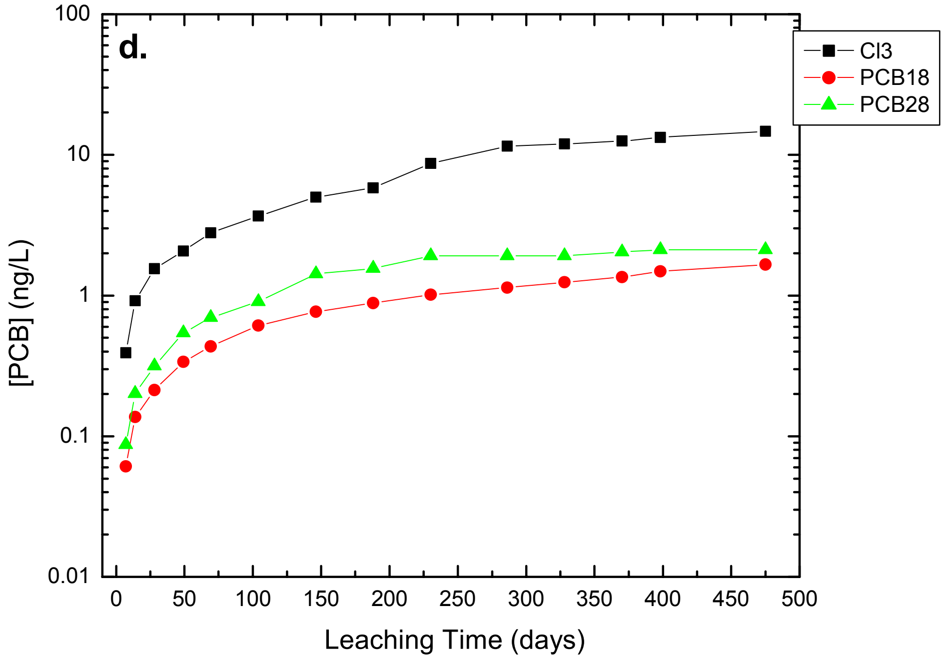
Black Rubber Pipe Hanger Liner (BRPHL) Leaching Behavior

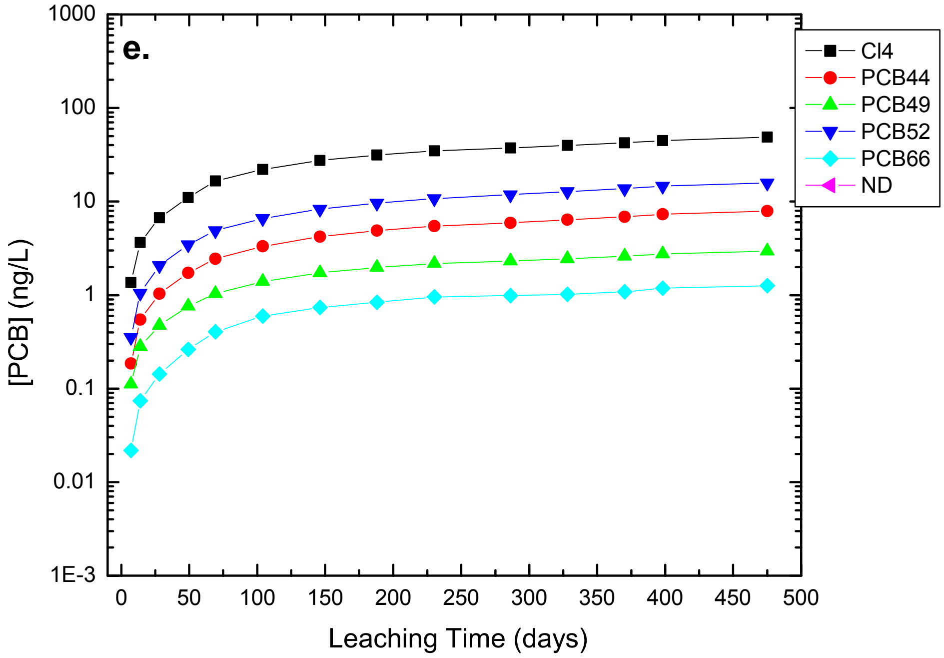
Leaching concentration behaviors for BRPHL leached at 25°C and ~1 bar, are plotted below for tPCBs and homologue groups Cl1-Cl5, and Cl7 (Figure 16(a). Plots for homologue groups and target congeners within each homologue group are shown in Figure 16(b-g). The BRPHL subsample (2.911 g) containing 4.7 mg (0.16 wt%) tPCB was exposed over a leaching time of nearly 500 days to a total leachate volume of 14.82 L.




b.
Cl1
100
10
1
0.1
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


c.
Cl2
PCB8
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


d.
Cl3
PCB18
PCB28
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


e.
Cl4
PCB44
PCB49
PCB52
PCB66
ND
1000
100
10
1
0.1
0.01
1E-3
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)

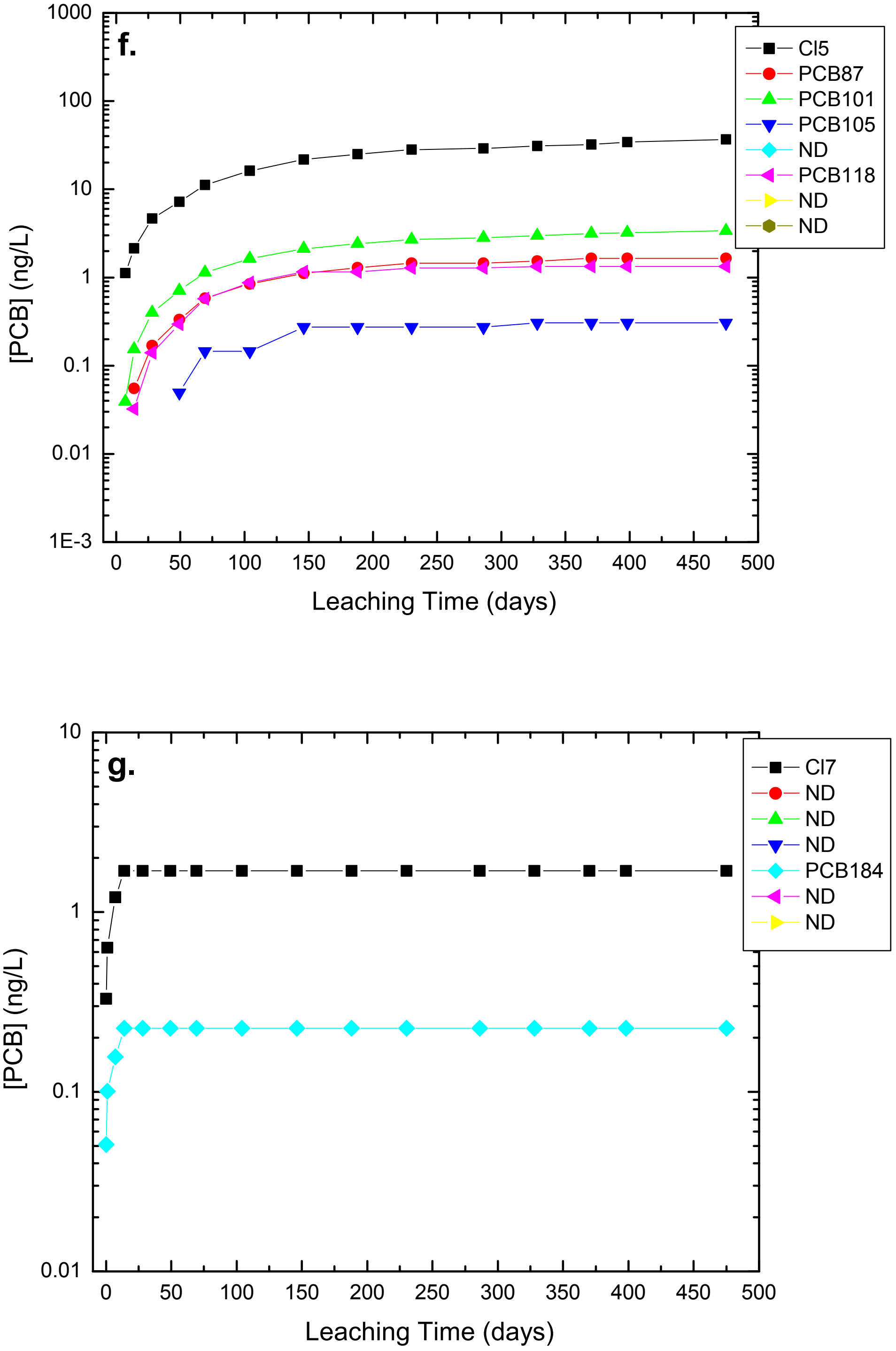


Figure 16 (a-g). Experimental PCB concentration vs. leaching time for BRPHL containing 0.16 wt% (4.7 mg) tPCBs exposed to a total volume of 14.82 L of seawater leachate. Plot a) shows tPCBs concentration and contributing homologue group concentration vs. leaching time, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-g) are homologue group concentrations and corresponding target congener concentrations within homologue groups Cl1-Cl5, and Cl7 vs. leaching time.

Total released homologue and congener distributions or fingerprints are shown in Figure 17, compared with the initial PCB signatures determined for BRPHL solid. All homologues and congeners detected are normalized and plotted as percent of measured tPCBs in each matrix (leachate vs. solid). In many instances the percent contribution of an analyte to tPCBs was < 0.1%, which can still be significant if it leaches into seawater, as shown in the leachate PCB signatures. The most significant levels of release from BRPHL were from homologue groups Cl1-Cl5 and Cl7.

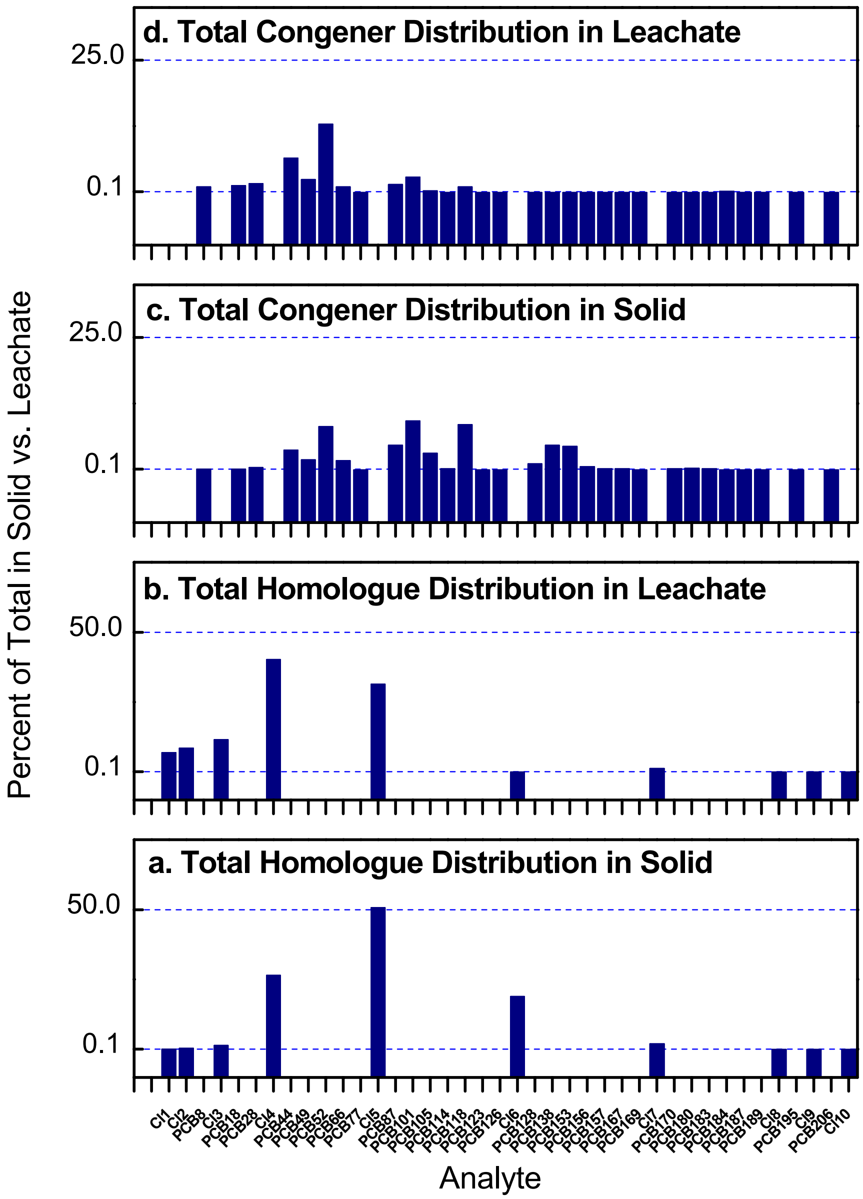


Figure 17(a-d). Experimental homologue and congener PCB signatures for BRPHL solid (a & c) compared with total homologue and congener distributions of PCBs leached from BRPHL into seawater (b & d). The leachate distributions are derived from all PCBs released, also depicted as the cumulative leachate concentration endpoint for detected analytes in **Figure 16** The solid distributions correspond to the pre-leaching PCB content in BRPHL solid, derived from the mass balance performed for the leaching experiment. Analytes at levels below 0.1% are plotted using an offset linear scale to indicate their presence. Variances at these very low sub-percentage levels are not visible on the scale shown here, but are in the mass balance tables in APPENDIX C.

Fingerprints for specific BRPHL leachate samples are plotted below at key intervals across the entire leaching experiment (exposure time). Figure 18corresponds to the homologue groups in samples at a) the maximum leach rate, b) the narrowest homologue distribution, c) a "typical" homologue distribution, and d) the final empirical leach rate. The respective target congener fingerprints in these samples are shown in Figure 19(a-d).

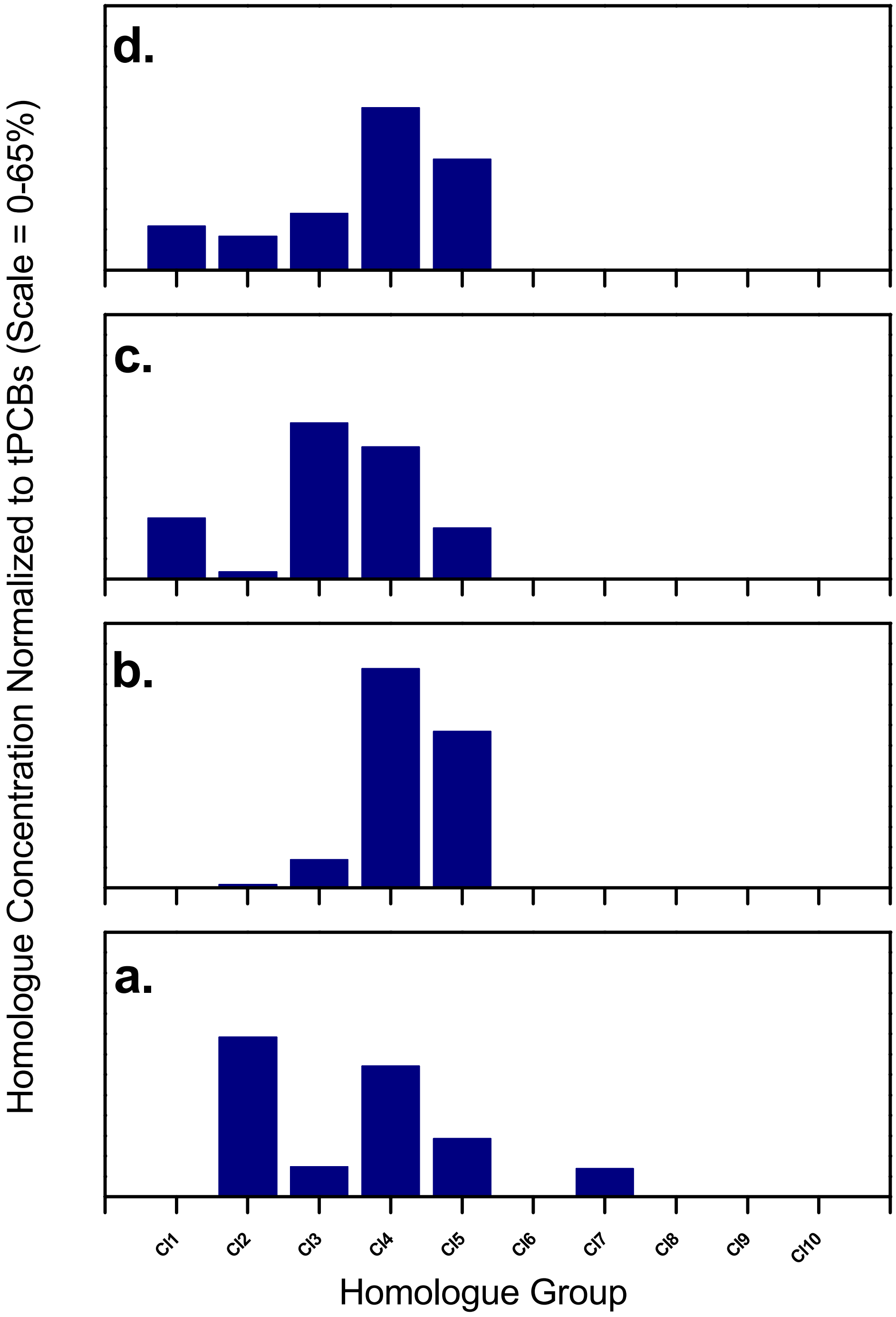


Figure 18 (a-d). Homologue fingerprints during the BRPHL leaching experiment, normalized as percent of total, corresponding to leaching intervals a) 7 to 14 days, b) 49 to 69 days, c) 230 to 286 days, d) 398 to 475 days.

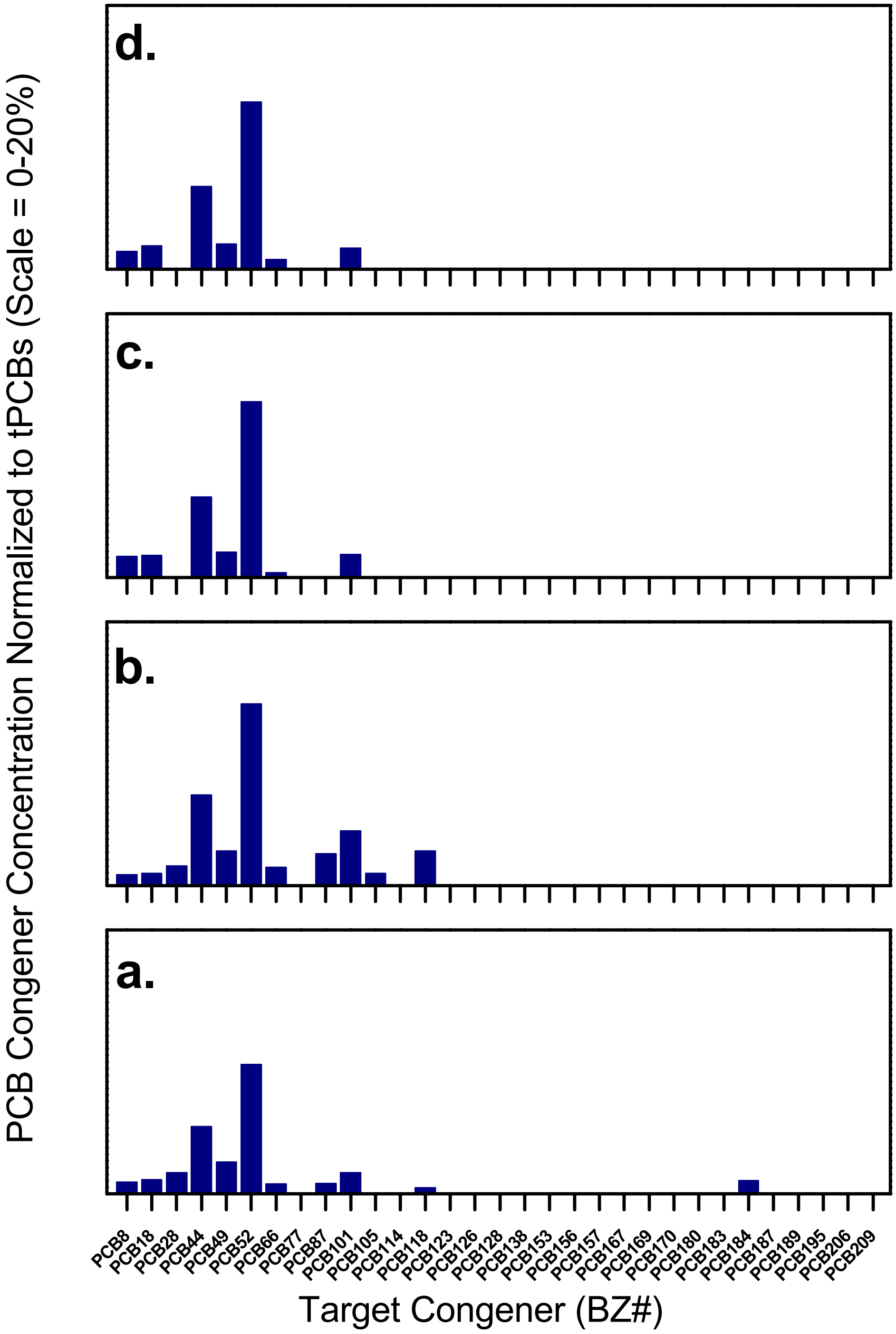
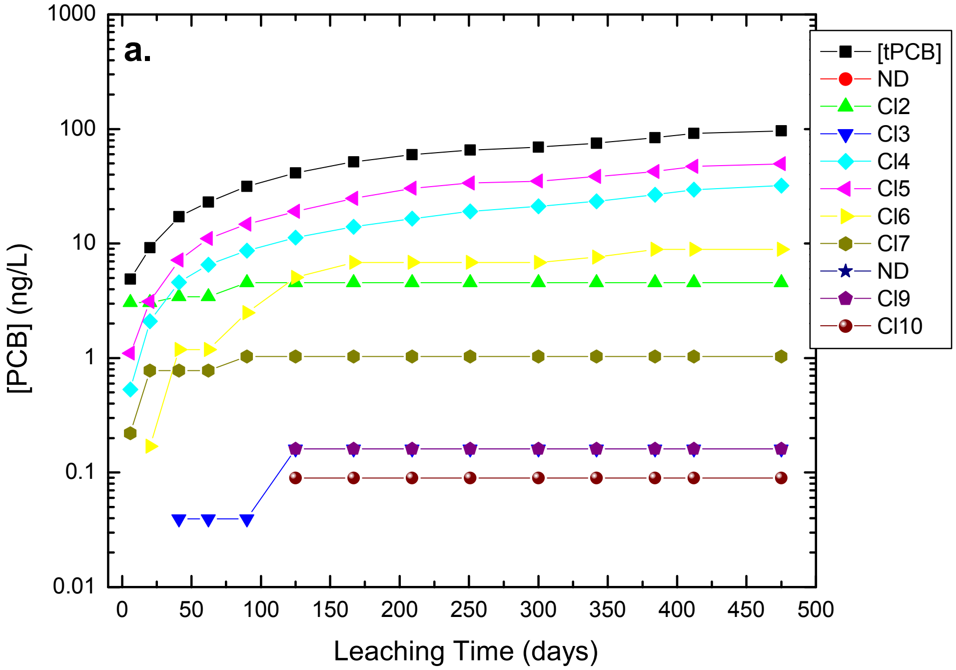
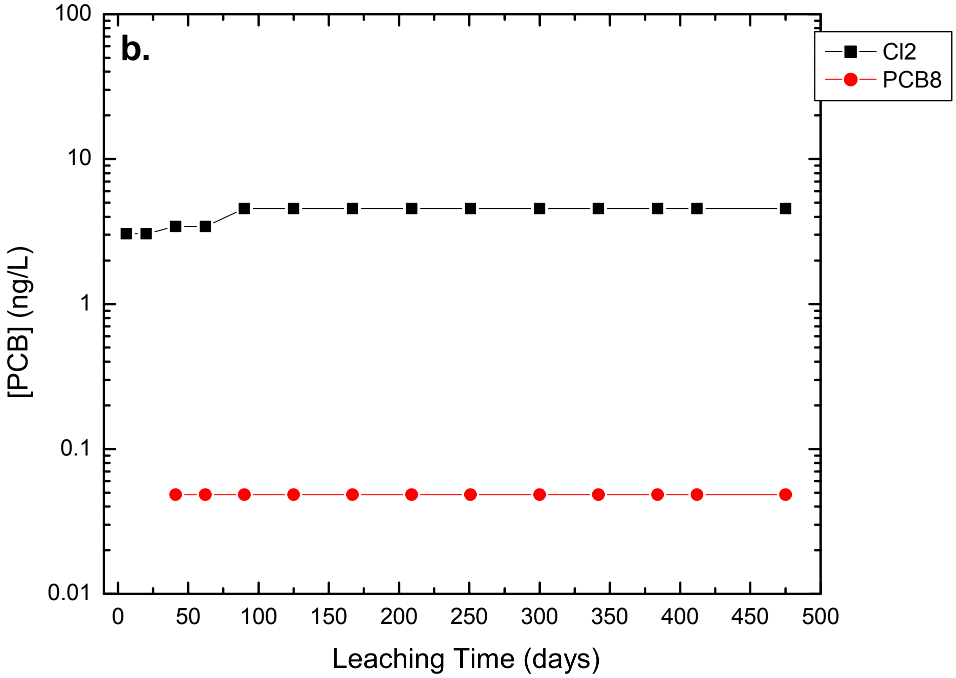


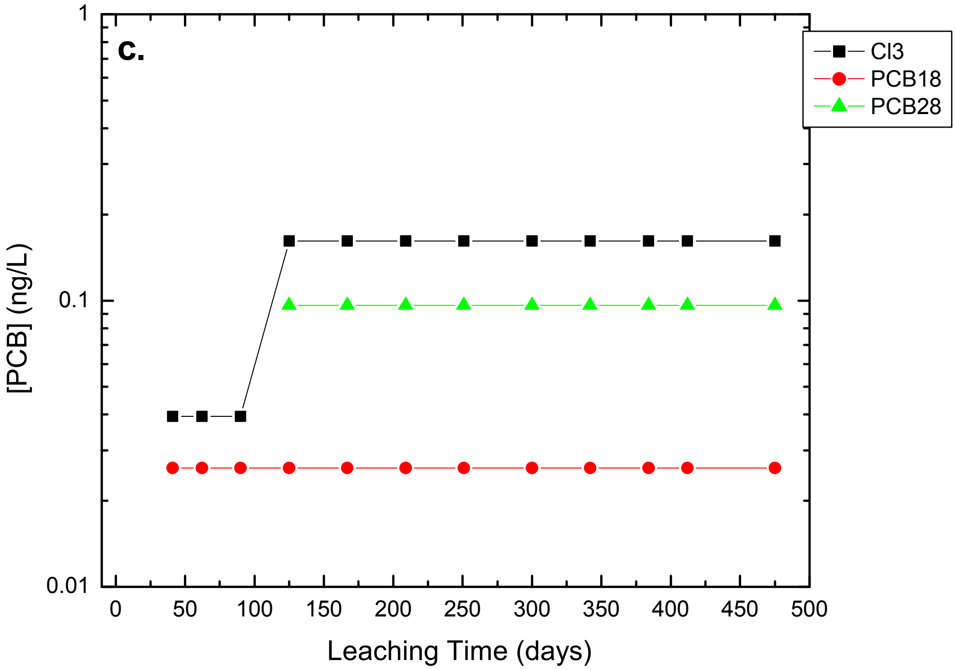
Figure 19 (a-d). Congener fingerprints during the BRPHL leaching experiment, normalized as percent of total, corresponding to leaching intervals a) 7 to 14 days, b) 49 to 69 days, c) 230 to 286 days, d) 398 to 475 days.

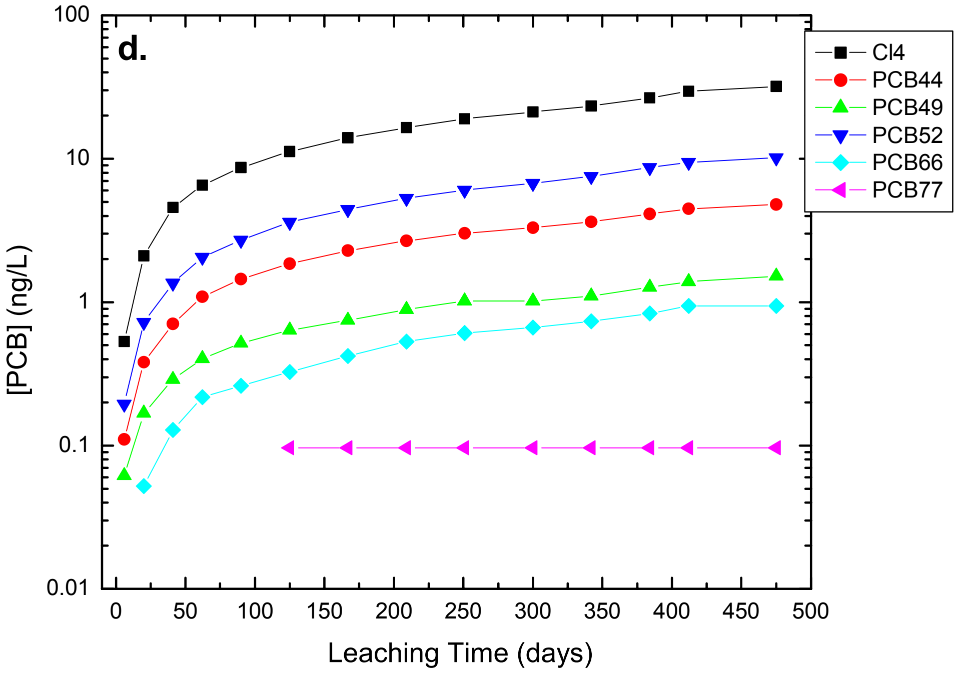
Electrical Cable (EC) Leaching Behavior

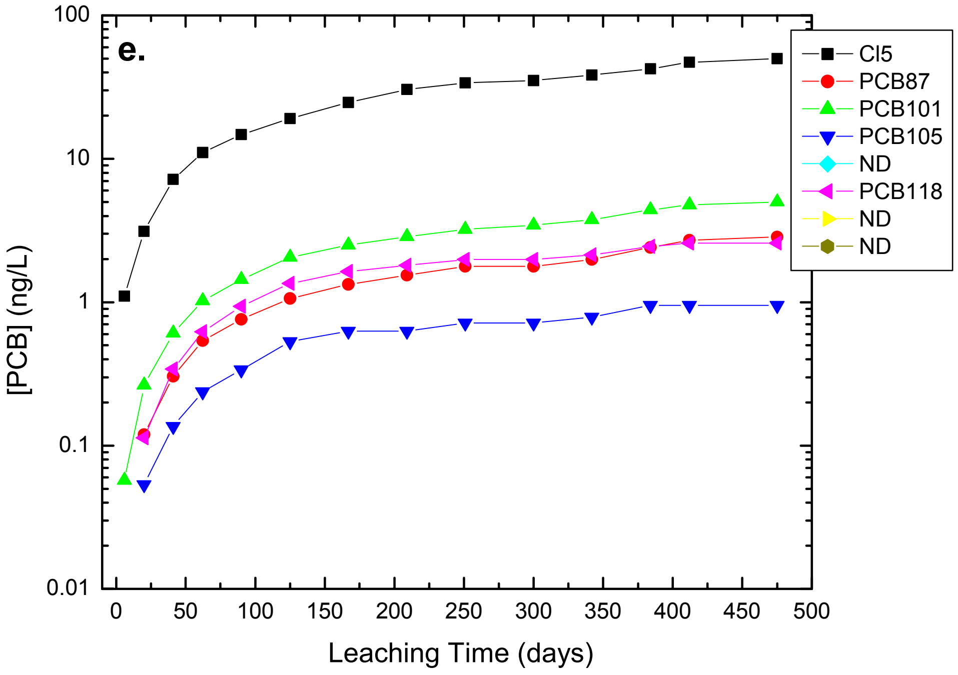
Leaching concentration behaviors for EC leached at 25°C and ~1 bar includes contributions from homologues Cl2-Cl7, Cl9, and Cl10 as shown in Figure 20(a). Each of these homologue groups and contributions from target congeners are plotted in Figure 20(b-i). The total exposure volume of seawater leachate was 14.49 L for EC (26.5474 g) containing 32.1 mg tPCBs (0.12 wt%). Note also that there is significant leaching suppression (horizontal line behavior), even though most homologue groups were detected over the nearly 500 day leaching experiment.

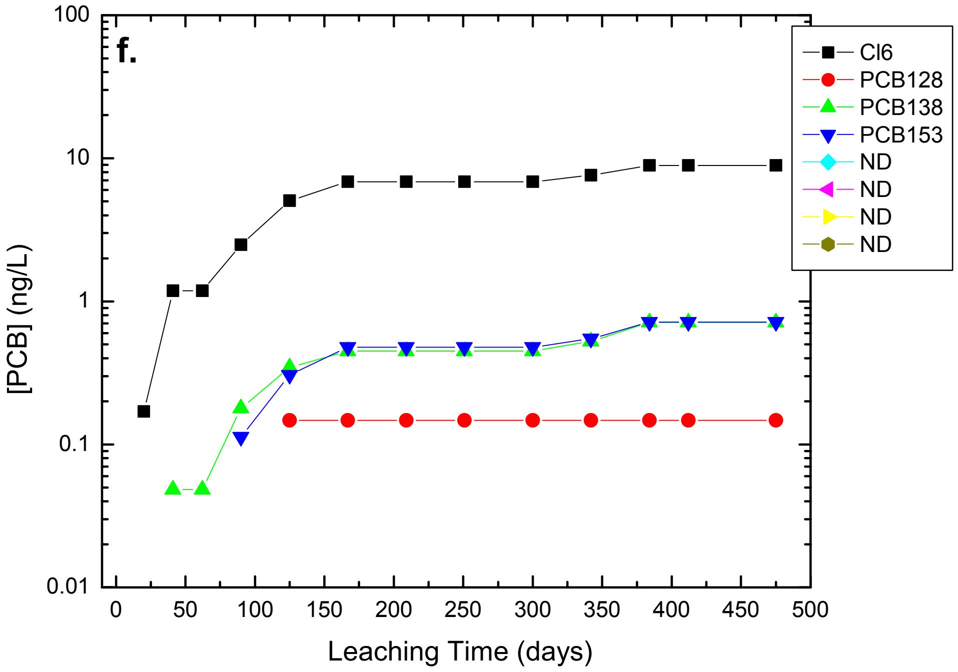


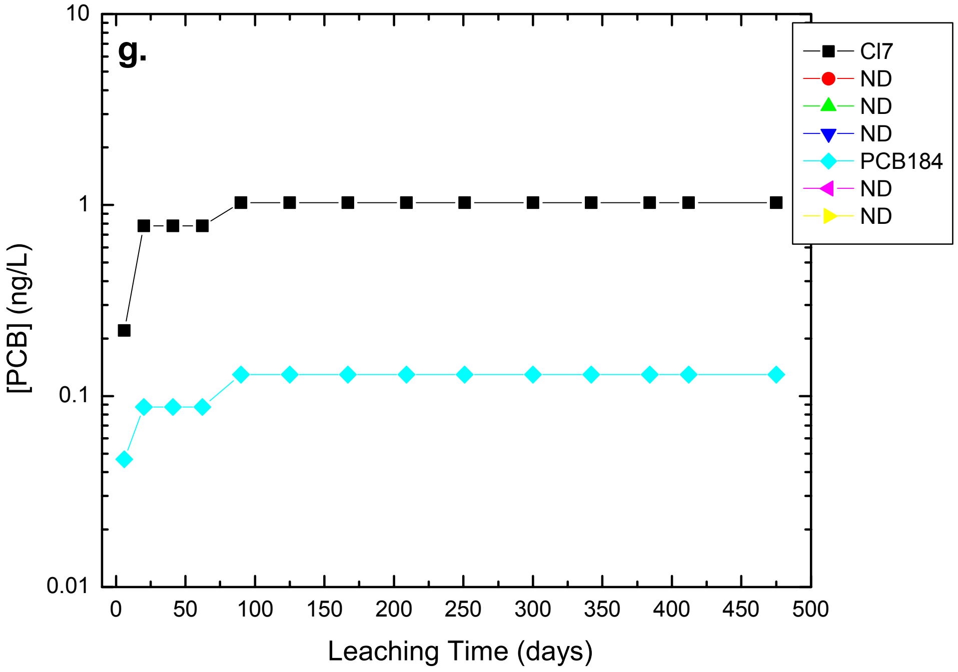

b.
Cl2
PCB8
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


c.
Cl3
PCB18
PCB28
[PCB] (ng/L)
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


d.
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77


e.
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
ND
PCB118
ND
ND


f.
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl6
PCB128
PCB138
PCB153
ND
ND
ND
ND


g.
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl7
ND
ND
ND
PCB184
ND
ND

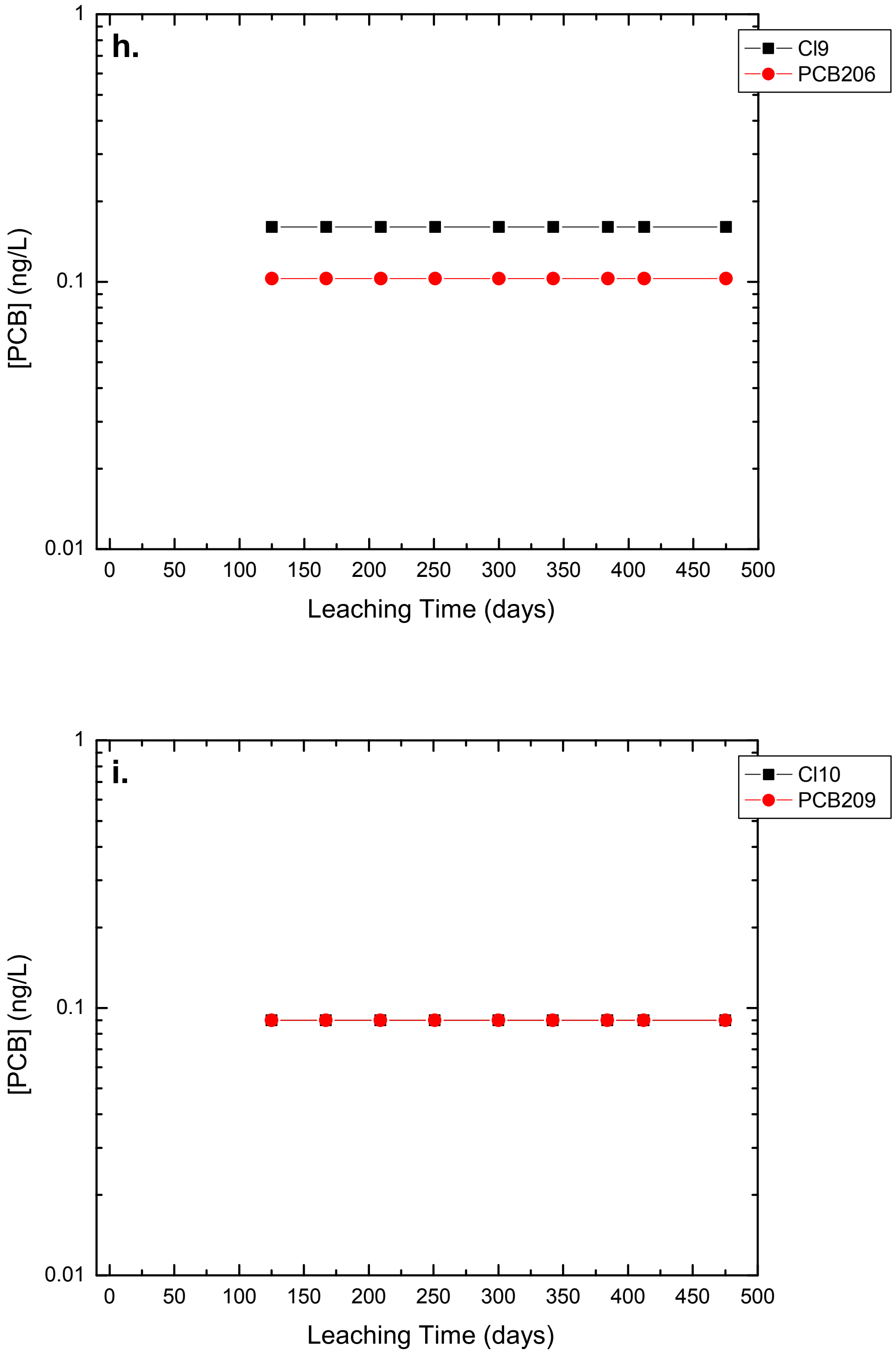


Figure 20 (a-i). Experimental PCB concentration vs. leaching time for EC containing 0.21 wt% (32.1 mg) tPCBs exposed to a total volume of 14.49 L of seawater leachate. Plot a) shows the tPCBs concentration and contributing homologue group concentrations vs. leaching time for EC, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-i) are homologue group concentrations and corresponding target congener concentrations within homologue groups Cl2-Cl7, Cl9 and Cl10 vs. leaching time.

Total released homologue and congener distributions or fingerprints are compared with the initial PCB signatures determined for EC solid in Figure 21. All detected homologues and congeners are normalized and plotted as percent of measured tPCBs in each matrix (leachate vs. solid). In many instances the percent contribution of tPCBs was < 0.1%, which can still be significant if they leach into seawater, as shown in the leachate PCB signatures. The most significant levels of release from EC solid were from homologue groups Cl2, and Cl4-Cl7.

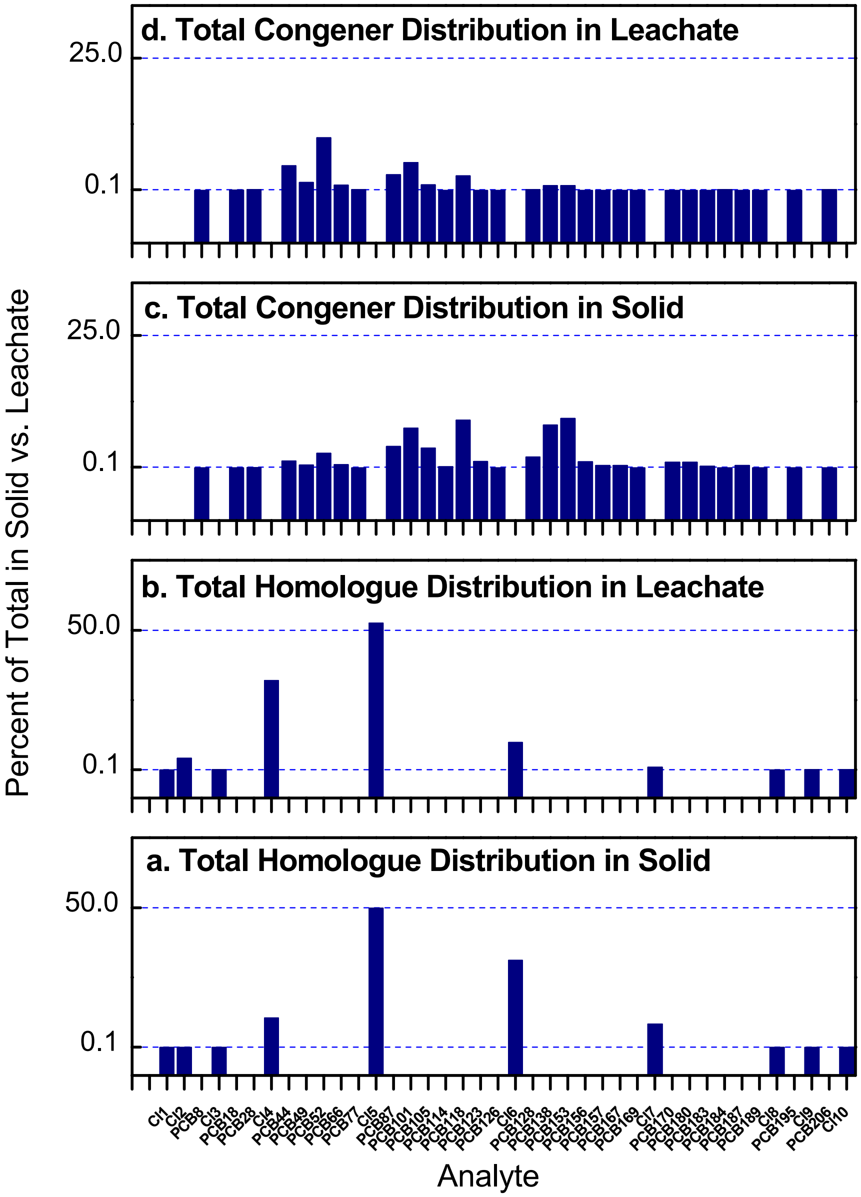


Figure 21 (a-d). Experimental homologue and congener PCB signatures for EC solid (a & c) compared with total homologue and congener distributions of PCBs leached from EC into seawater (b & d). Leachate distributions are derived from all PCBs released, which also corresponds to the cumulative leachate concentration endpoint for analytes plotted in **Figure 20**. Solid distributions correspond to the initial PCB content in EC solid, from the leaching experiment mass balance performed at the end of the leaching experiment. An offset linear scale is used to indicate analyte levels present below 0.1%. Though not visible on the scale shown here, the degree of variance at these very low sub-percentage levels can be seen in the mass balance tables in APPENDIX C.

Normalized fingerprints for specific EC leachate samples are presented below at key intervals across the entire leaching experiment (exposure time). Figure 22shows the homologue group fingerprints corresponding to a) the initially observed and also maximum observed leach rate, b) the final appearance of dichlorobiphenyl and heptachlorobiphenyl groups, c) the broadest homologue and congener distributions observed, and d) the final empirical leach rate. The respective target congener fingerprints are shown in Figure 23(a-d).

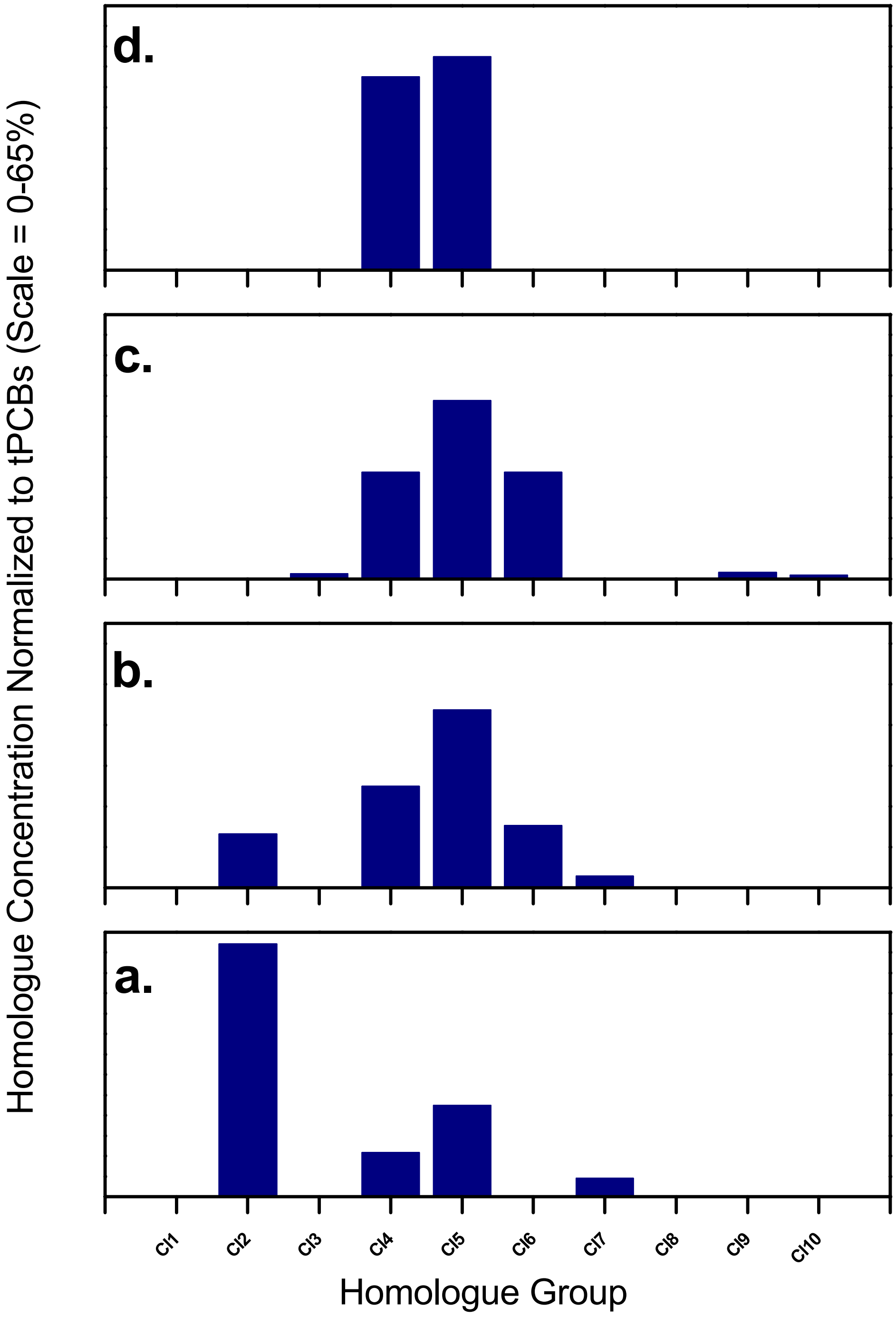


Figure 22 (a-d). Homologue fingerprints during the EC leaching experiment, normalized as percent of total, corresponding to leaching intervals a) 1 to 6 days, b) 62 to 90 days, c) 90 to 125 days, d) 412 to 475 days.

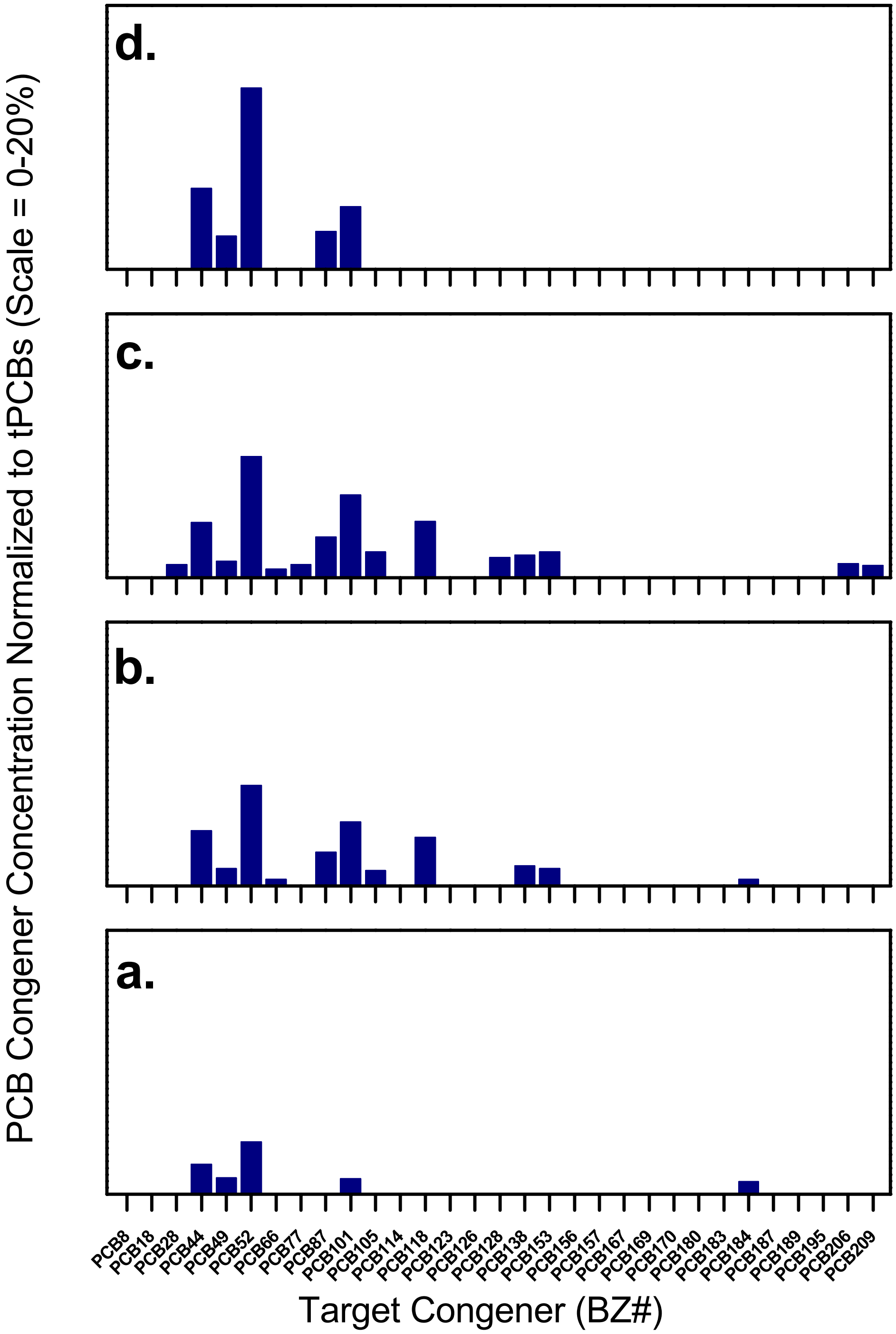
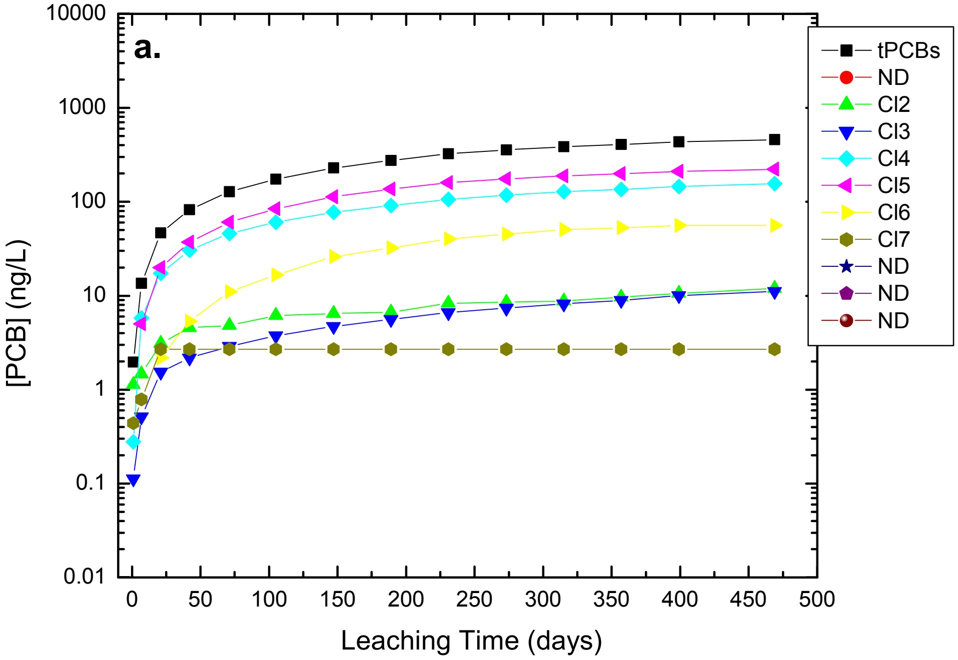
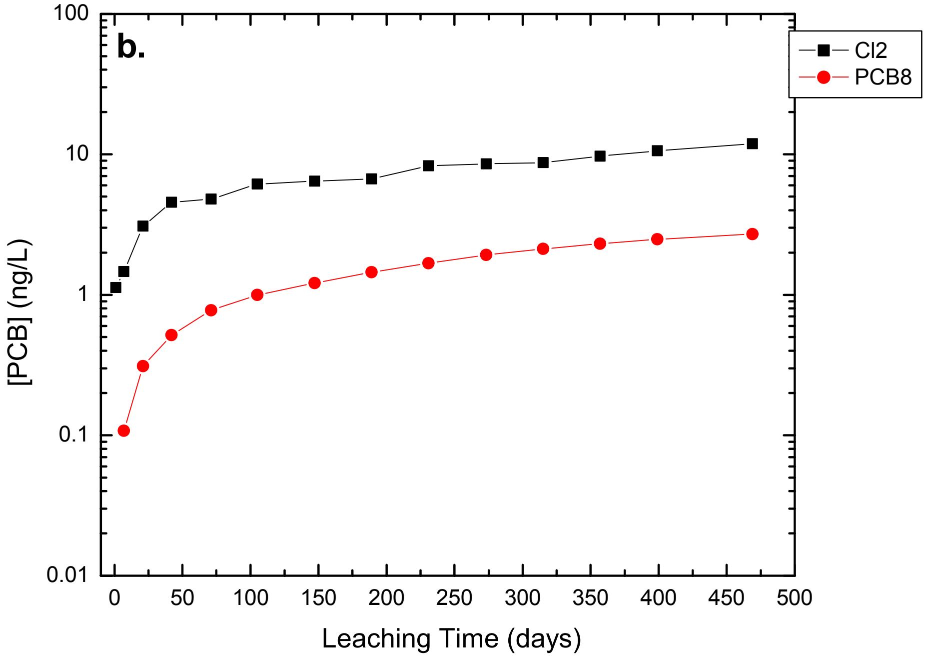


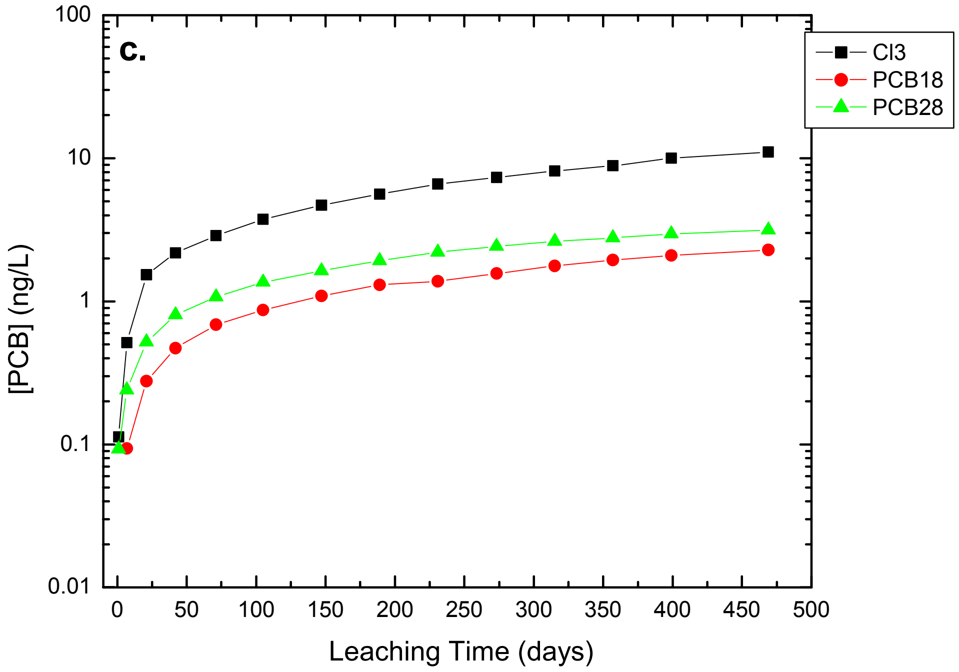
Figure 23 (a-d). Congener fingerprints during the EC leaching experiment, normalized as percent of total, corresponding to leaching intervals a) 1 to 6 days, b) 62 to 90 days, c) 90 to 125 days, d) 412 to days.

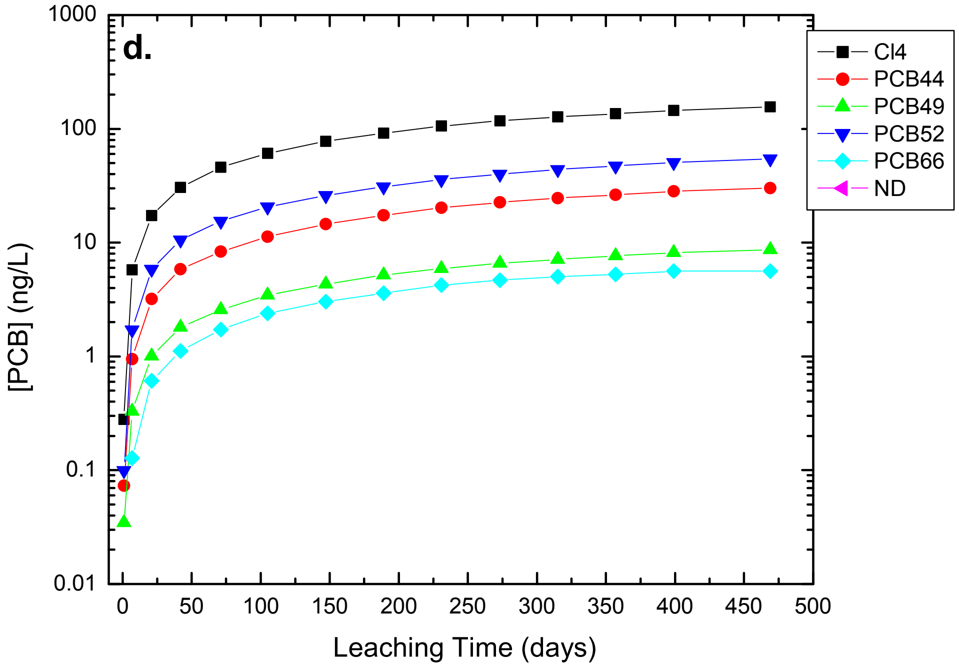
Foam Rubber/Ensolite^{TM} (FRE) Leaching Behavior

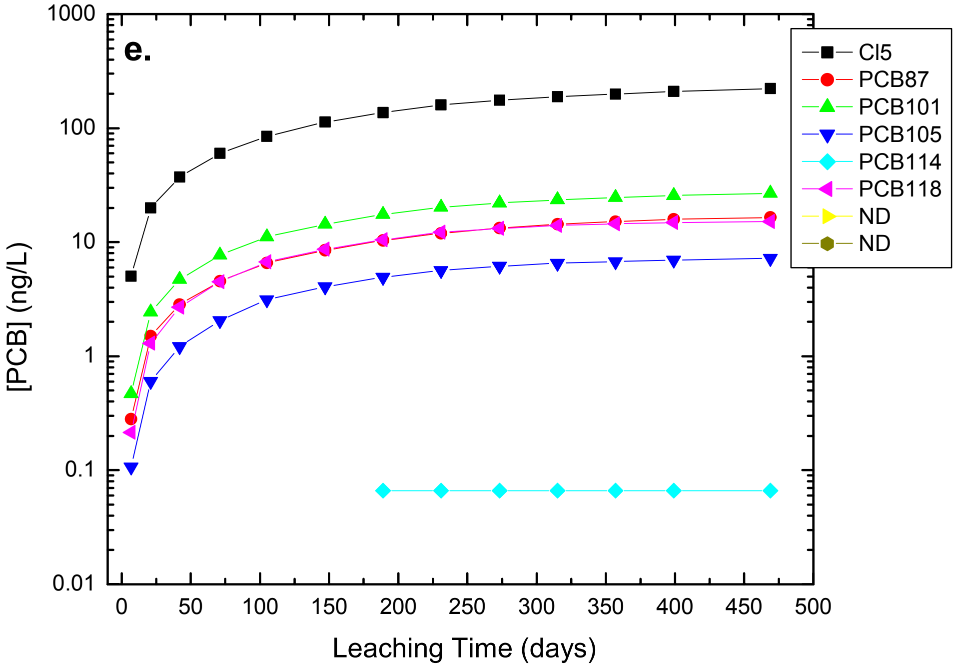
Figure 24(a) includes contributions from homologues Cl2-Cl7 to the tPCB concentration behavior for FRE leached at 25°C and ~1 bar. The FRE solid (2.608 g) contained 23.2 mg tPCBs (0.89 wt%) and was exposed to a total volume of 13.86 L of seawater leachate over the leaching period of nearly 500 days. Target PCB congener concentration curves that contribute to each of these homologue group behaviors are shown in Figure 24(b-g).

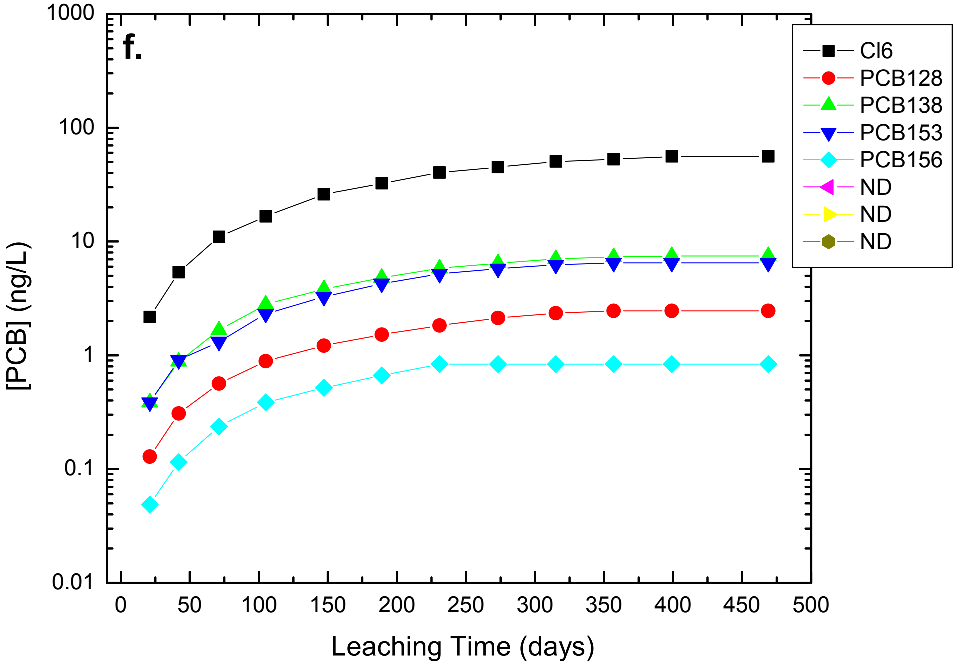





c.
Cl3
PCB18
PCB28
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


d.
Cl4
PCB44
PCB49
PCB52
PCB66
ND
[PCB] (ng/L)
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


e.
[PCB] (ng/L)
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
PCB114
PCB118
ND
ND


f.
[PCB] (ng/L)
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl6
PCB128
PCB138
PCB153
PCB156
ND
ND
ND

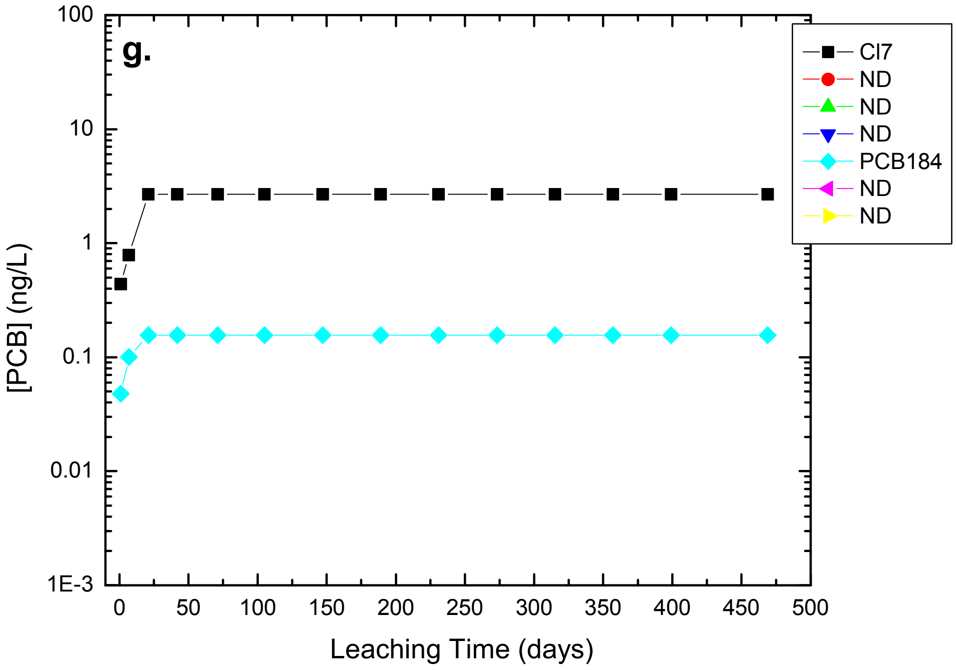


Figure 24 (a-g). Experimental PCB concentration vs. leaching time for FRE containing 0.89 wt% (23.2 mg) tPCBs exposed to a total volume of 13.86 L of seawater leachate. Plot a) shows the tPCBs concentration and contributing homologue group concentrations vs. leaching time, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-g) are homologue group concentrations and corresponding target congener concentrations within homologue groups Cl2-Cl7 vs. leaching time.

Total released homologue and congener distributions or fingerprints are shown in Figure 25, compared with the initial PCB signatures determined for FRE solid. Detected homologues and congeners are normalized and plotted as percent of measured tPCBs in each matrix (leachate vs. solid). In many instances the percent contribution of an analyte to tPCBs was < 0.1%, which can still be significant if those analytes leach into seawater, as shown in the leachate PCB signatures. The most significant levels of release from BRPHL were from homologue groups Cl2-Cl7.

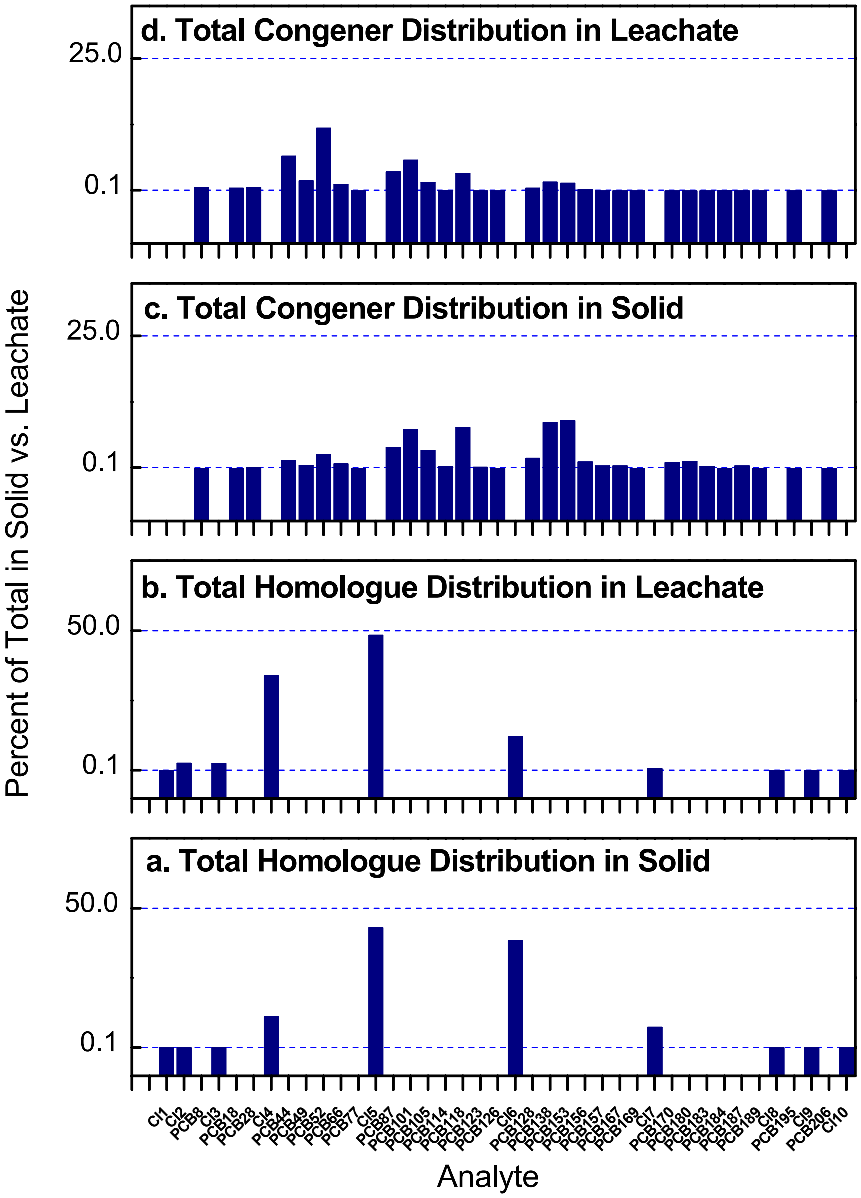


Figure 25 (a-d). Experimental homologue and congener PCB signatures for FRE solid (a & c) compared with total homologue and congener distributions of PCBs leached from FRE into seawater (b & d). The leachate distributions correspond to all PCBs released over the leaching experiment, also represented by the cumulative leachate concentration endpoint for analytes plotted in **Figure 24**. The solid distributions correspond to the pre-leaching PCB content in FRE solid, determined from the leaching experiment mass balance. Analytes at levels below 0.1% are shown on an offset linear scale to indicate their presence, but the degree of variance is not visible on the scale shown here. Variance at these very low sub-percentage levels can be seen in the mass balance tables in APPENDIX C.

Normalized fingerprints corresponding to specific FRE leachate samples are presented below at key intervals across the entire leaching experiment (exposure time). Figure 26corresponds to the homologue group fingerprints at a) the maximum leach rate and broadest homologue distribution, b) and c) "typical" homologue and congener distributions, and d) the final empirical leach rate, also the minimum observed distribution. The corresponding target congener fingerprints are shown in Figure 27(a-d).

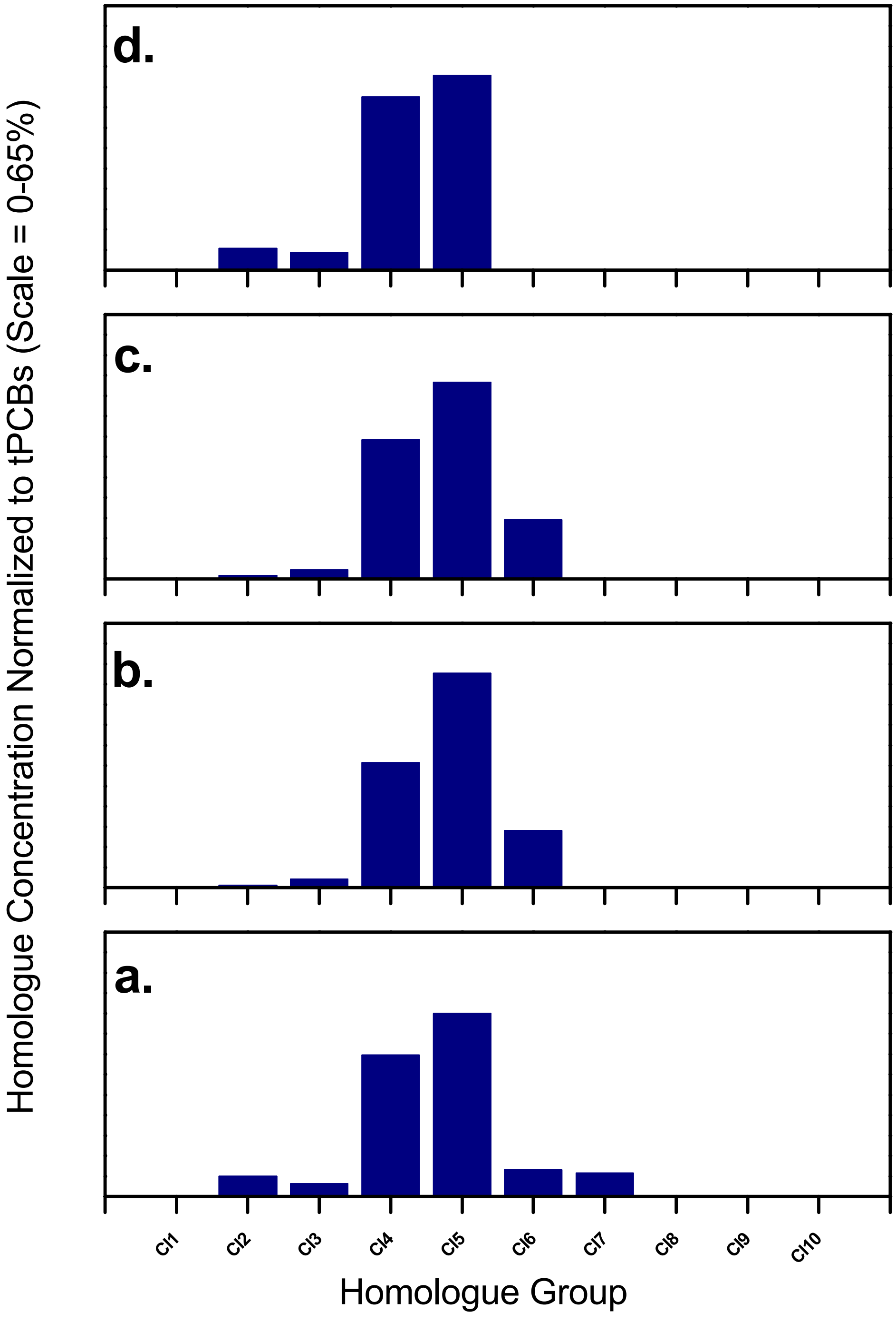


Figure 26 (a-d). Homologue fingerprints during the FRE leaching experiment, normalized as percent of total, for leaching intervals a) 7 to 21 days, b) 147 to 189 days, c) 189 to 273 days, d) 399 to 469 days.

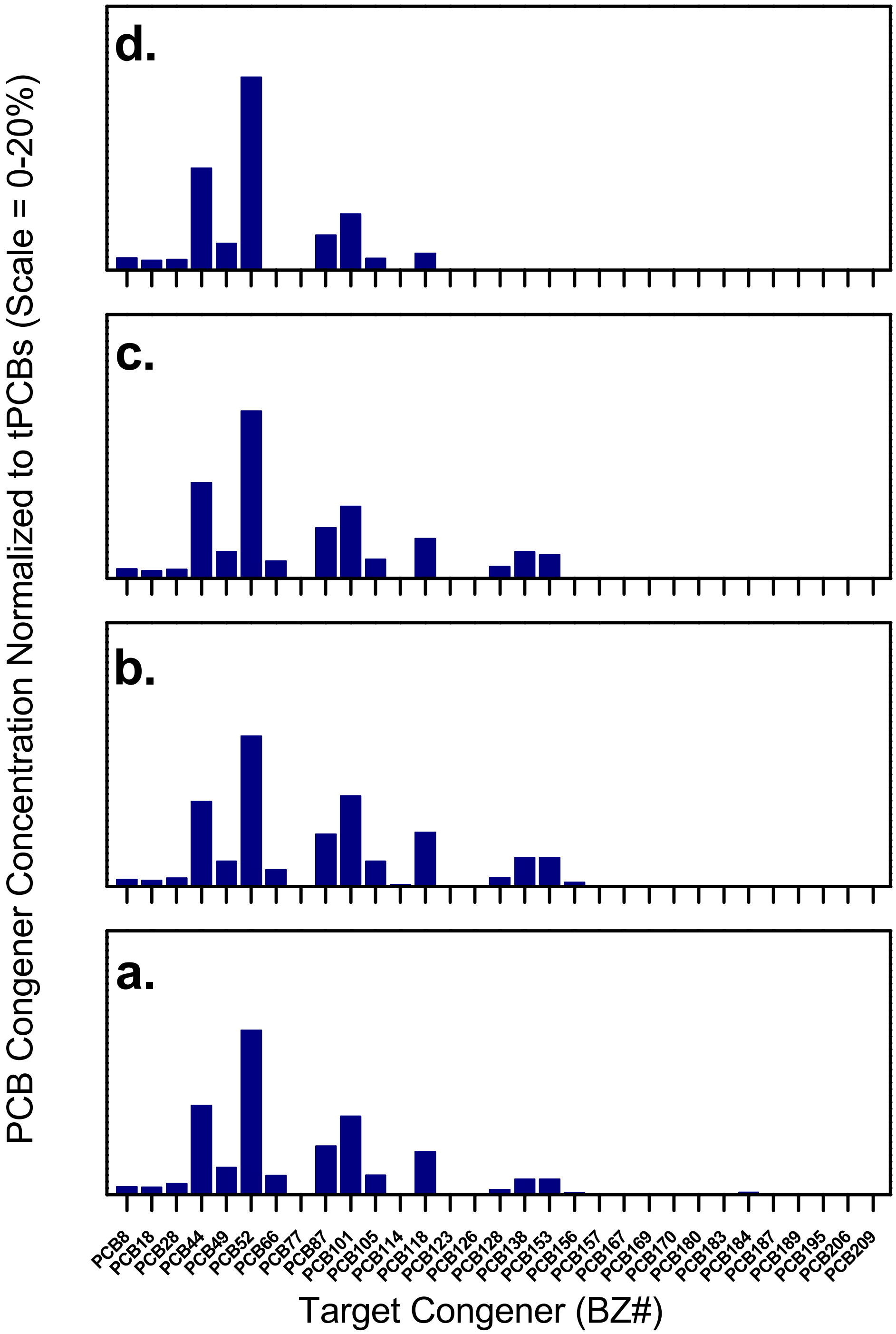
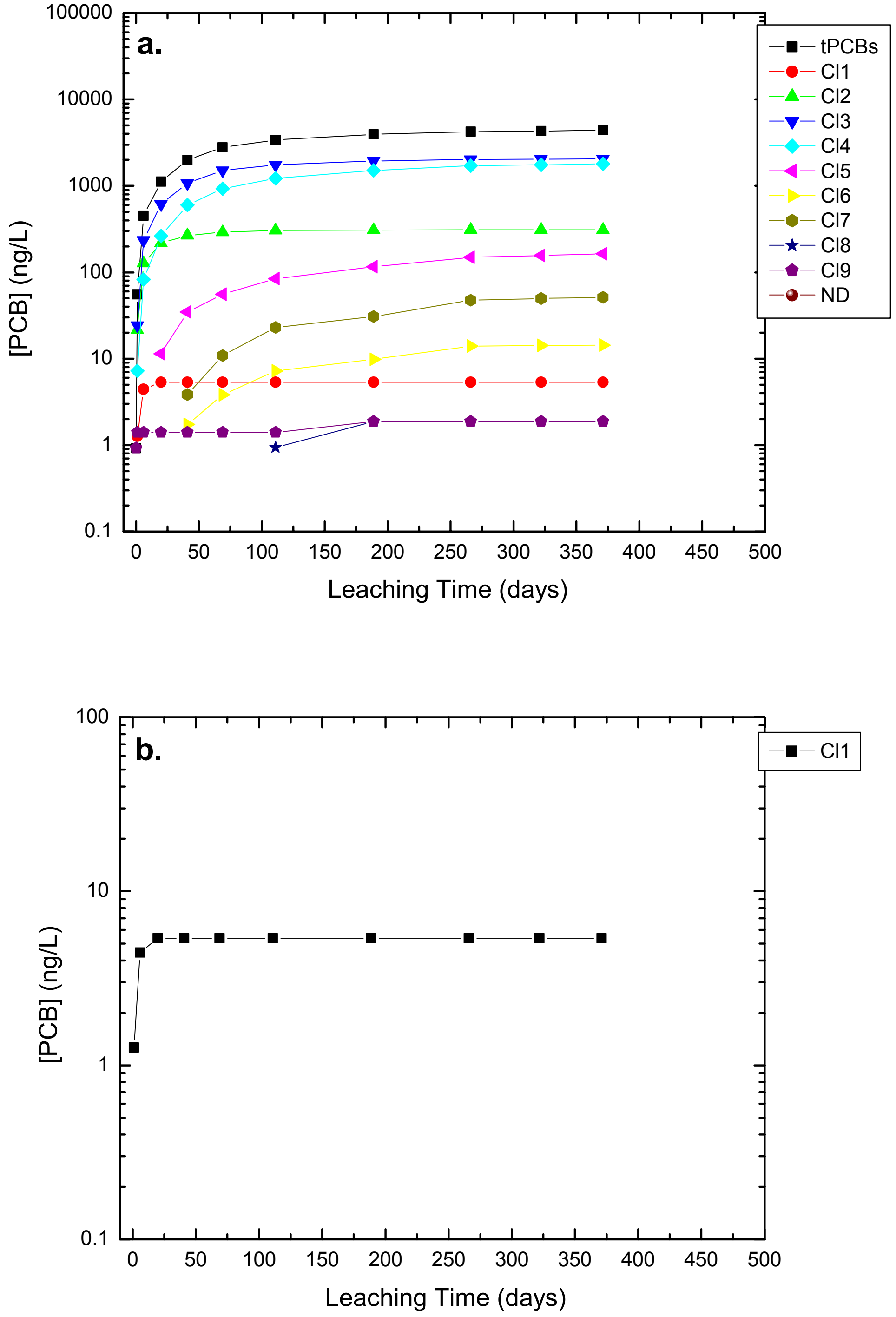
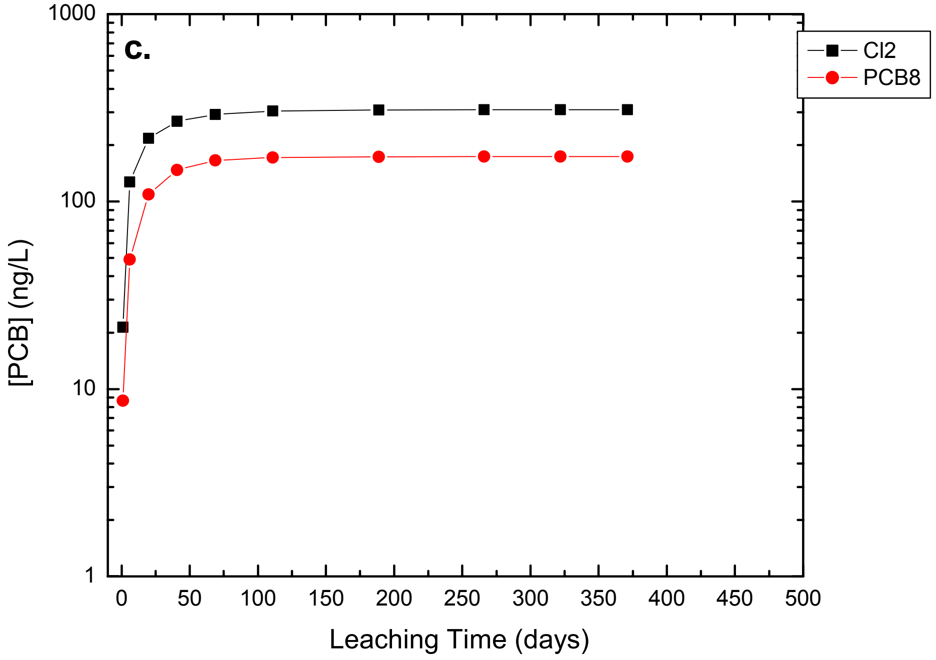


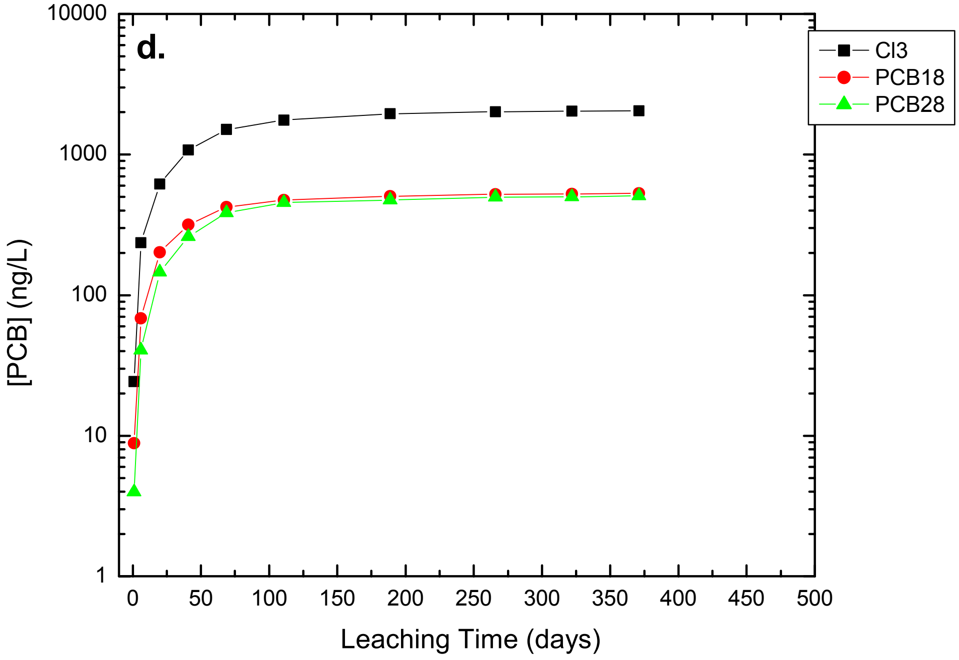
Figure 27 (a-d). Congener fingerprints during the FRE leaching experiment, normalized as percent of total, for leaching intervals a) 7 to 21 days, b) 147 to 189 days, c) 189 to 273 days, d) 399 to 469 days.

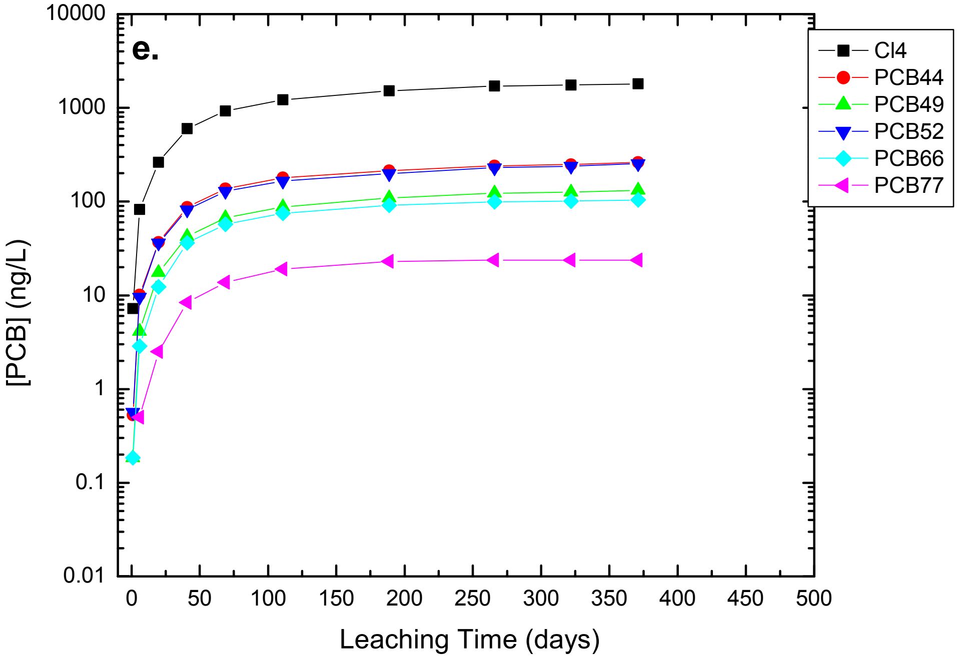
Aroclor 1268 (A1268) Analytical Control Dissolution Behavior

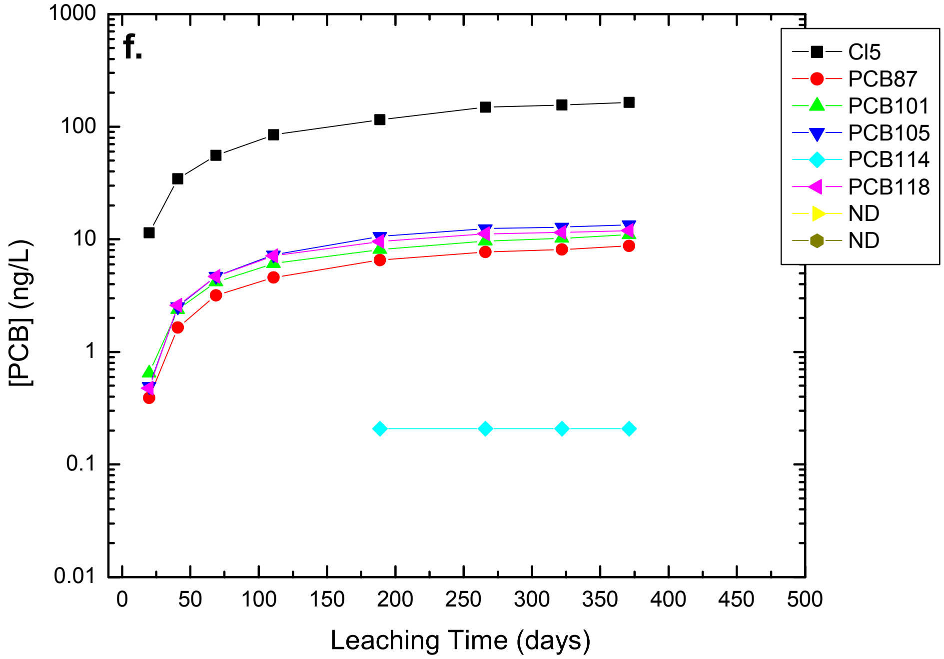
The 25^{o}C/~1 bar results for this positive analytical control, 20.2 mg exposed to a total of 9.77 L of seawater over the nearly 400 day experiment, is shown in Figure 28(a), and includes contributions to the tPCB concentration from homologue groups Cl1-Cl9. These homologues are plotted with their corresponding target congeners in Figure 28(b-j). Note that the slopes of these curves increase sharply and become smaller with time very quickly as compared with the A1254 control curves in Figure 12 presented previously.

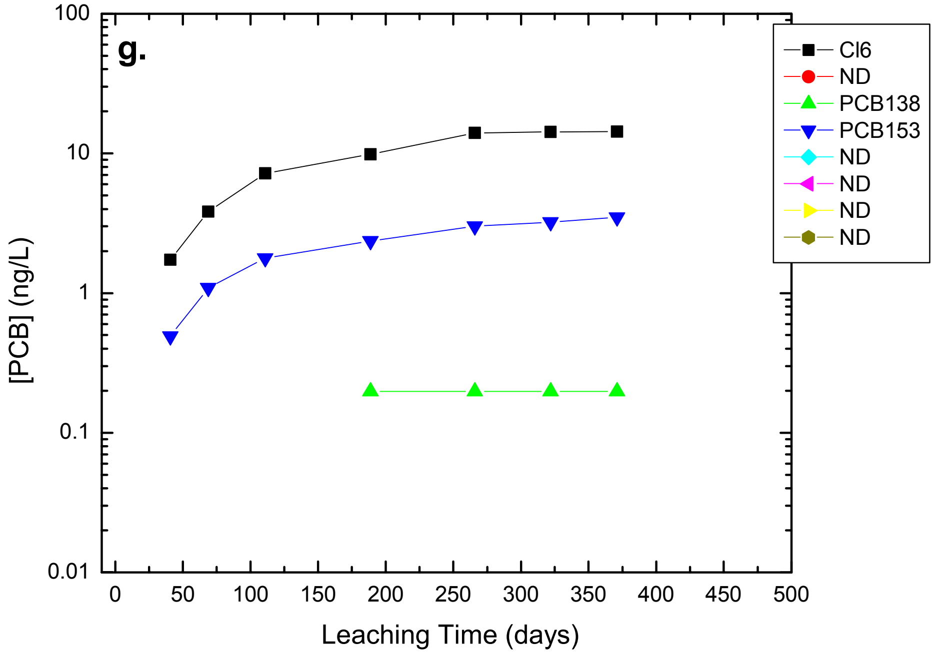


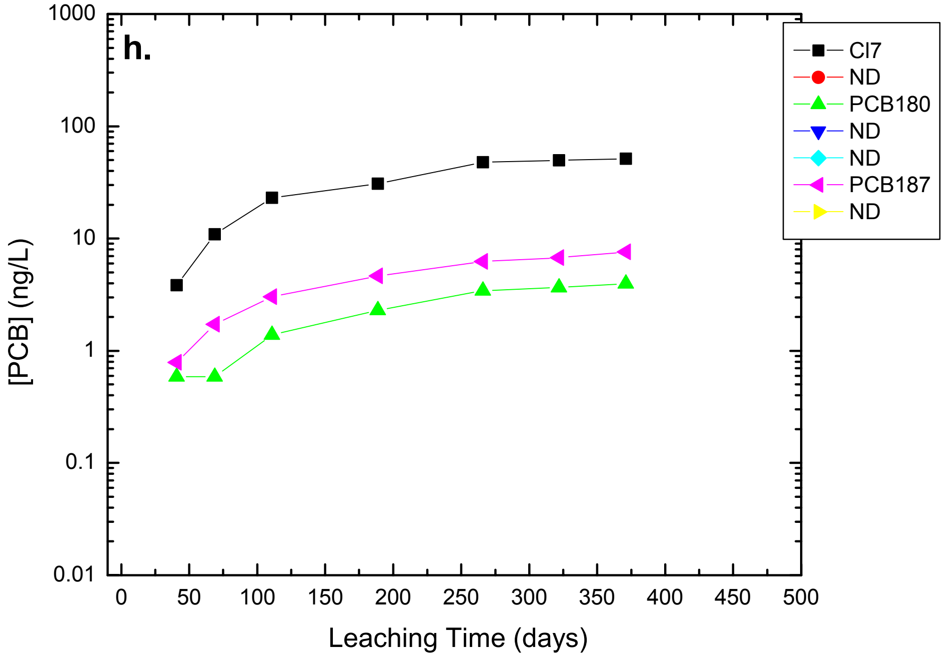

c.
Cl2
PCB8
[PCB] (ng/L)
1000
100
10
1
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)

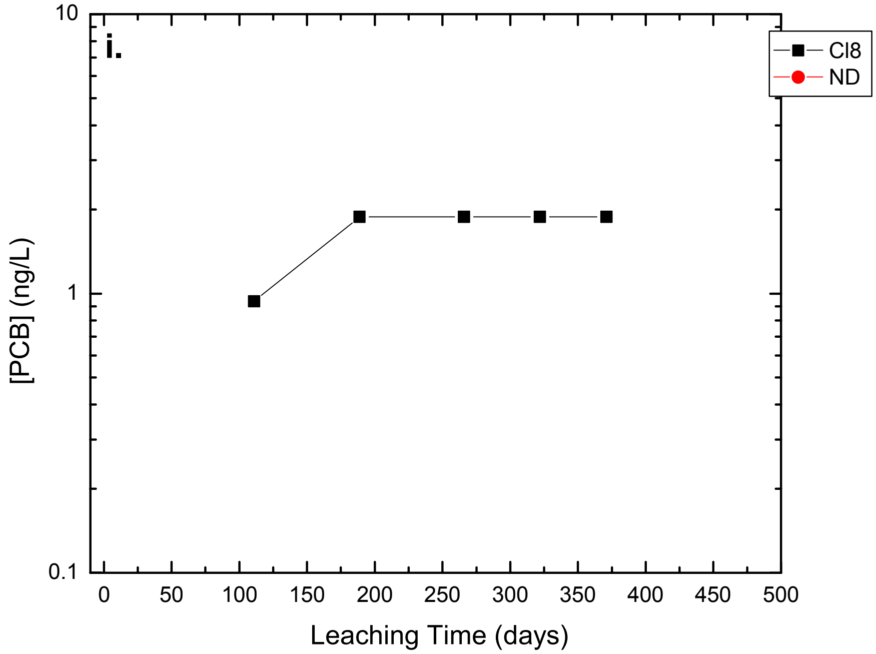

d.
Cl3
PCB18
PCB28
[PCB] (ng/L)
10000
1000
100
10
1
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


e.
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77
[PCB] (ng/L)
10000
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


f.
Cl5
PCB87
PCB101
PCB105
PCB114
PCB118
ND
ND
[PCB] (ng/L)
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


g.
[PCB] (ng/L)
Leaching Time (days)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Cl6
ND
PCB138
PCB153
ND
ND
ND
ND


h.
[PCB] (ng/L)
Leaching Time (days)
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Cl7
ND
PCB180
ND
ND
PCB187
ND



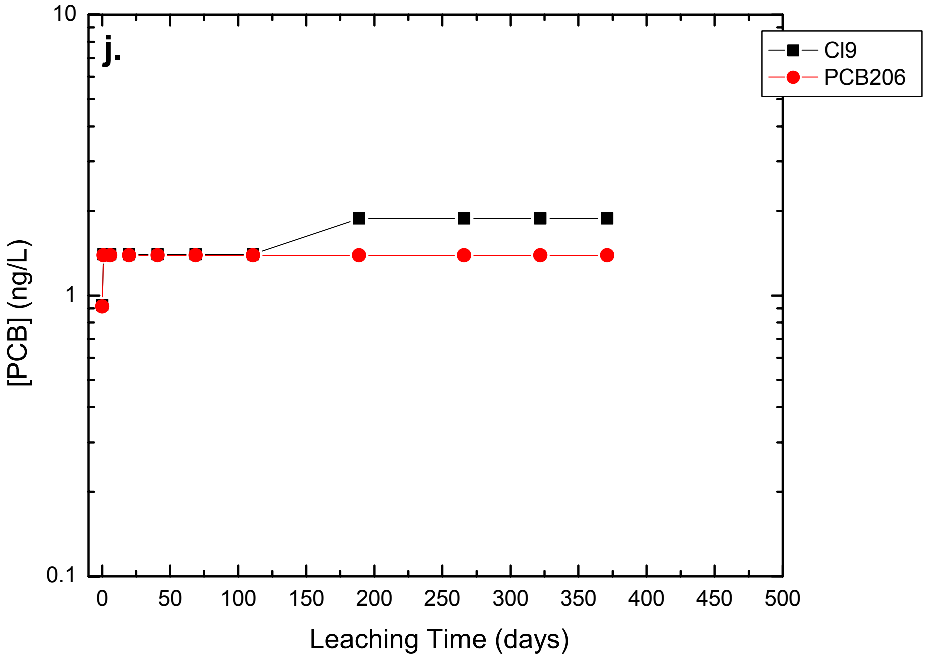


Figure 28 (a-j). Experimental PCB concentration vs. exposure time for 20.2 mg of A1268 in a total volume of 9.77 L of seawater. Plot a) shows experimental tPCBs concentration and contributing homologue group concentrations vs. time, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-j) are homologue group concentrations and target congener concentrations within homologue groups Cl1-Cl9 vs. time.

Total released homologue and congener distributions are shown in Figure 29, compared with the initial PCB signatures determined for neat A1268 "solid". All homologues and congeners detected are normalized and plotted as percent of measured tPCBs in each matrix (seawater vs. solid). In many instances the percent contribution of an analyte to tPCBs was < 0.1%, which can still be significant if the analyte dissolves into seawater, as shown in the seawater PCB signatures. The most significant levels of release from pure A1268 were from homologue groups Cl2-Cl5 and Cl7.

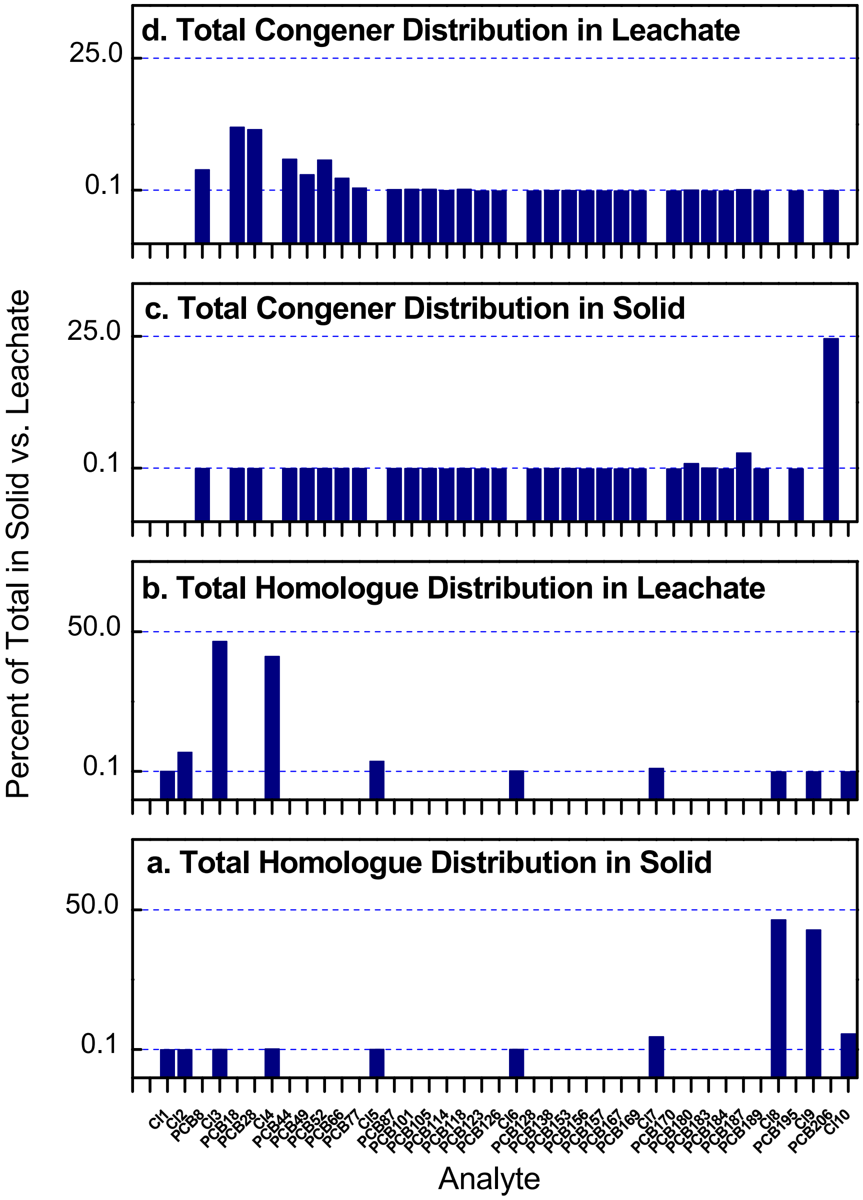


Figure 29 (a-d). Experimental homologue and congener PCB signatures for neat A1268 solid (a & c) compared with total homologue and congener distributions of PCBs released from neat A1268 into seawater (b & d). Seawater distributions correspond to all PCBs released from A1268 during the experiment and also to the cumulative concentration endpoint for analytes plotted in **Figure 28**. Solid distributions correspond to the initial pre-exposure PCB content in A1268 solid, determined from the experiment mass balance. Some analytes contribute to tPCBs at levels below 0.1% and are plotted using an offset linear scale. This is useful to indicate their presence, however the degree of variance at these very low sub-percentage levels is not visible on the scale shown here. These experimental variances can be seen in the mass balance tables included in APPENDIX C.

Fingerprints for specific A1268 seawater samples are included below at key intervals across the entire experiment (exposure time). Figure 30shows homologue groups corresponding to a) the maximum observed dissolution rate and narrowest distribution of congeners and homologues, b) the observed increase in tetrachlorobiphenyl and decrease in dichlorobiphenyl homologue contributions, c) the broadest homologue and congener distributions, and d) the final empirical dissolution rate. The corresponding target congener fingerprints are shown in Figure 31(a-d).

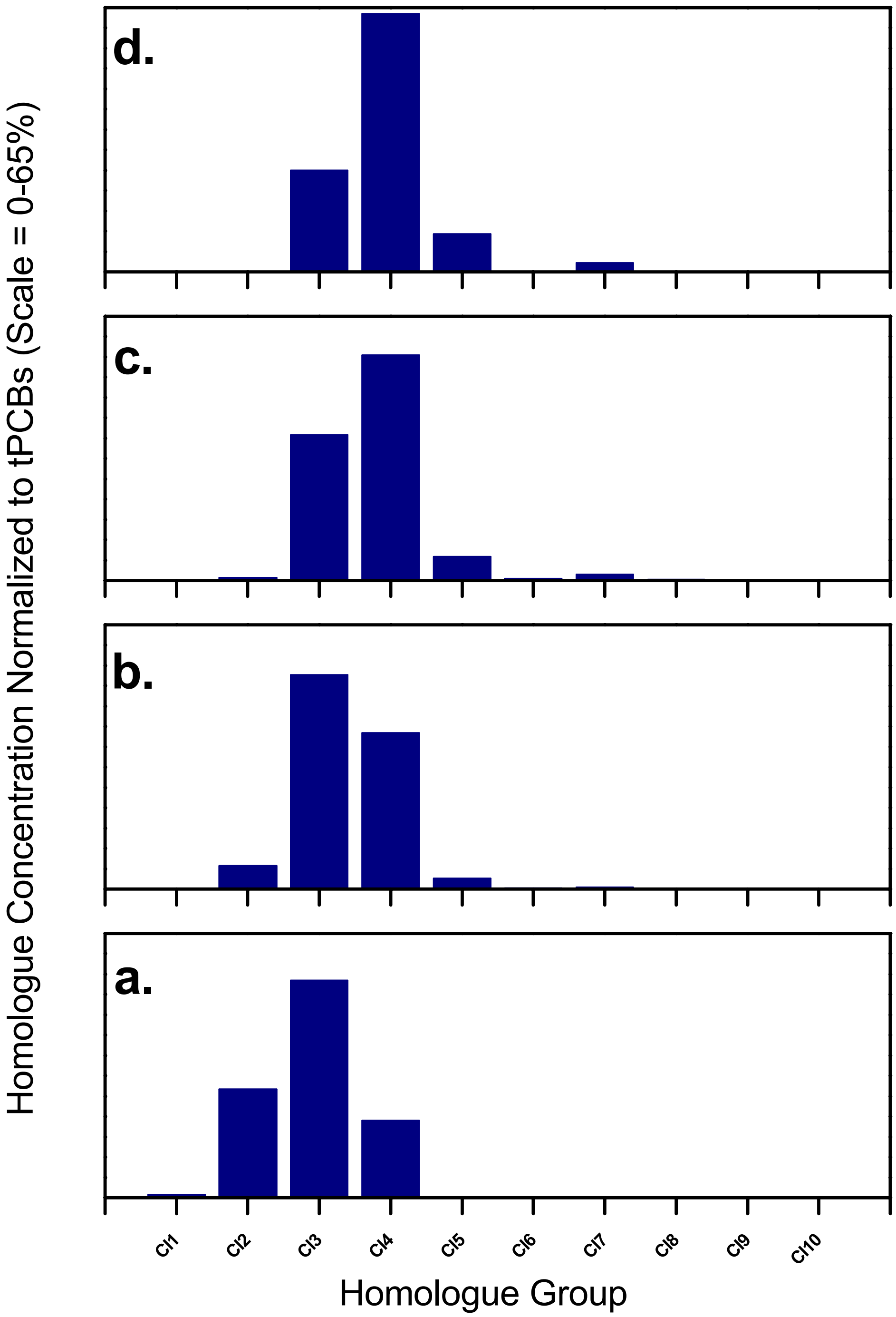


Figure 30 (a-d). Homologue fingerprints during the A1268 dissolution experiment, normalized as percent of total, for exposure intervals a) 1 to 6 days, b) 20 to 41 days, c) 111 to 189 days, d) 322 to 371 days.

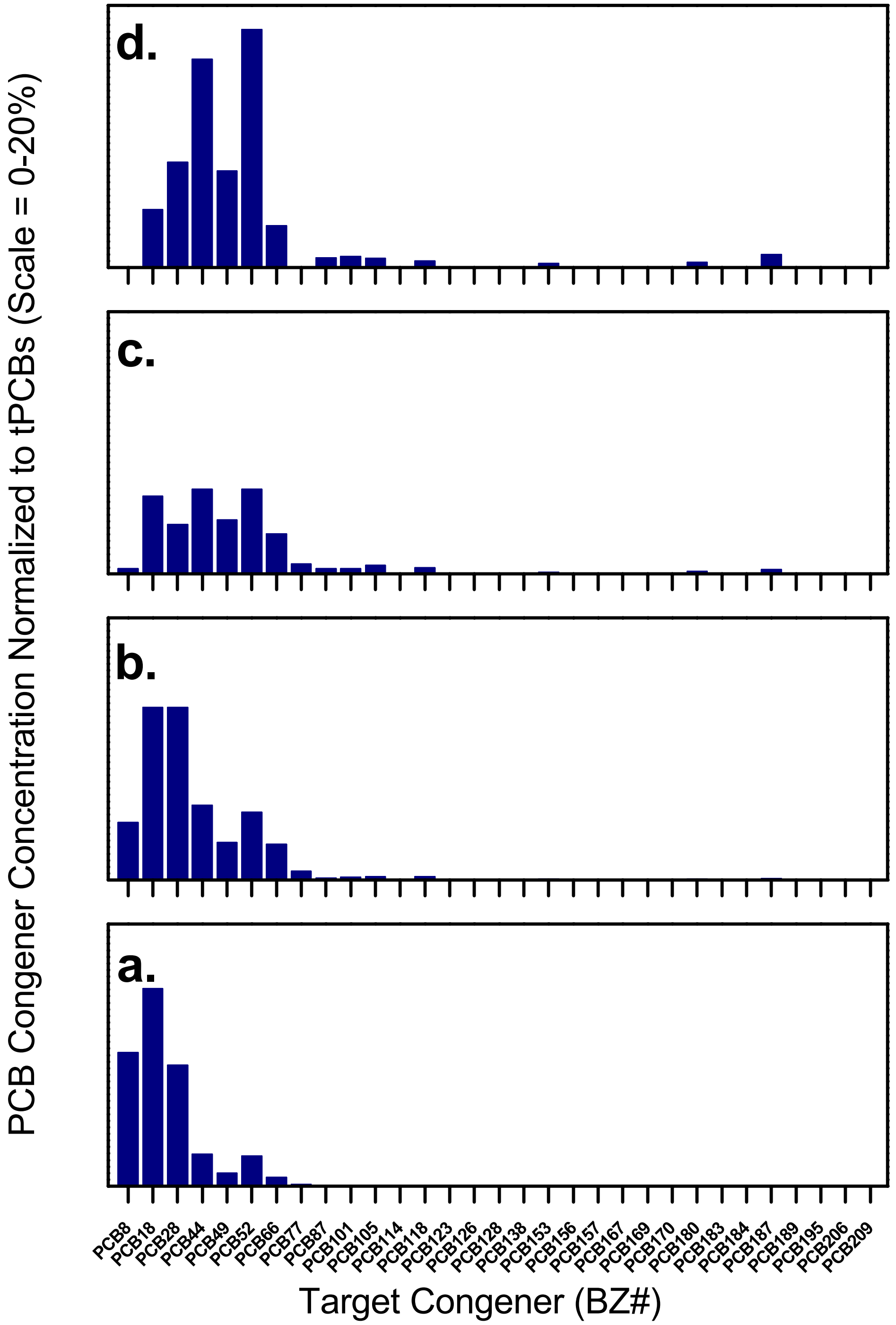


Figure 31 (a-d). Congener fingerprints during the A1268 dissolution experiment, normalized as percent of total, for exposure intervals a) 1 to 6 days, b) 20 to 41 days, c) 111 to 189 days, d) 322 to 371 days.

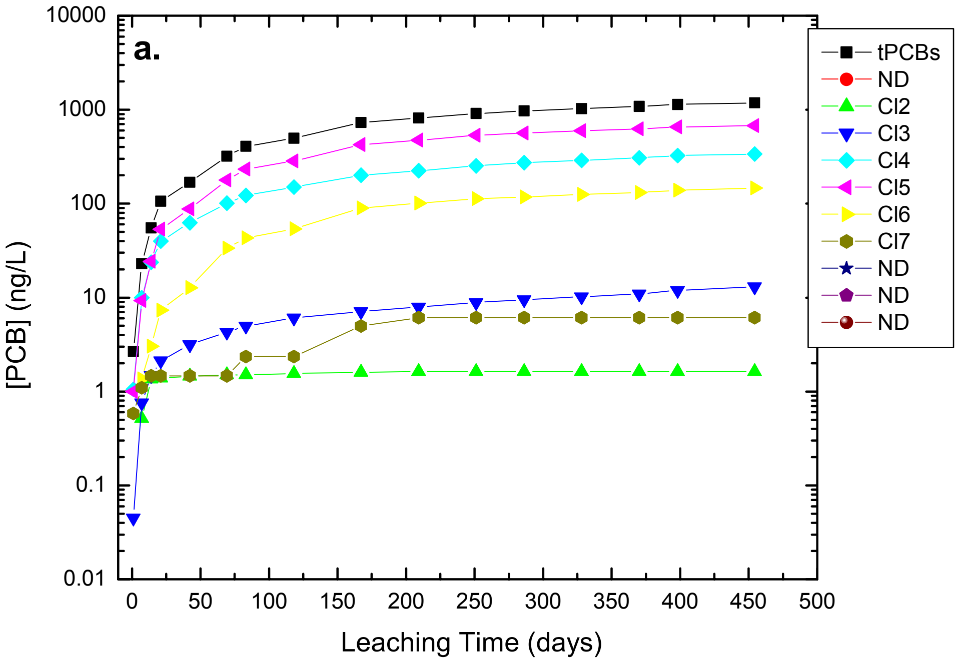
The most concentrated seawater sample observed in the Aroclor 1268 dissolution series was evaluated in an effort to establish an effective saturation limit for A1268 PCB analytes leaching from solids that contain A1268 under these conditions. (Analytical concentration data are included in APPENDIX C.) This sample (214-59B-S1-T10) occurred over the interval 20 - 41days, significantly less than the longest time-interval in the experiment, with a maximum tPCB concentration of 9118 pptr (ng/L), and contributions from homologue groups Cl2-Cl7. However, this particular sample contained only the maxima for Cl3 and Cl4 homologues (4800 and 3500 pptr, respectively) across the entire A1268 experimental series. The maxima for Cl1 and Cl2 (33 and 1100 pptr, respectively) occurred in the leachate sample collected at 6 days, whereas the maximum concentrations for Cl5-Cl7 (350, 44, and 180 pptr, respectively) occurred in the leachate sample collected at 266 days. The Cl8 homologue maximum (10 pptr) occurred in the leachate sample at 111 days and then (an equivalent amount) again at 189 days. The maximum concentration for Cl9 (9.7 pptr) occurred in the first sample collected immediately after submersing the A1268 solid for the first time. Cl10 (PCB209) was never detected in any of the A1268 seawater samples. The effective A1268 saturation limit is estimated as the sum of all maximum homologue concentrations observed (10,000 pptr) and assumes that the solubility of any given homologue group would not be significantly affected (suppressed) by the presence of other dissolved homologue groups at their maximum observed concentrations. It must also be recognized that the true solubility for such a complex mixture is likely time-dependent, but as postulated for A1254, A1268 should exhibit a solubility value above the highest concentration observed (9118 pptr = 0.009118 ppm). In the absence of solubility data for A1268, we can follow the same approach demonstrated for A1254, and estimate the solubility for Aroclor 1268 from the homologue solubilities compiled by Mackay, *et al*[51]. Applying the homologue signature for A1268 in this study to these values, the solubility range is estimated as 0.00026 - 0.0015 mg/L (ppm). However, as demonstrated for A1254, the estimation based on homologue solubilities was severely underestimated relative to empirical observed solubilities. If it is assumed that this would also be the case for A1268, the adjusted range for A1268 becomes 0.001- 0.025 mg/L, giving reasonable assurance that we are below saturation across the A1268 leaching experiment, except perhaps in this particular sample. Again, as for A1254, the solubility of A1268 should be suppressed slightly in seawater.

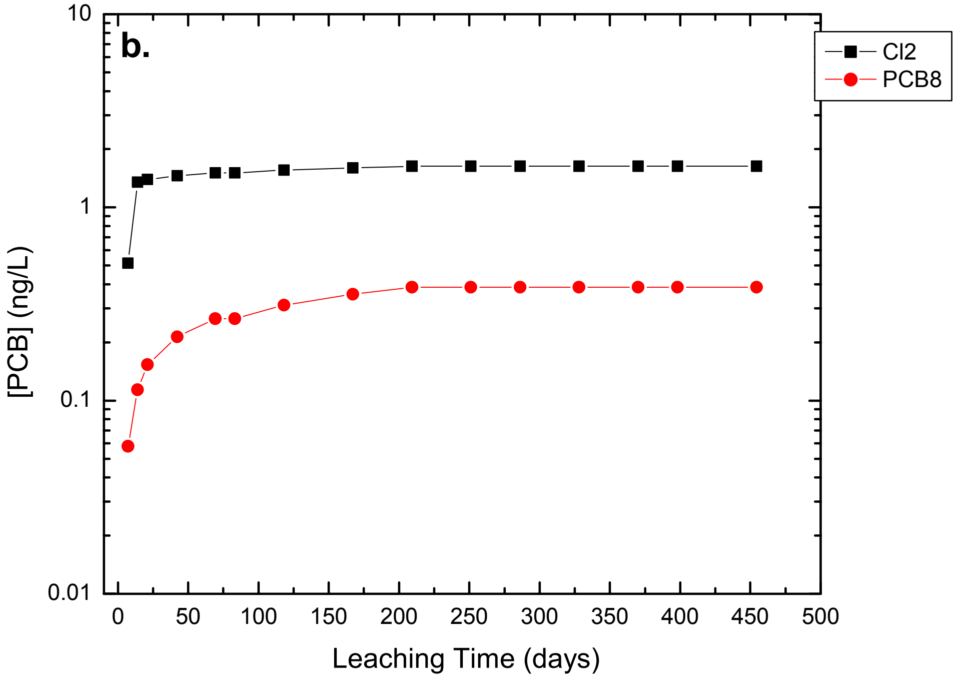
The concentration maxima of target congeners, if detected within each of these homologue groups, deviated from their corresponding homologue group maxima as follows: Cl2/PCB8 at 20 days, Cl3/PCB18 & 28 at 20 & 69 days, respectively, Cl4/PCB44, 49, & 52 at 69 days), Cl5/PCB87, 101, 105, 114, & 118 at 189 days (PCBs 123 & 126 not detected), Cl6/PCB138 & 153 at 189 & 111 days, respectively (PCBs 128, 156, 157, 167, 169 not detected), and Cl7/PCBs 170, 183, 184, & 189 not detected. As with A1254, these exceptions indicate that solubility of PCBs in seawater leachate is not the only factor contributing to the leaching mechanism, i.e it is likely that the presence of insoluble PCBs in the Aroclor matrix is retarding the solvation of other congener.

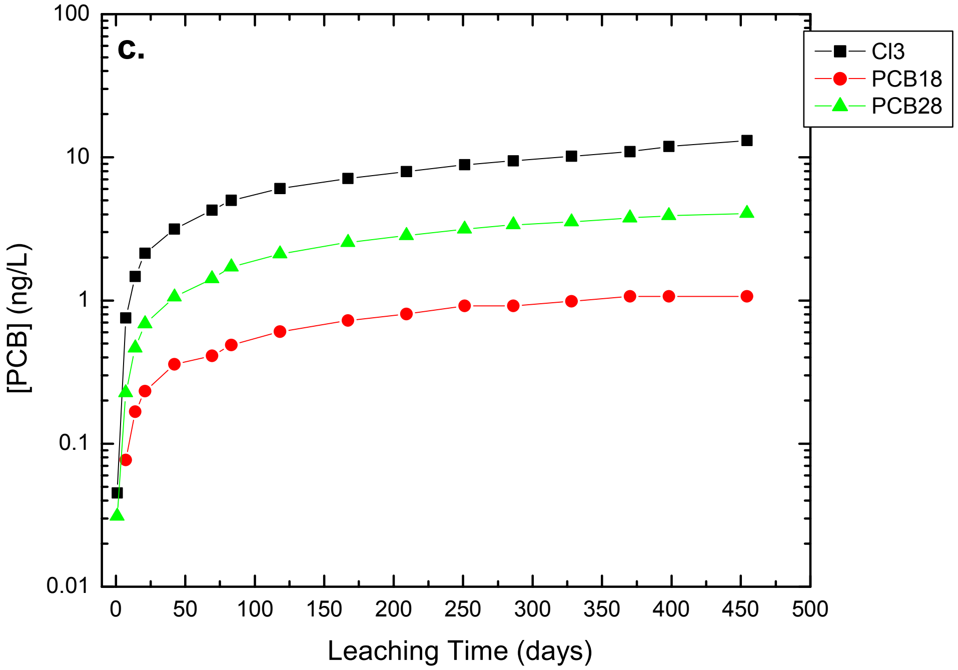
If one considers that the maximum concentration observed was 9118 pptr as indicated above (all other leachate concentrations were observed below this value), an estimated A1268 PCB saturation limit of 10,000 pptr was calculated, and the concentration in the total experimental volume was 4401 pptr (as indicated by the final concentration value in Figure 56a and in the cumulative concentration table in APPENDIX D, Aroclor 1268 (A1268) Results), then the observed dissolution behavior must be limited by the pure Aroclor 1268 solid matrix itself. If the Aroclor could have released PCBs, then it would have been reflected as a cumulative leachate concentration increase, at least up to the value experimentally shown to be possible in an experimental A1268 seawater sample, i.e. 9118 pptr, and very likely up to the estimated saturation limit of 10,000 pptr. All of these combined observations demonstrate that this neat Aroclor 1268 experiment is a valid upper limit dissolution behavior for A1268 PCB congeners leaching from solid matrices. This leaching occurs from the most closely related PCB solid matrix possible, pure Aroclor 1268 itself, a mixture of PCBs.

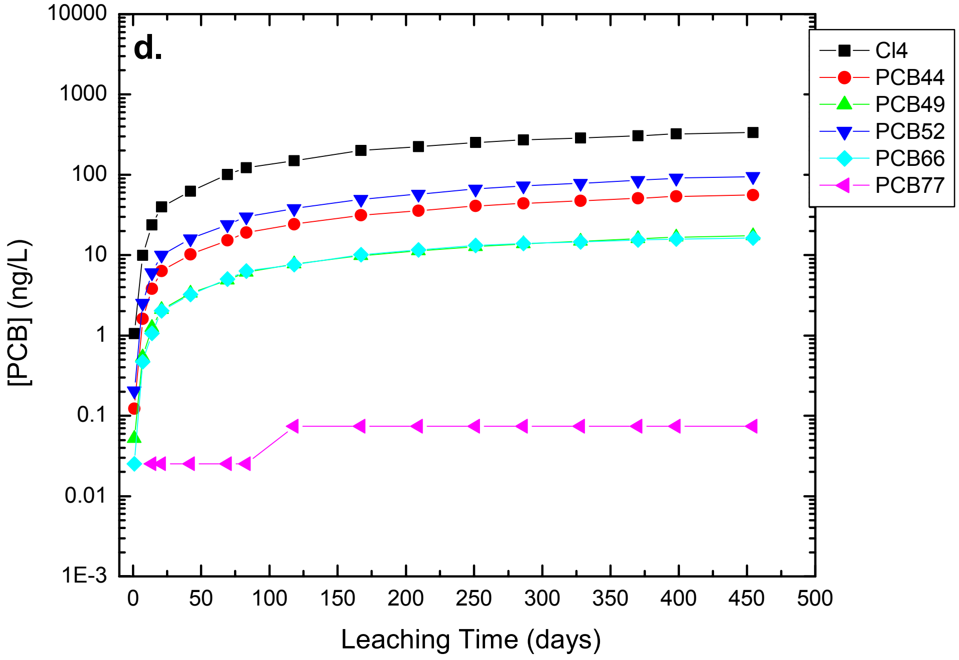
Bulkhead Insulation (BHI) Leaching Behavior

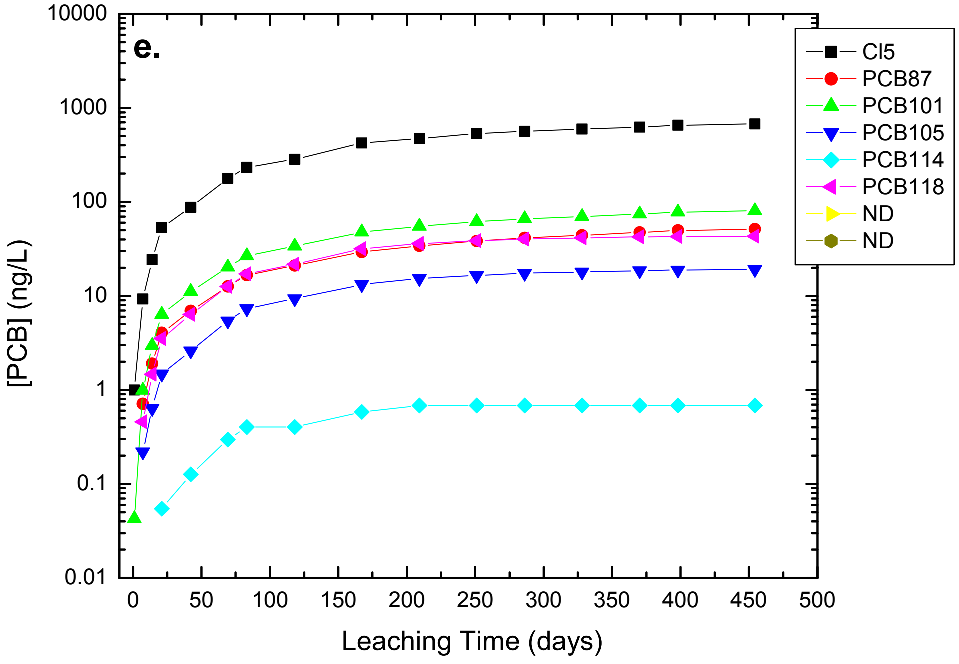
Leaching concentration curves for BHI at 25^{o}C/~1 bar are shown in Figure 32(a) for tPCBs and contributing homologue groups, Cl2-Cl7, which are separately plotted with target congeners in Figure 32(b-g). BHI (.520 g), containing 0.23 mg (0.044 wt%) tPCBs, was exposed to a 15.71 L total volume of seawater leachate over a leaching time of nearly 500 days and exhibited the maximum leach rate curve for all shipboard solids tested. It also approached the leach rate for the positive control curve to within three orders of magnitude. The very open/porous nature of this solid, leading to a high surface area, combined with the likelihood that PCBs are primarily coating the inorganic nature of the solid surfaces (vice PCBs incorporated into an organic/polymer matrix), very likely results in greater PCB mobility. This would lead to an increase in observed PCB "leaching", similar to what was observed for both a neat Aroclor PCB matrices in results presented in this study.

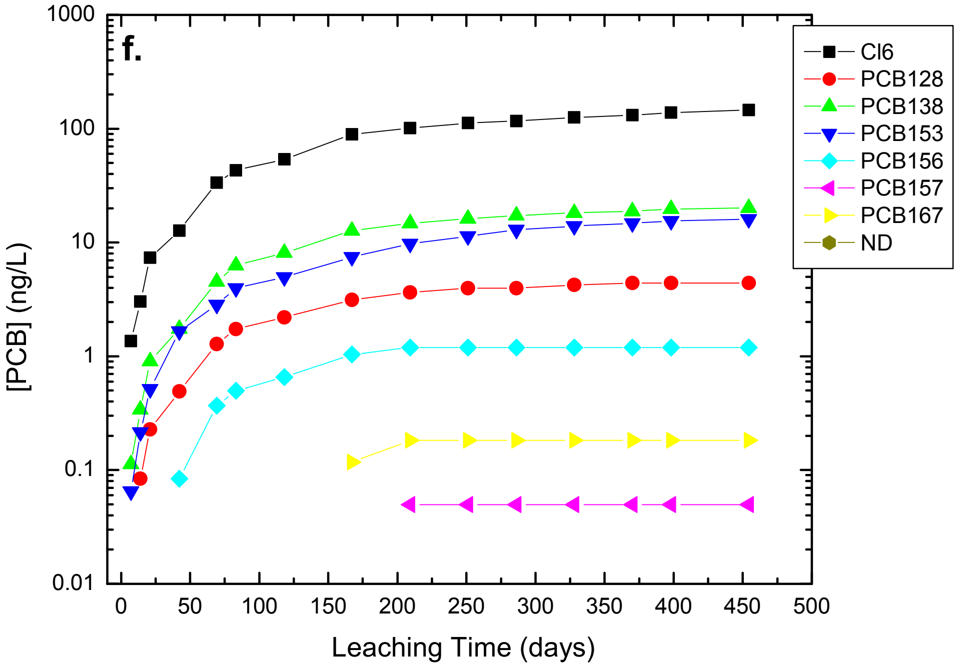



b.
Cl2
PCB8
[PCB] (ng/L)
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


c.
Cl3
PCB18
PCB28
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


d.
[PCB] (ng/L)
10000
1000
100
10
1
0.1
0.01
1E-3
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77


e.
[PCB] (ng/L)
10000
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
PCB114
PCB118
ND
ND



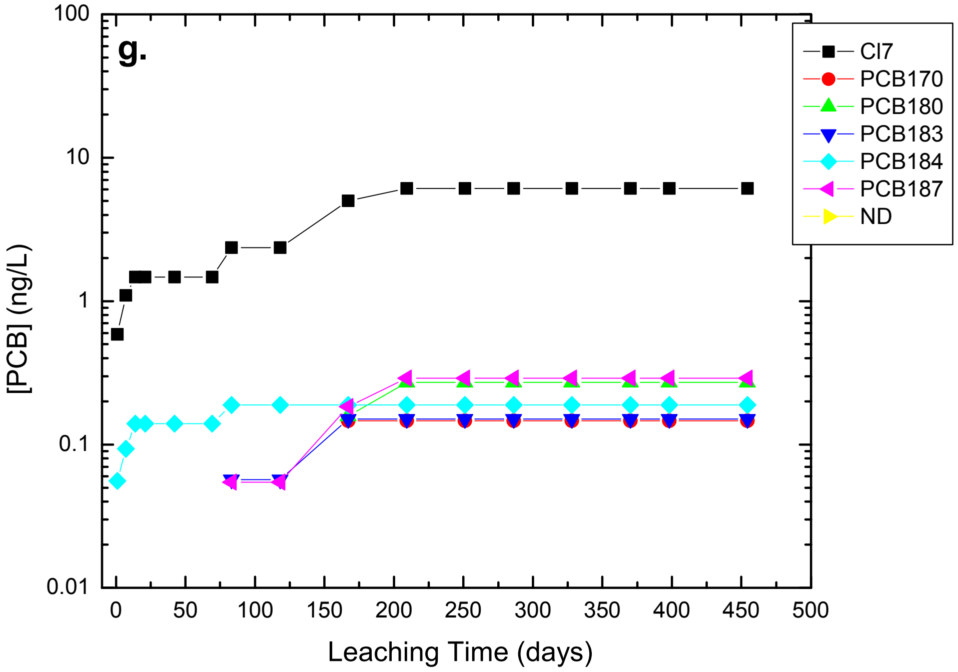


Figure 32 (a-g). Experimental PCB concentration vs. leaching time for BHI containing 0.23 mg (0.044 wt%) tPCBs exposed to a total volume of 15.71 L of seawater leachate. Plot a) shows the tPCBs concentration and contributing homologue group concentrations vs. leaching time, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-g). are homologue group concentrations and target congener concentrations within homologue groups Cl2-Cl7 vs. leaching time.

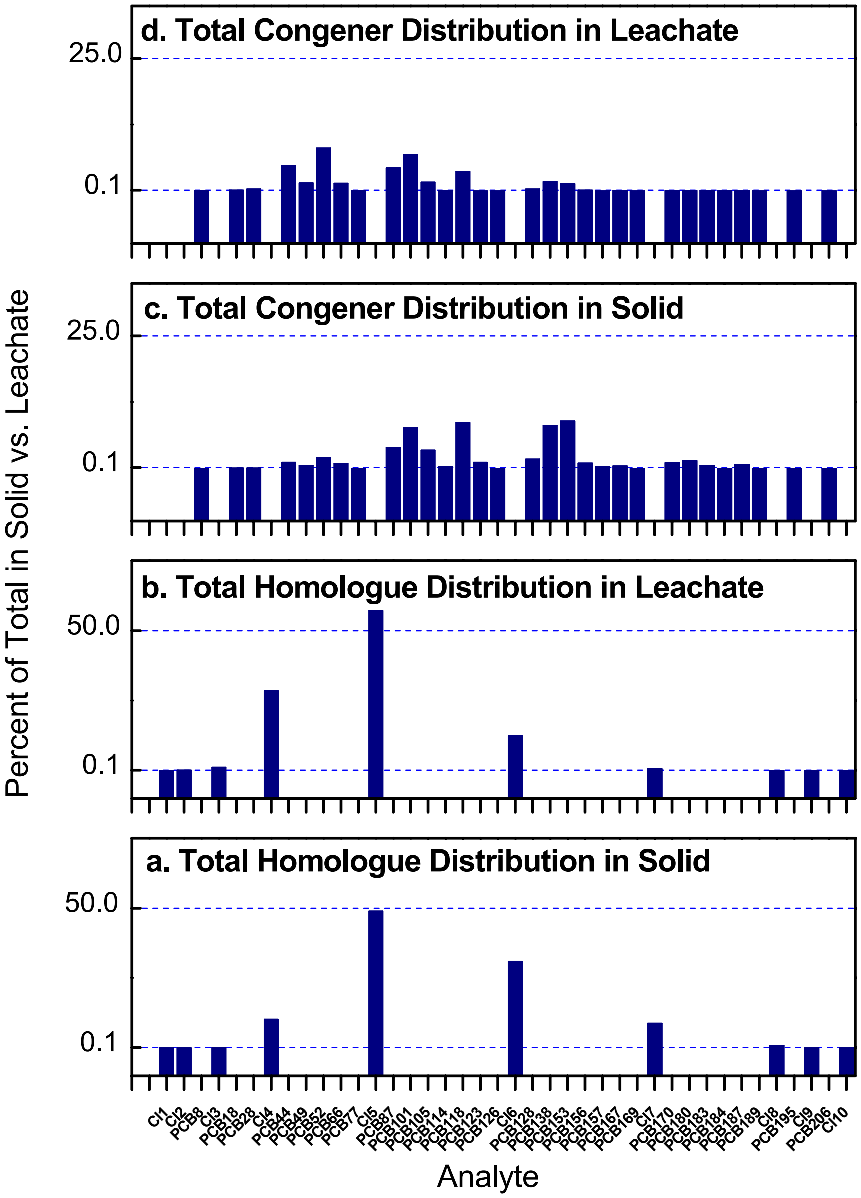


Figure 33 (a-d). Experimental homologue and congener PCB signatures for BHI solid (a & c) compared with total homologue and congener distributions of PCBs leached into seawater from BHI (b & d). The leachate distributions correspond to all released PCBs, which is also the cumulative leachate concentration endpoint for analytes presented in **Figure 32**. Solid distributions correspond to the initial PCB content in the BHI solid, determined using the mass balance performed at the conclusion of the leaching experiment. Analytes present below 0.1% are indicated using an offset linear scale. However, variances at these very low sub-percentage levels are not visible on the scale shown here. The mass balance tables in APPENDIX C should be consulted for these experimental variance values.

Fingerprints for specific samples of BHI leachate are shown below at key intervals across the entire leaching experiment (exposure time). Figure 34homologue group fingerprints correspond to a) the maximum leach rate, b) the observed increase in tetrachlorobiphenyl and decrease in dichlorobiphenyl groups, c) the broadest homologue and congener distributions, and d) the final empirical leach rate, also corresponding to the narrowest homologue and congener distributions. The respective target congener fingerprints are illustrated in Figure 35(a-d).

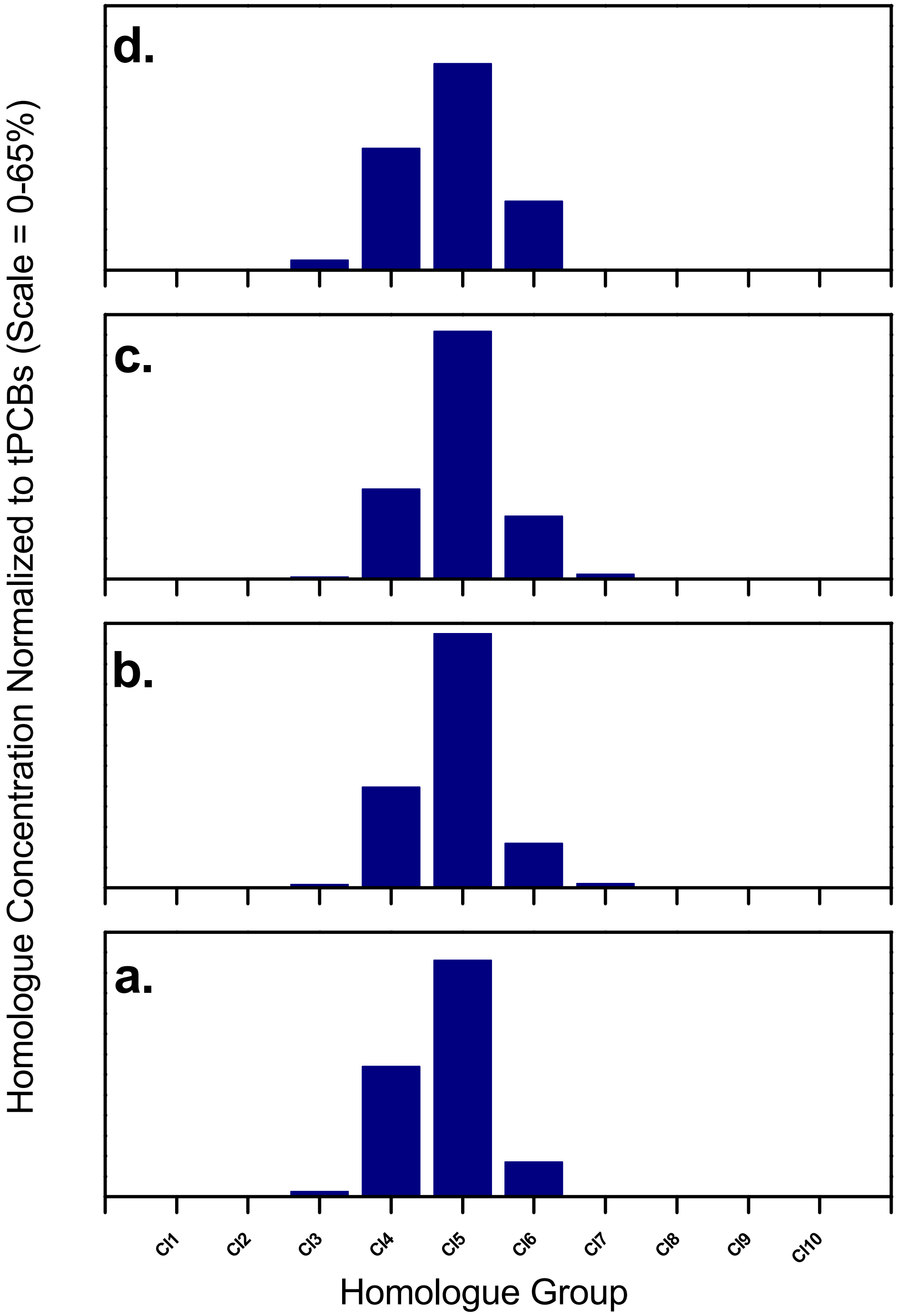


Figure 34 (a-d). Homologue fingerprints during the BHI leaching experiment, normalized as percent of total, corresponding to leaching intervals a) 14 to 21 days, b) 69 to 83 days, c) 118 to 167 days, d) 398 to 454 days.

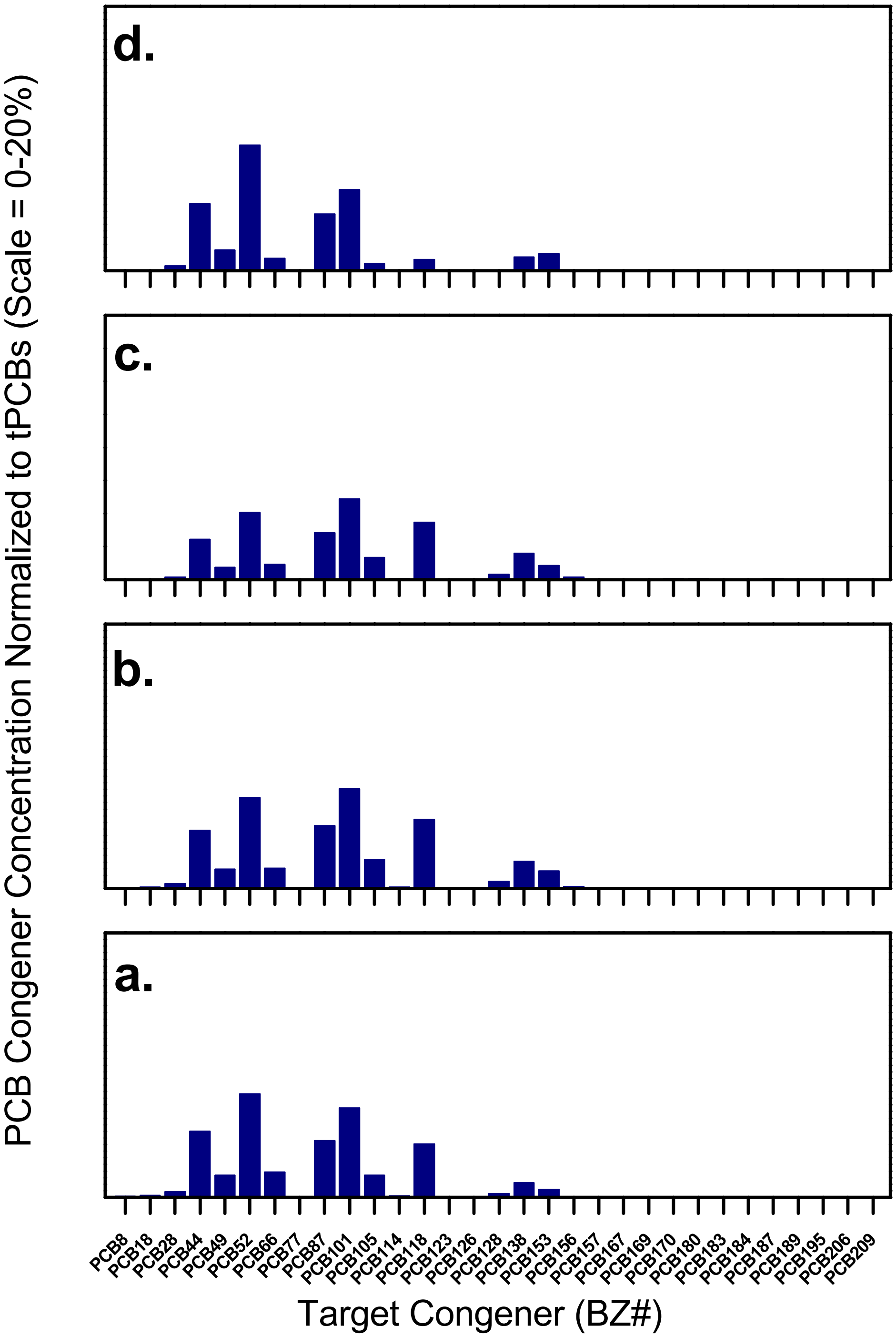
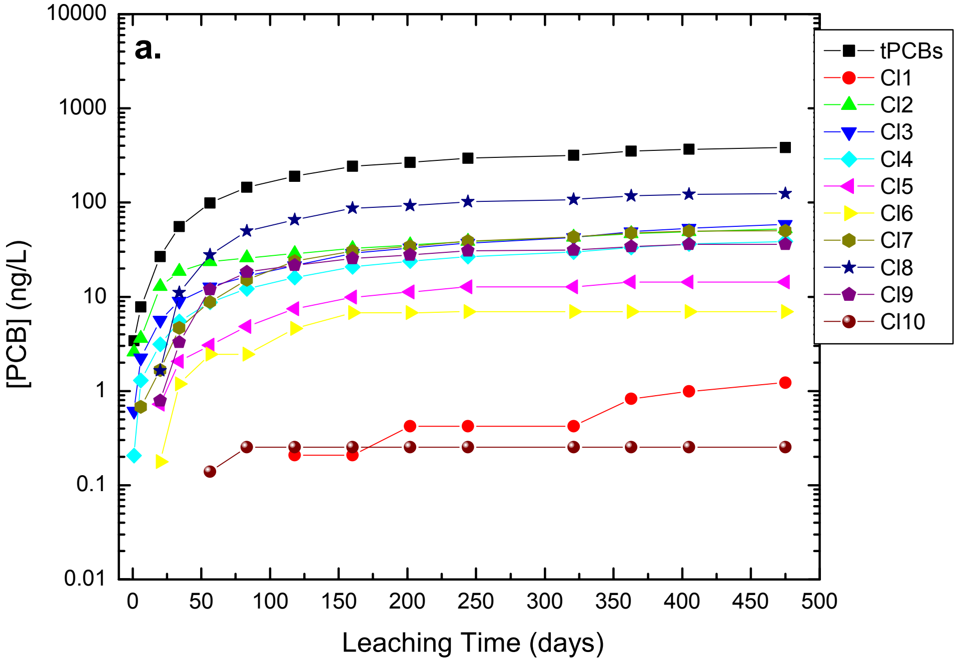


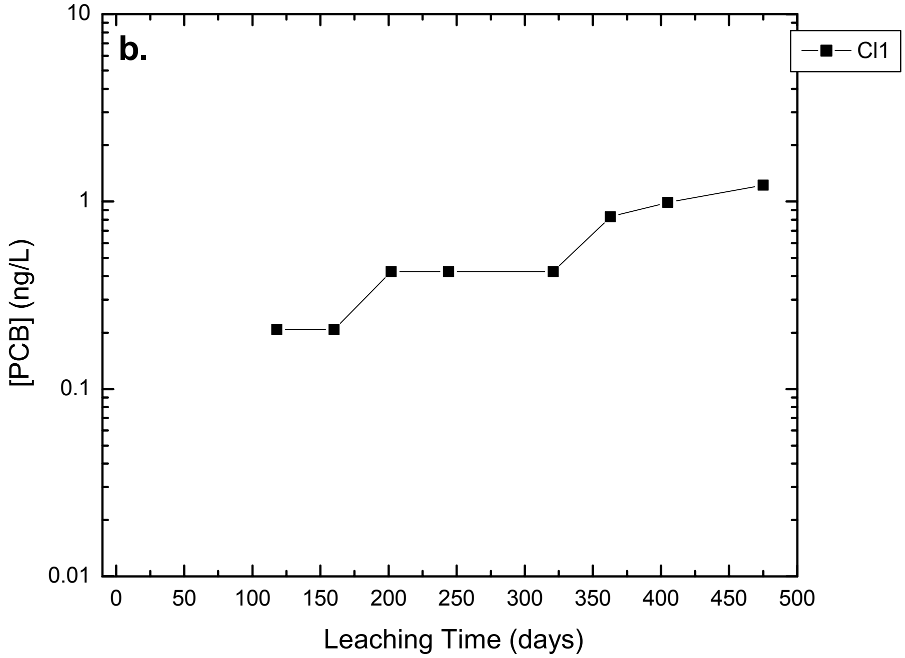
Figure 35 (a-d). Congener fingerprints during the BHI leaching experiment, normalized as percent of total, corresponding to leaching intervals a) 14 to 21 days, b) 69 to 83 days, c) 118 to 167 days, d) 398 to 454 days.

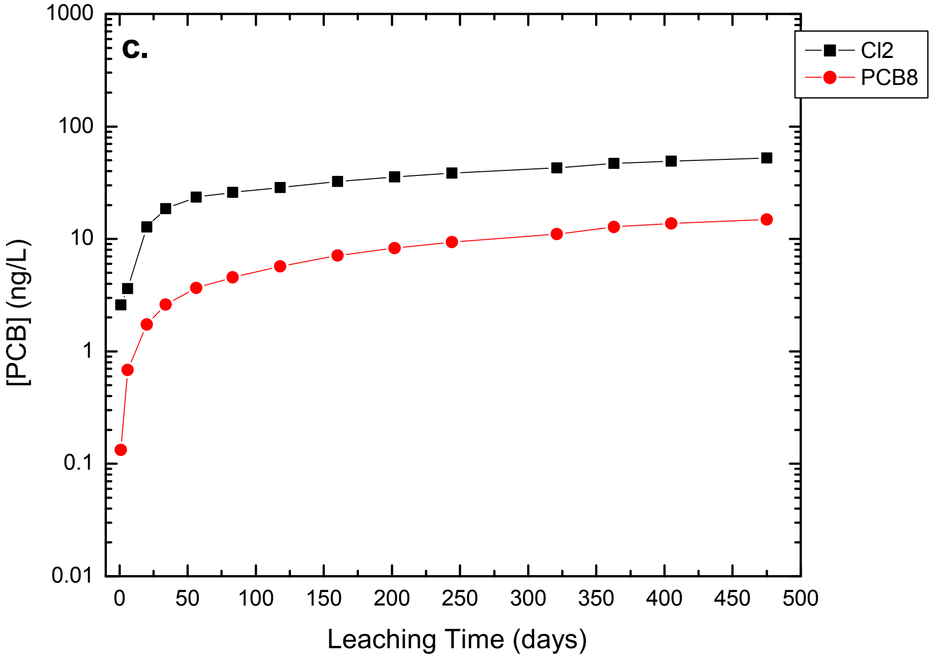
Felt Gasket/Inner (FGI) Leaching Behavior

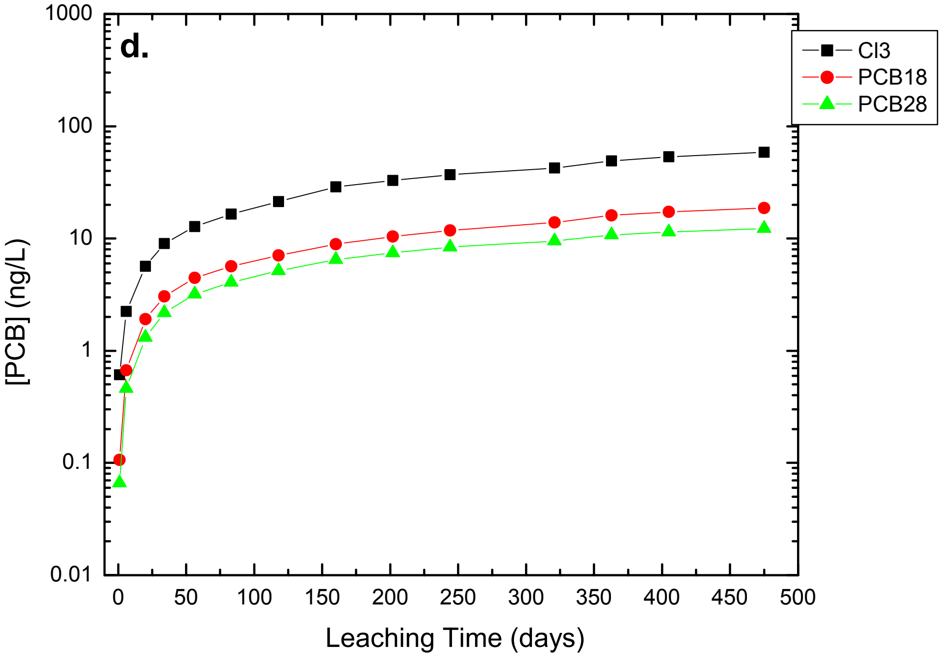
PCB concentration behaviors for FGI (2.9609 g), containing 682.0 mg (23.0 wt%) tPCBs exposed to a total leaching volume of 13.85 L at 25°C/~1 bar for nearly 500 days are shown in Figure

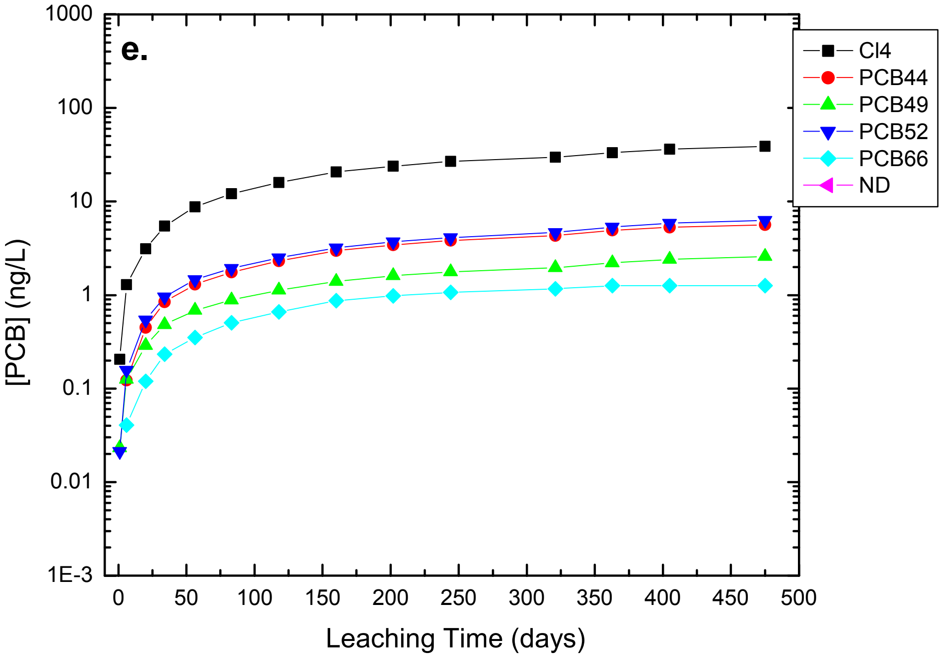
36(a), for which all ten homologue groups (Cl1-Cl10) contributed to the tPCB concentration curve behavior as a function of leaching time. Each of these ten homologue group curves is plotted with the corresponding target congeners in Figure 36(b-k). This sample was the only shipboard solid that exhibited some leaching of all possible homologue groups. One might consider that this sample perhaps has the highest probability of leaching the largest number of different target congeners, but it does not. Rather, the bulkhead insulation achieved this distinction, because the BHI sample likely contain both Aroclor 1254 and Aroclor 1268, overlapping well with the target congener list, which is biased towards a larger number of more common lower chlorinated congeners found in environmental samples.

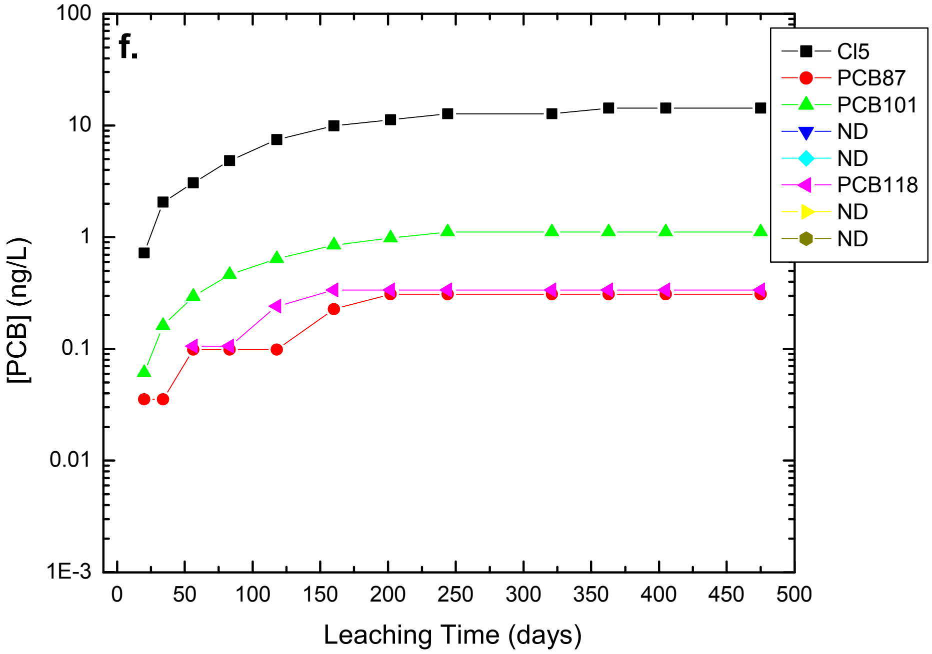


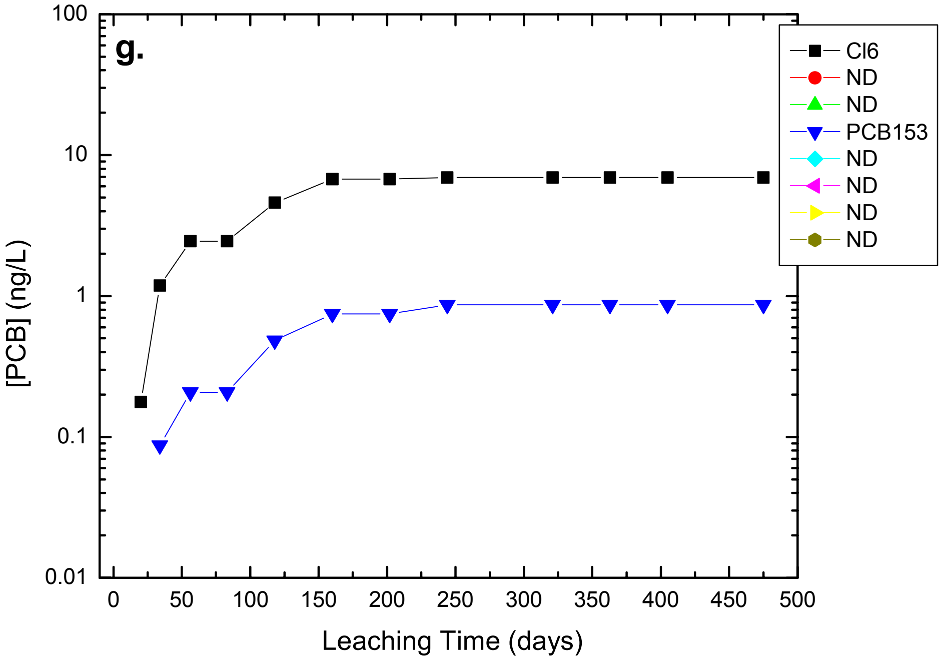

b.
Cl1
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)

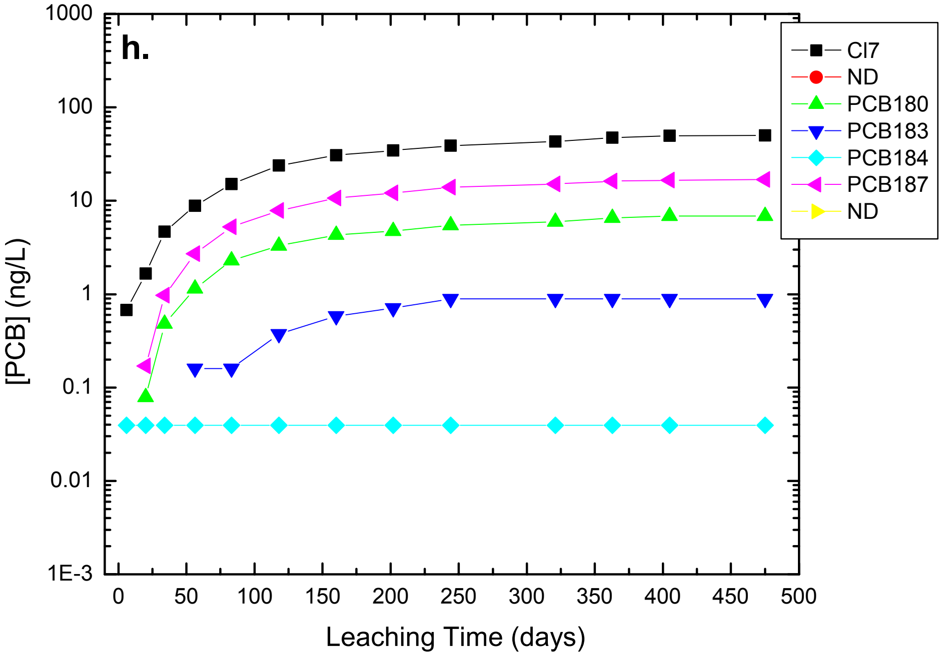

c.
Cl2
PCB8
1000
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)

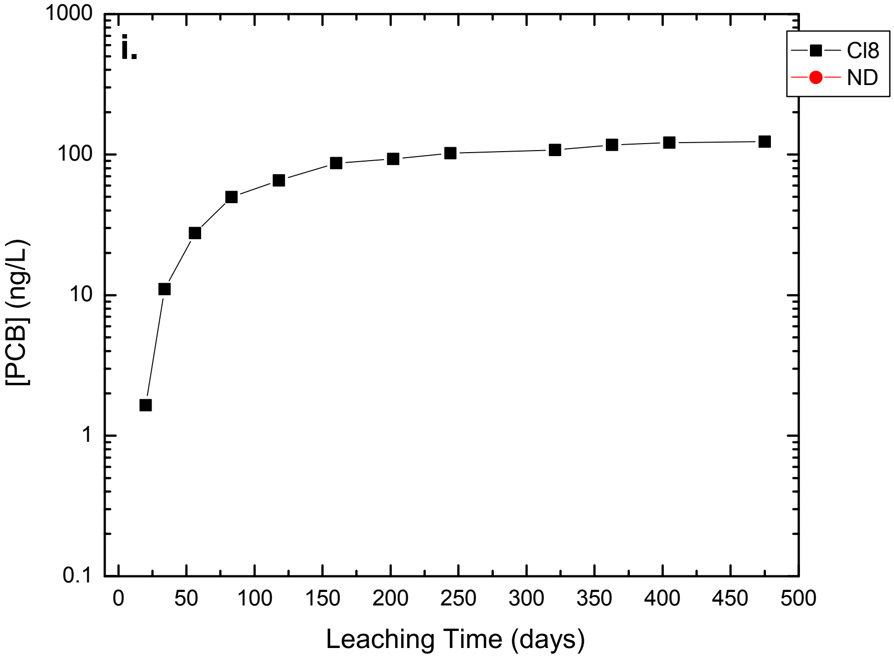

d.
Cl3
PCB18
PCB28
[PCB] (ng/L)
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)

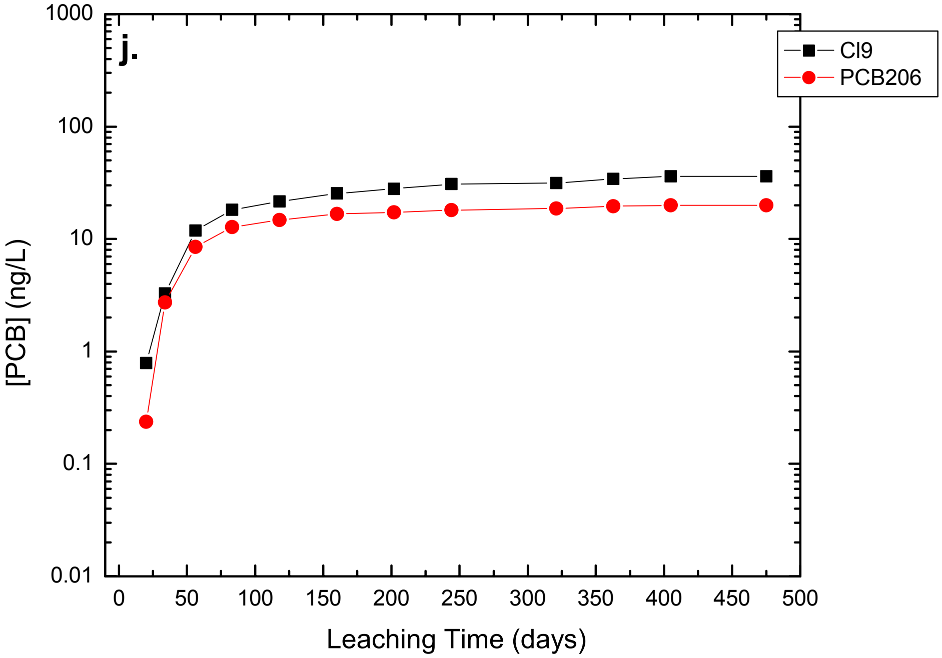

e.
Cl4
PCB44
PCB49
PCB52
PCB66
ND
[PCB] (ng/L)
1000
100
10
1
0.1
0.01
1E-3
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


f.
[PCB] (ng/L)
100
10
1
0.1
0.01
1E-3
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl5
PCB87
PCB101
ND
ND
PCB118
ND
ND


g.
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl6
ND
ND
PCB153
ND
ND
ND
ND


h.
1000
100
10
1
0.1
0.01
1E-3
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl7
ND
PCB180
PCB183
PCB184
PCB187
ND


i.
1000
100
10
1
0.1
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl8
ND



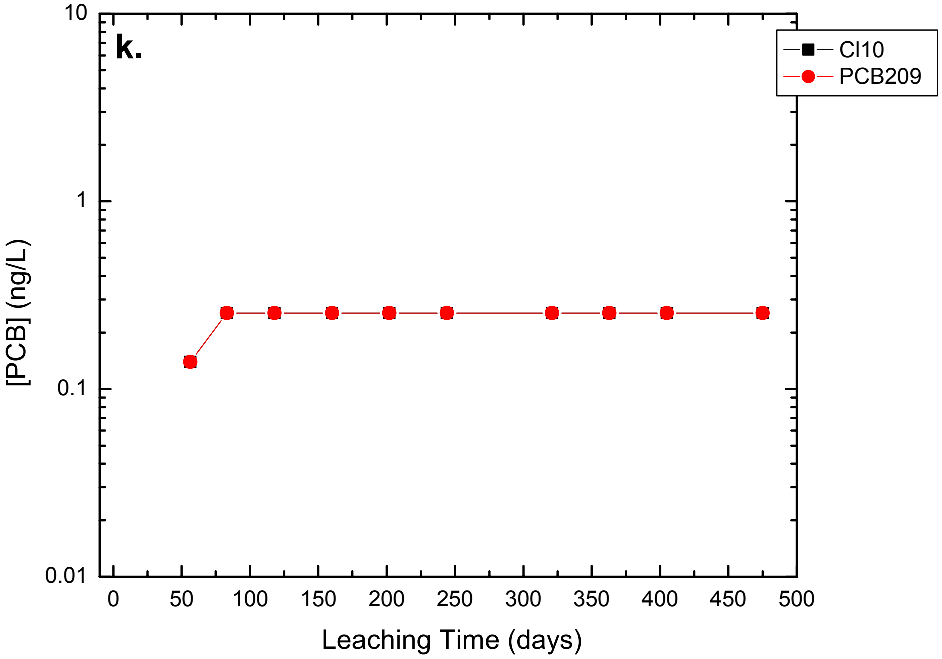


Figure 36 (a-k). Experimental PCB concentration vs. leaching time for FGI containing 682.0 mg (23.0 wt%) tPCBs exposed to a total volume of 13.85 L of seawater leachate. Plot a) shows tPCBs concentration and contributing homologue group concentrations vs. leaching time, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-k) are homologue group concentrations and target congener concentrations within homologue groups Cl1-Cl10 vs. leaching time.

Total released homologue and congener distributions are shown in Figure 37, compared with the initial PCB signatures for FGI solid. All detected homologues and congeners are normalized and plotted as percent of measured tPCBs in each matrix (leachate vs. solid). In many instances the percent contribution of an analyte to tPCBs was < 0.1%. Such a low level in the solid can still be significant if the analyte leaches into seawater, as shown in the leachate PCB signatures. The most significant levels of release from FGI were from homologue groups Cl2-Cl9.

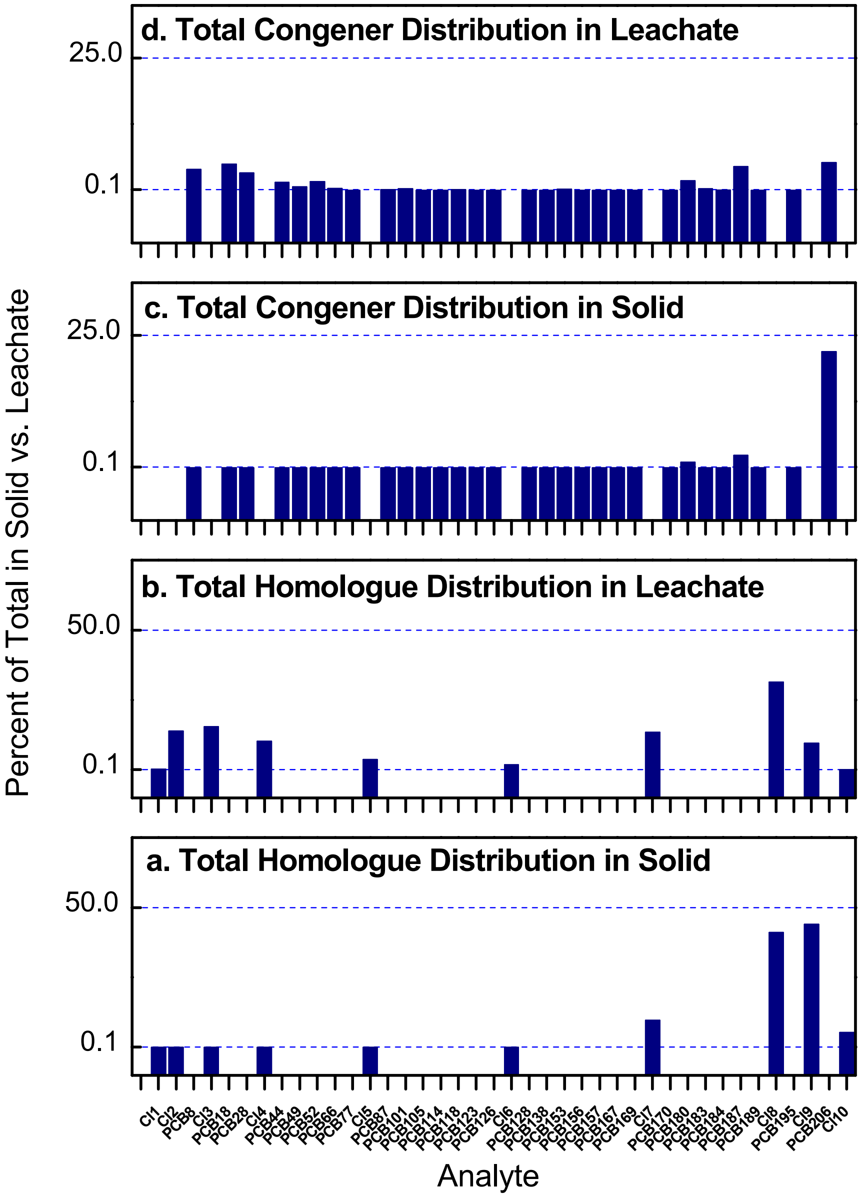


Figure 37 (a-d). Experimental homologue and congener PCB signatures for FGI solid (a & c) compared with total homologue and congener distributions of PCBs leached from FGI into seawater (b & d). The leachate distributions correspond to all PCBs released during the experiment and are derived from the cumulative leachate concentration endpoint analytes plotted in **Figure 36**. The solid distributions correspond to the initial PCB content in FGI solid, determined from the leaching experiment mass balance performed at the conclusion of the experiment. An offset linear scale is used to plot analytes present at levels below 0.1%, but the degree of experimental variance at these very low sub-percentage levels is not visible on the scale shown here. This can be seen in the mass balance tables found in APPENDIX C.

Normalized fingerprints for specific FGI leachate samples are presented below at key intervals across the entire leaching experiment (exposure time). Figure 38homologue group fingerprints correspond to a) the maximum leach rate, b) the broadest homologue and congener distributions, c) the first detection of monochlorobiphenyl, and d) the final empirical leach rate, at which point the narrowest homologue and congener distributions were observed, concurrent with a significant reduction in the octachlorobiphenyl group. The corresponding target congeners are depicted in Figure 39(a-d), where b) shows the first detection of decachlorobiphenyl, observed only twice during leaching in this experiment.

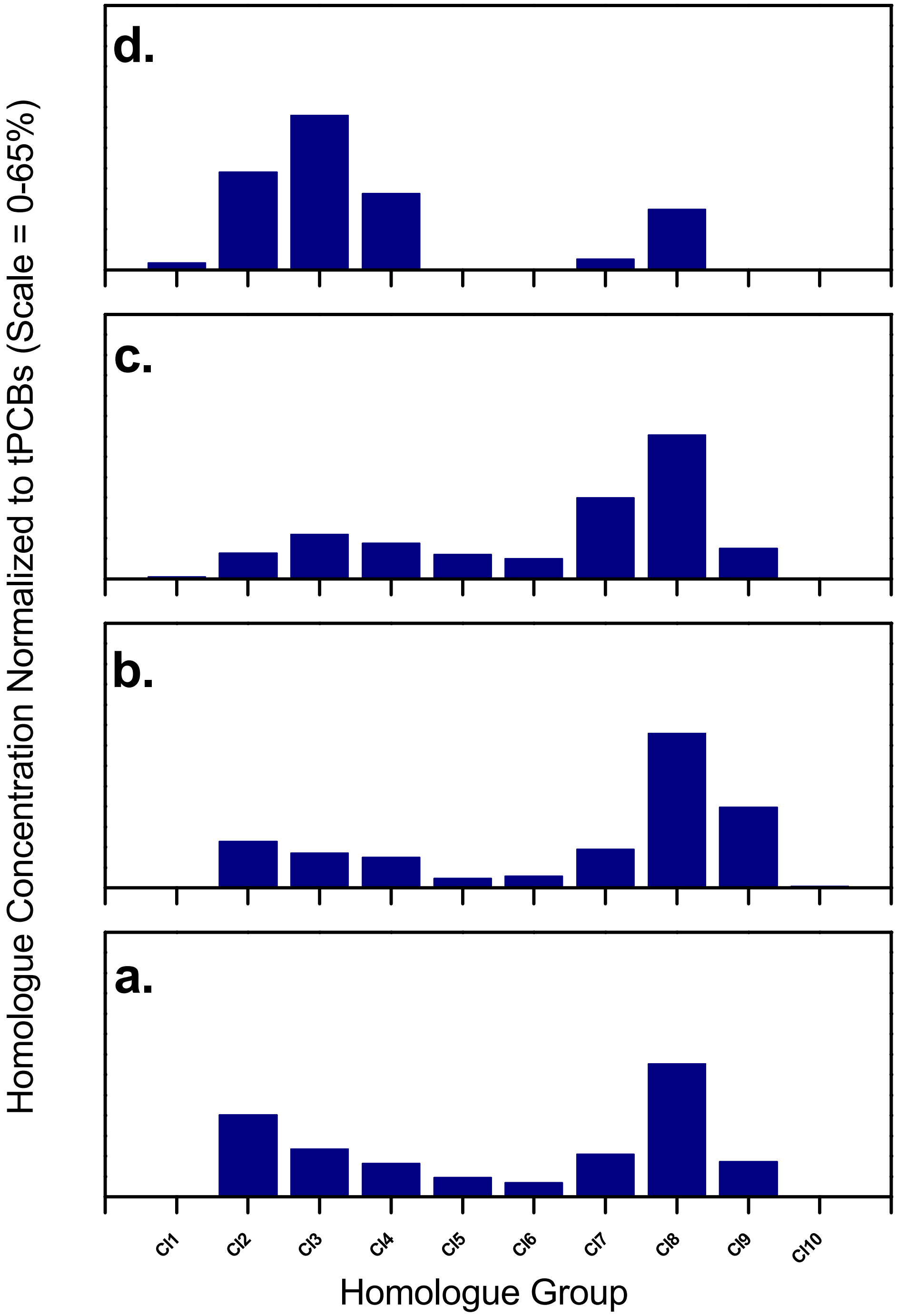


Figure 38 (a-d). Homologue fingerprints during the FGI leaching experiment, normalized as percent of total, for leaching intervals a) 20 to 34 days, b) 34 to 56 days, c) 83 to 118 days, d) 405 to 475 days.

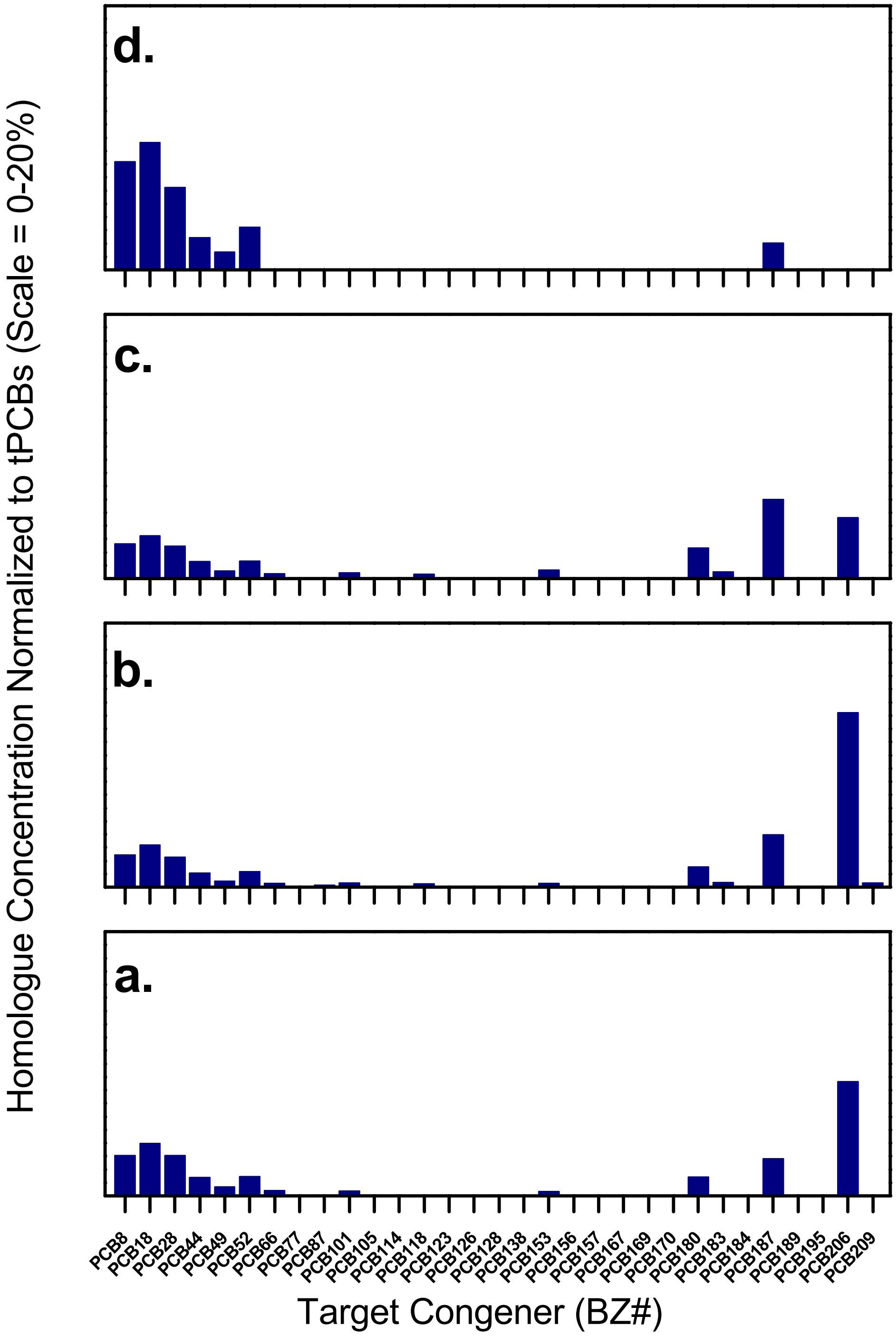
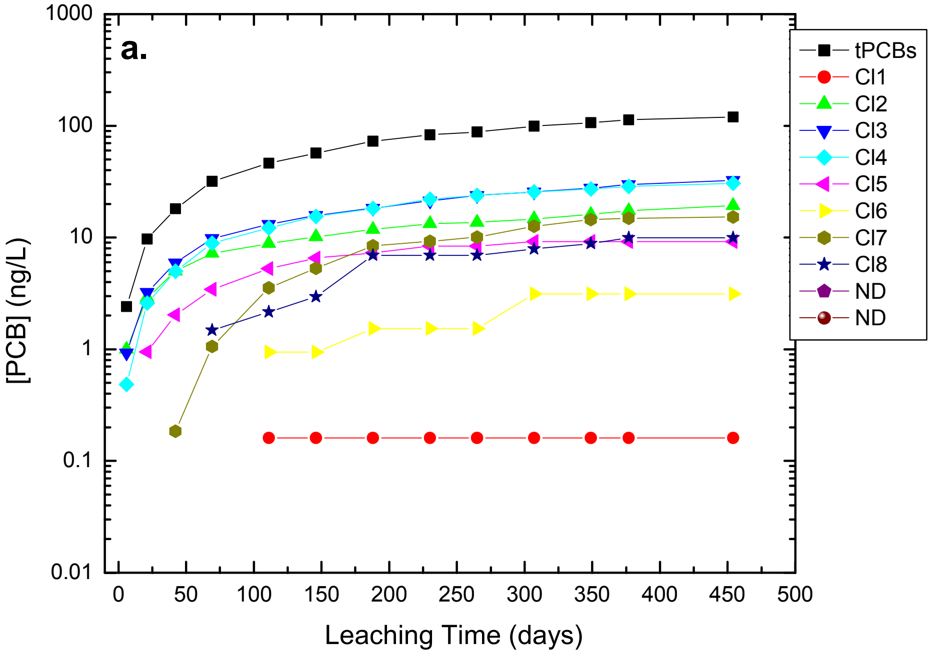
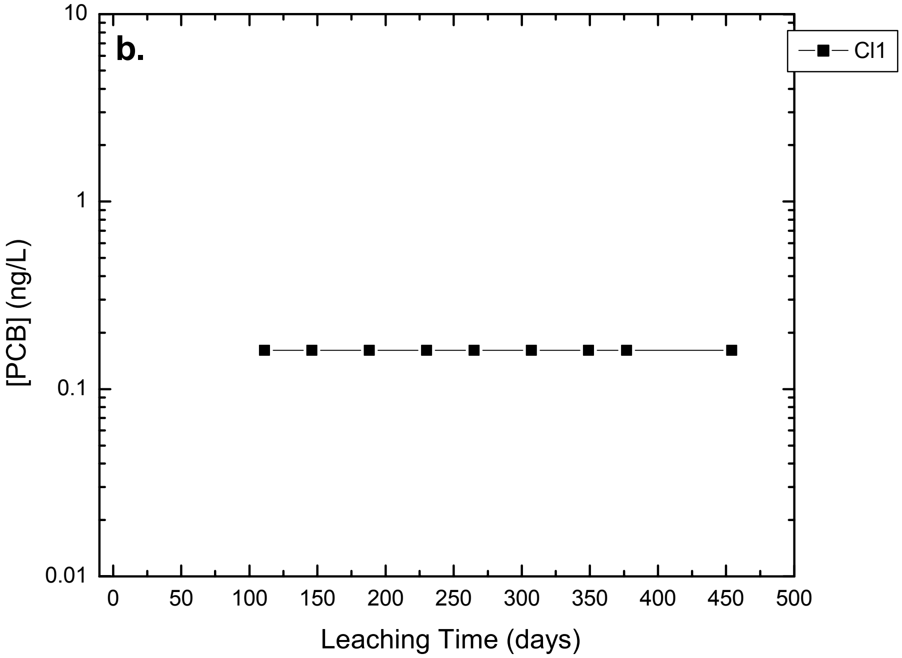


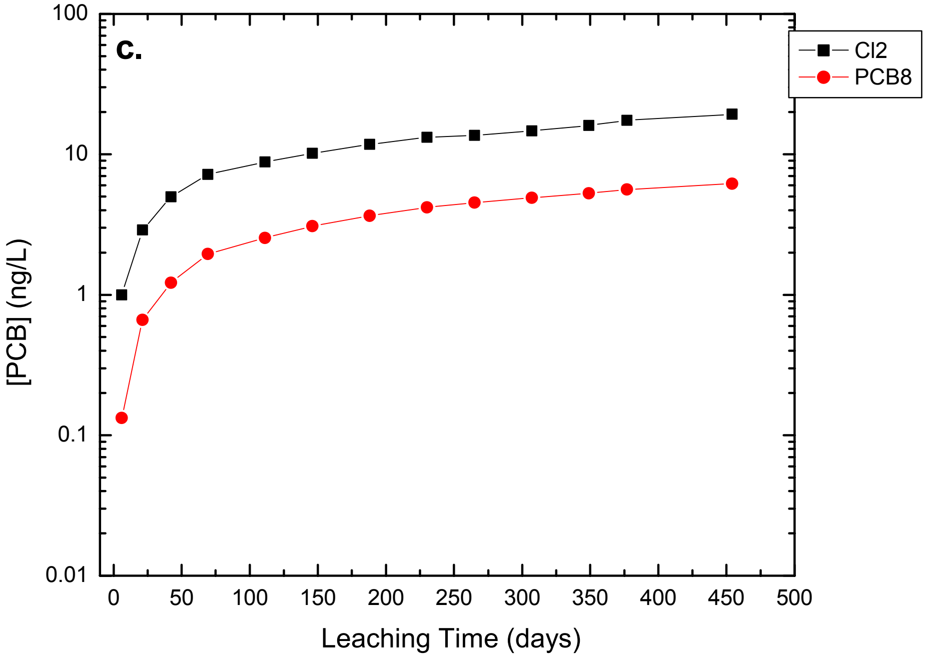
Figure 39 (a-d). Congener fingerprints during the FGI leaching experiment, normalized as percent of total, for leaching intervals a) 20 to 34 days, b) 34 to 56 days, c) 83 to 118 days, d) 405 to 475 days.

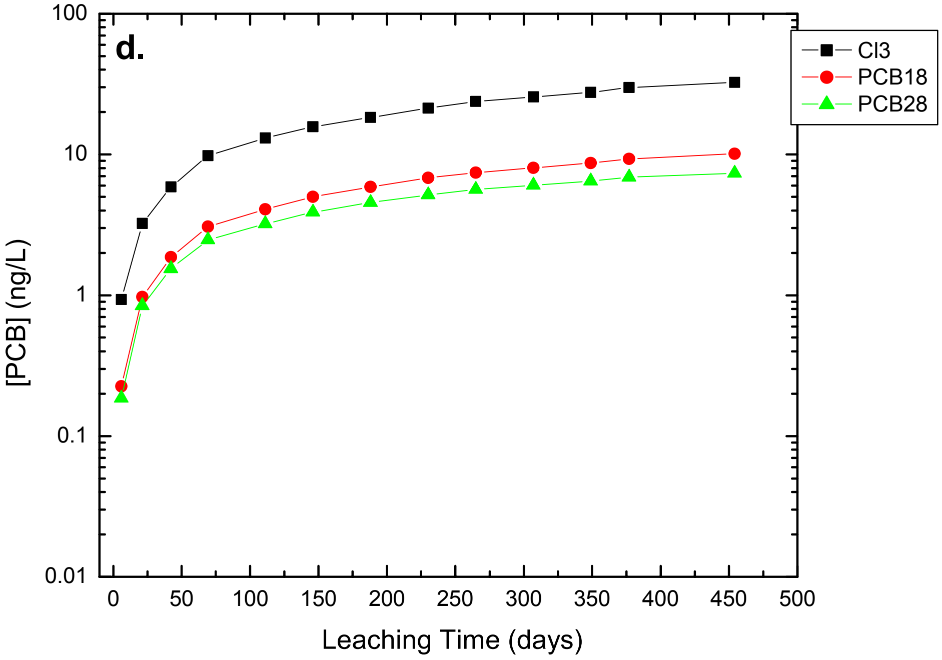
Felt Gasket/Outer (FGO) Leaching Behavior

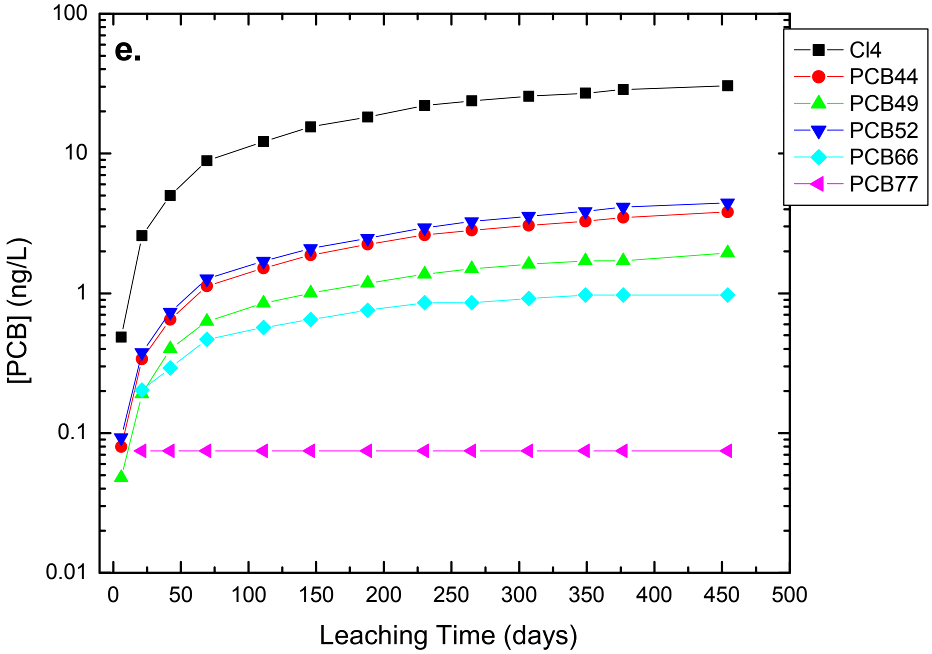
The leaching concentration behavior for FGO (0.955 g), containing 112.1 mg (11.7 wt%) tPCBs, leached at 25°C/~1 bar for nearly 500 days, and exposed to 13.86 L total seawater volume is shown in Figure 40(a) for tPCB and detected homologues Cl1-Cl8. These homologue curves are plotted in Figure 40(b-i) with the corresponding detected target congeners within each homologue group. This sample also exhibited an Aroclor 1268 signature and was associated with the same flange, i.e. was physically a part of the same felt gasket as the FGI sample. However, it was smaller, painted, and likely contained less Aroclor 1268 character. These differences were considered significant enough relative to FGI to expect it to exhibit a unique leaching behavior.

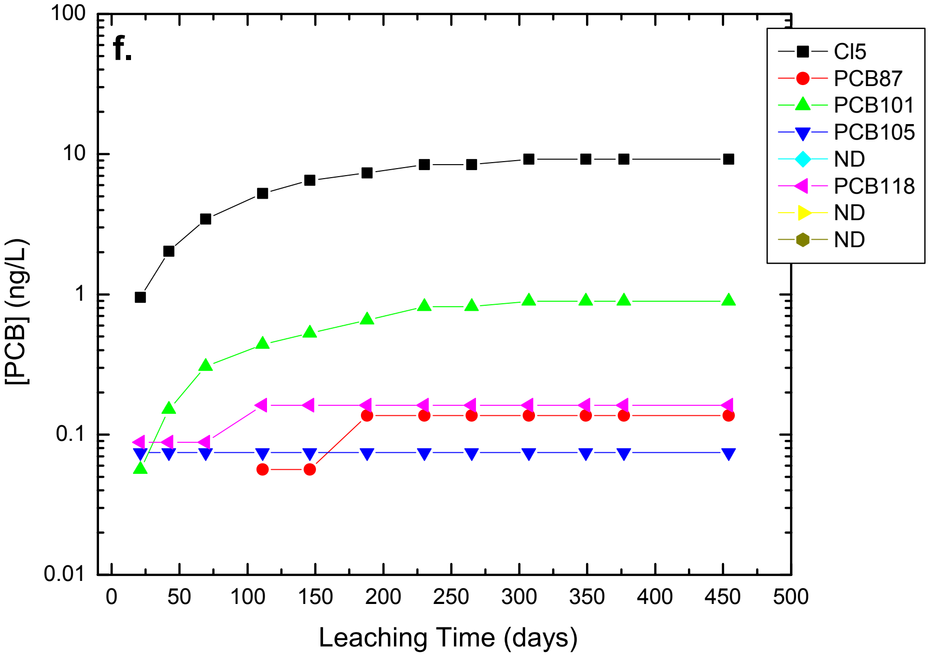


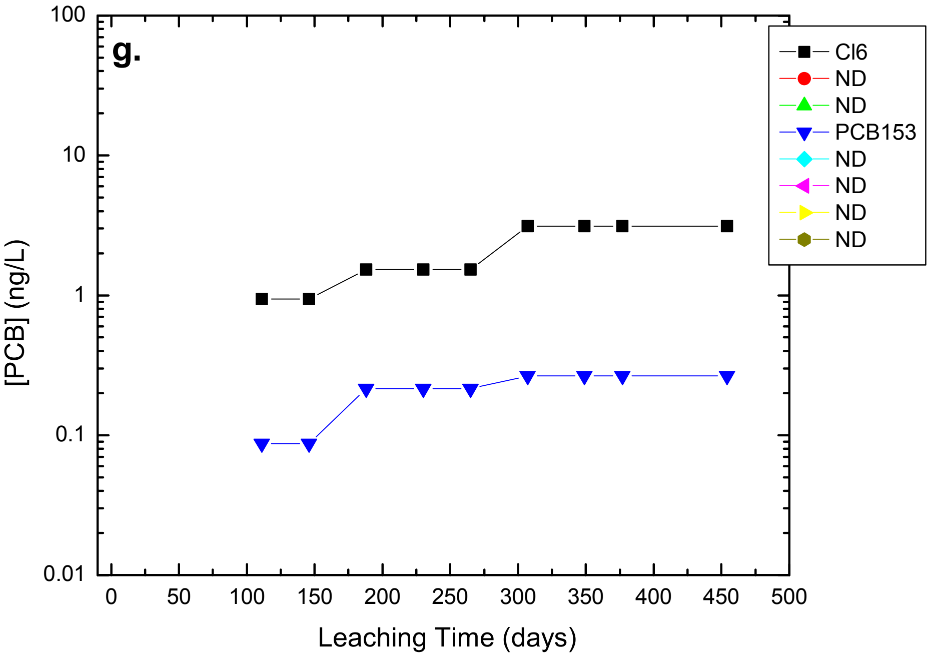

b.
Cl1
[PCB] (ng/L)
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)

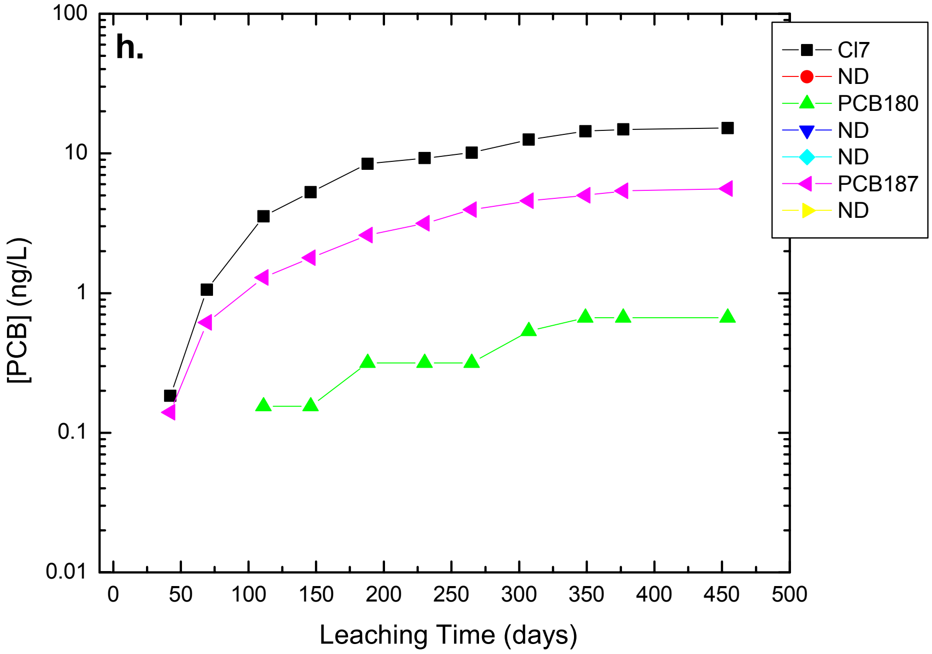

c.
Cl2
PCB8
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


d.
Cl3
PCB18
PCB28
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


e.
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)


f.
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
ND
PCB118
ND
ND


g.
100
10
1
0.1
0.01
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl6
ND
ND
PCB153
ND
ND
ND
ND



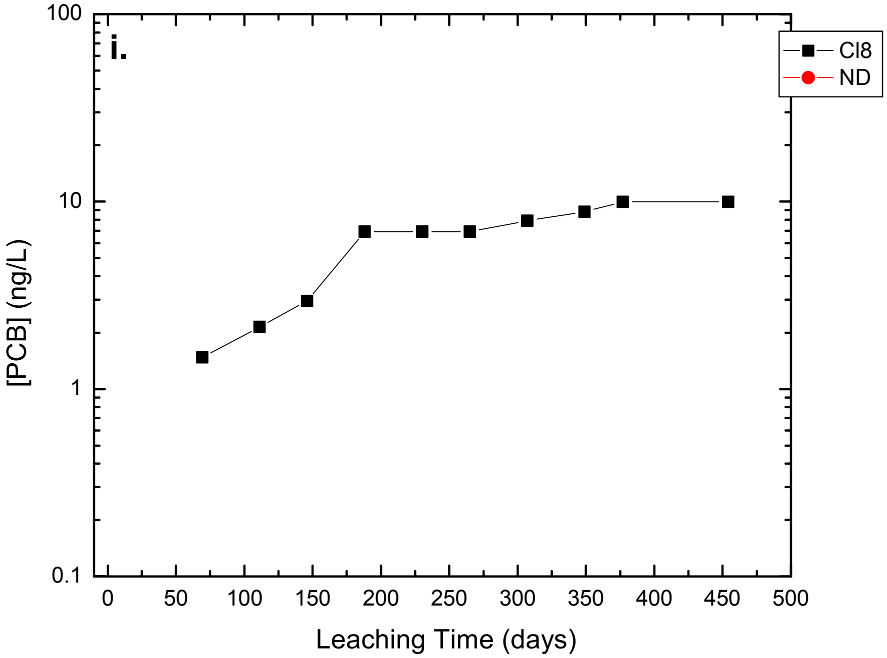


Figure 40 (a-i). Experimental PCB concentration vs. leaching time for FGO containing 112.1 mg (11.7 wt%) tPCBs exposed to a total volume of 13.86 L of seawater leachate. Plot a) shows the tPCBs concentration and contributing homologue group concentrations vs. leaching time, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-i) are . homologue group concentrations and target congener concentrations within homologue groups Cl1-Cl8 vs. leaching time.

Total released homologue and congener distributions are shown in Figure 41, compared with the initial PCB signatures determined for FGO solid. All detected homologues and congeners are normalized and plotted as percent of measured tPCBs in each matrix (leachate vs. solid). In many instances the percent contribution of an analyte to tPCBs was < 0.1%, however this content level in the solid can still be significant if the analyte leaches into seawater, as shown in the leachate PCB signatures. The most significant levels of release from FGO were from homologue groups Cl2-Cl9.

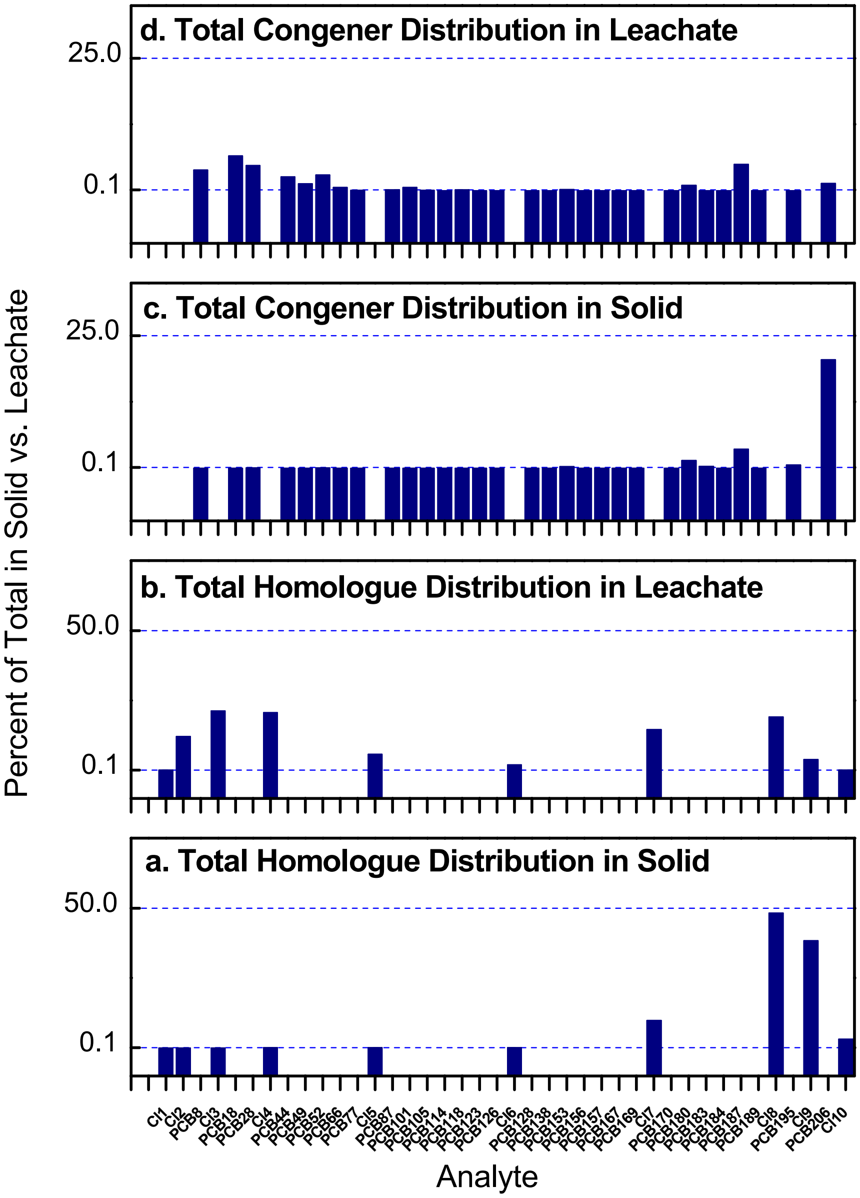


Figure 41 (a-d). Experimental homologue and congener PCB signatures for FGO solid (a & c) compared with total homologue and congener distributions of PCBs leached from FGO into seawater (b & d). Leachate distributions are derived from the accumulative leachate concentration endpoint for analytes plotted in **Figure 24** and correspond to all PCBs released during the leaching experiment. The solid distributions correspond to the initial pre-leaching PCB content in FGO solid, derived from the leaching experiment mass balance performed at the experiment conclusion. Analytes present at levels below 0.1% are plotted using an offset linear scale to indicate the presence of the analyte, but experimental variances are not visible on the scale shown. The experimental values that show the degree of variance at these very low sub-percentage levels can be found in the mass balance tables in APPENDIX C.

Specific leachate fingerprints are included below at key intervals across the entire FGO leaching experiment (exposure time). Figure 42homologue group fingerprints correspond to a) the maximum leach rate, b) the broadest homologue and congener distributions observed, characterized by intermittent appearance of the hexachlorobiphenyl group and a single detection of the monochlorobiphenyl group, c) the narrowest homologue distribution, characterized by a decrease in pentachlorbiphenyl and octachlorbiphenyl group contributions, and d) the final empirical leach rate. The respective target congener fingerprints are shown in Figure 43(a-d), where b) illustrates the last detections for PCB 87 and PCB 118 over the leaching experiment.

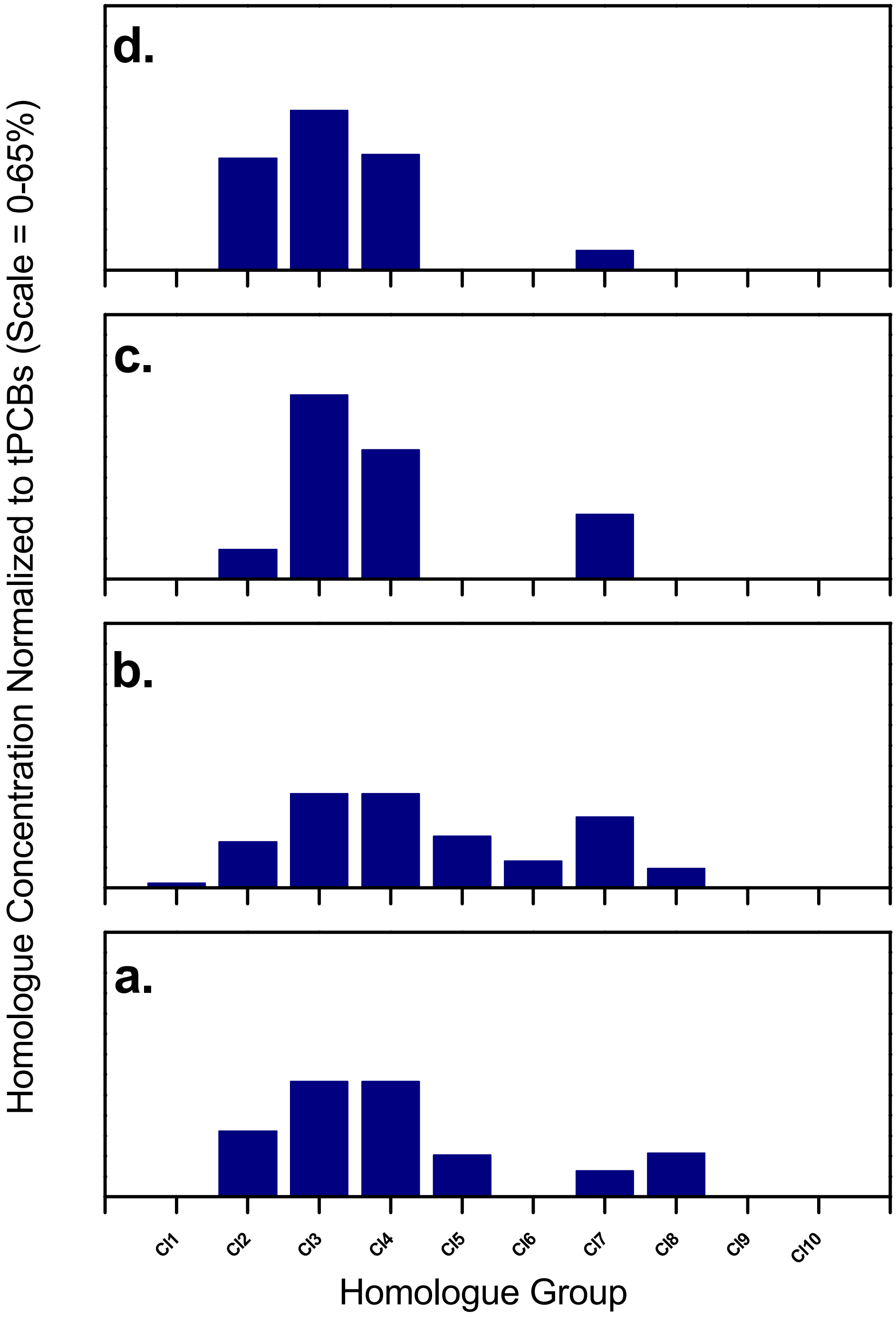


Figure 42 (a-d). Homologue fingerprints during the FGO leaching experiment, normalized as percent of total, corresponding to leaching intervals a) 42 to 69 days, b) 69 to 111 days, c) 230 to 265 days, d) 377 to 454 days.

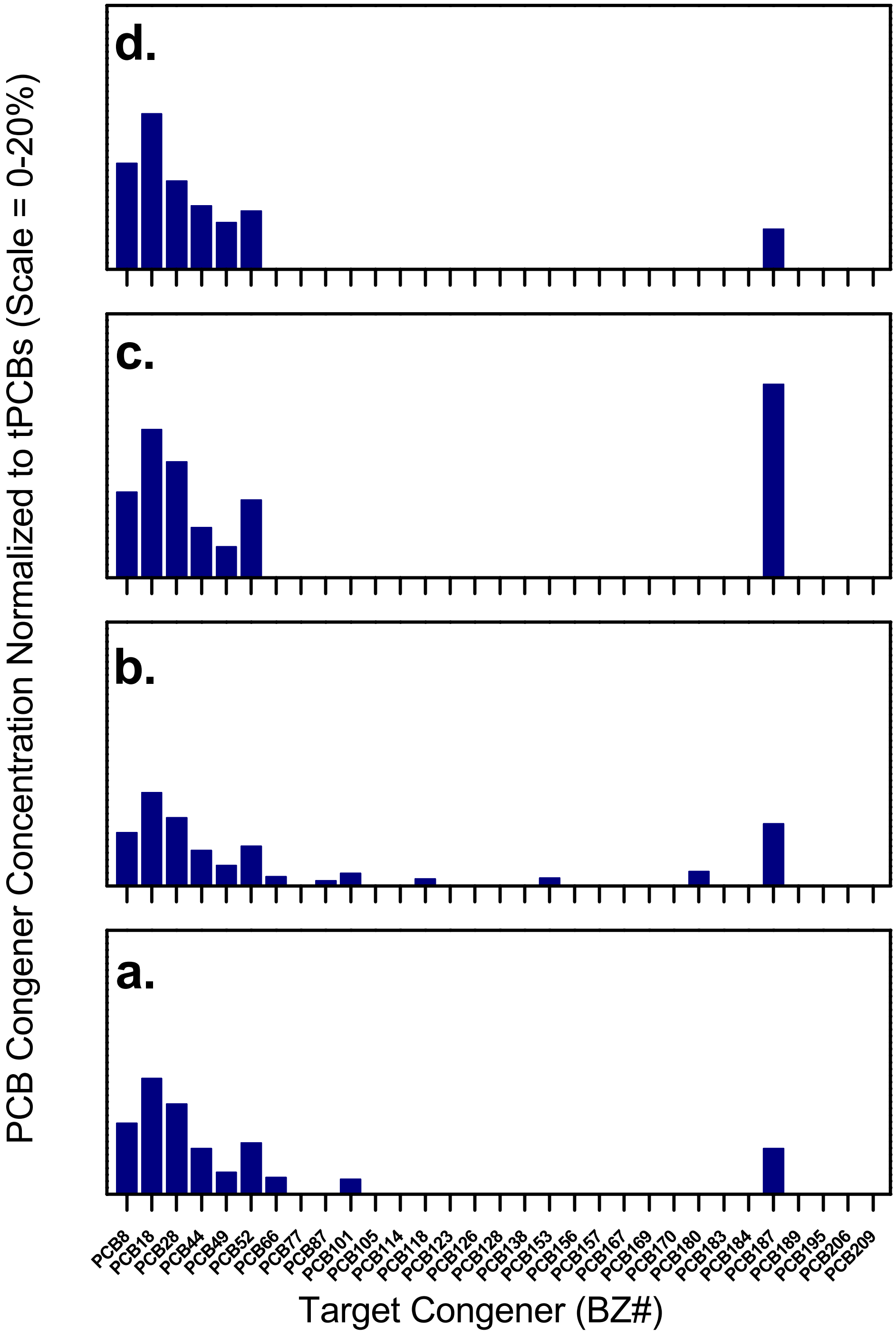
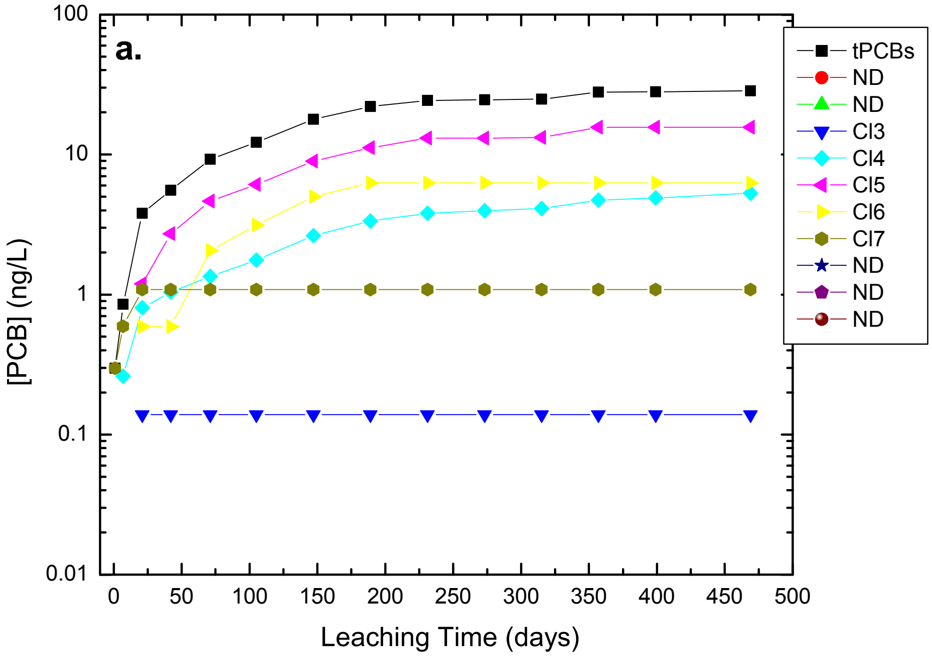
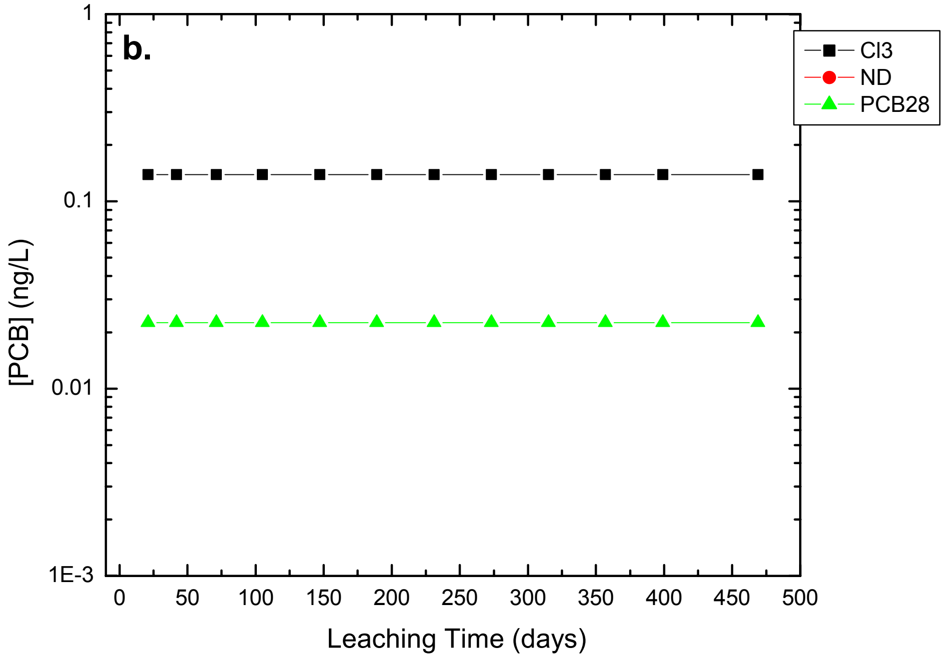


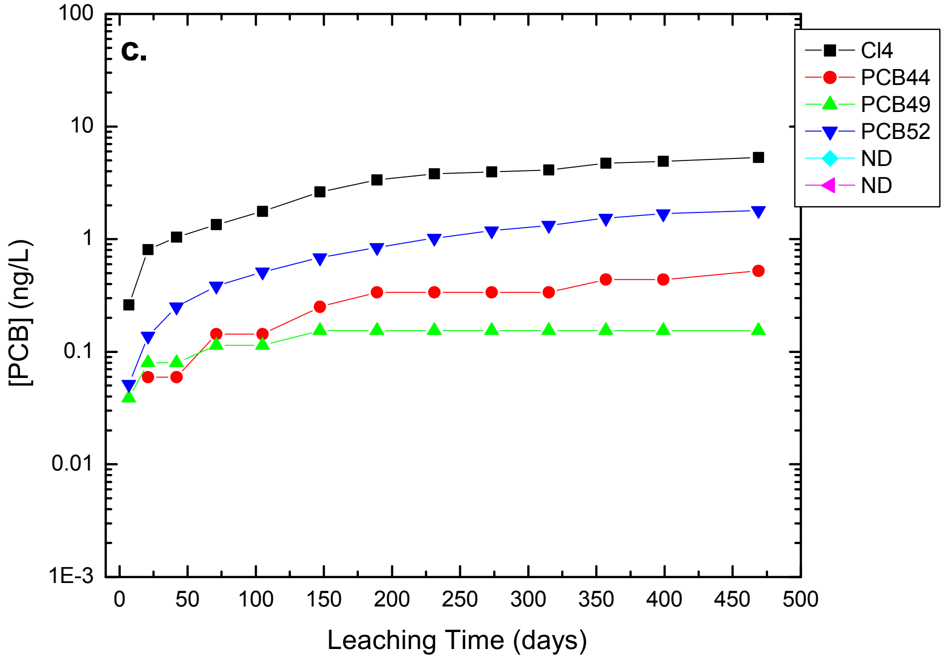
Figure 43 (a-d). Congener fingerprints during the FGO leaching experiment, normalized as percent of total, corresponding to leaching intervals a) 42 to 69 days, b) 69 to 111 days, c) 230 to 265 days, d) 377 to 454 days.

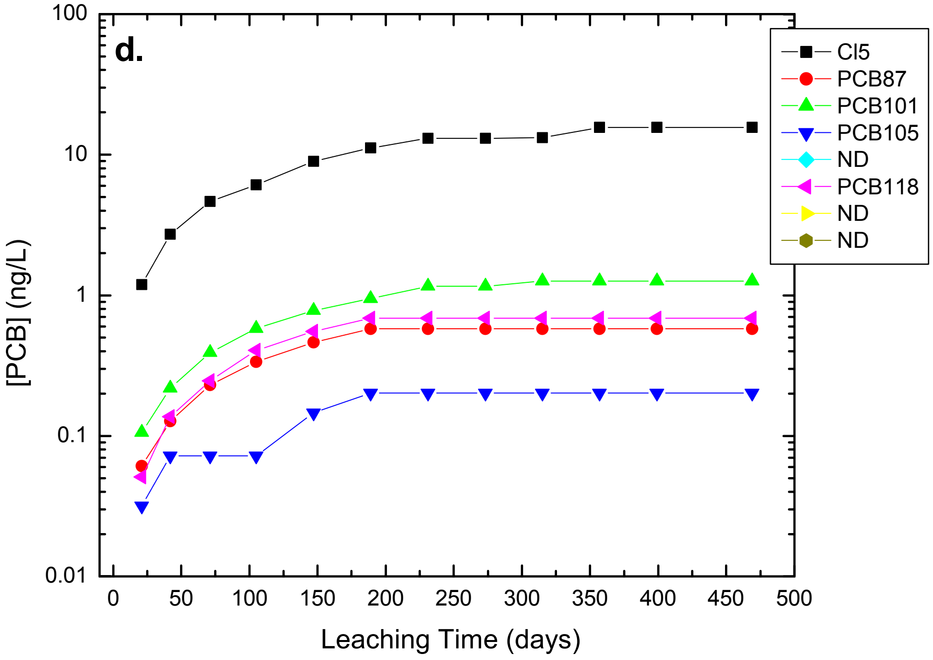
Aluminized Paint (AP) Leaching Behavior

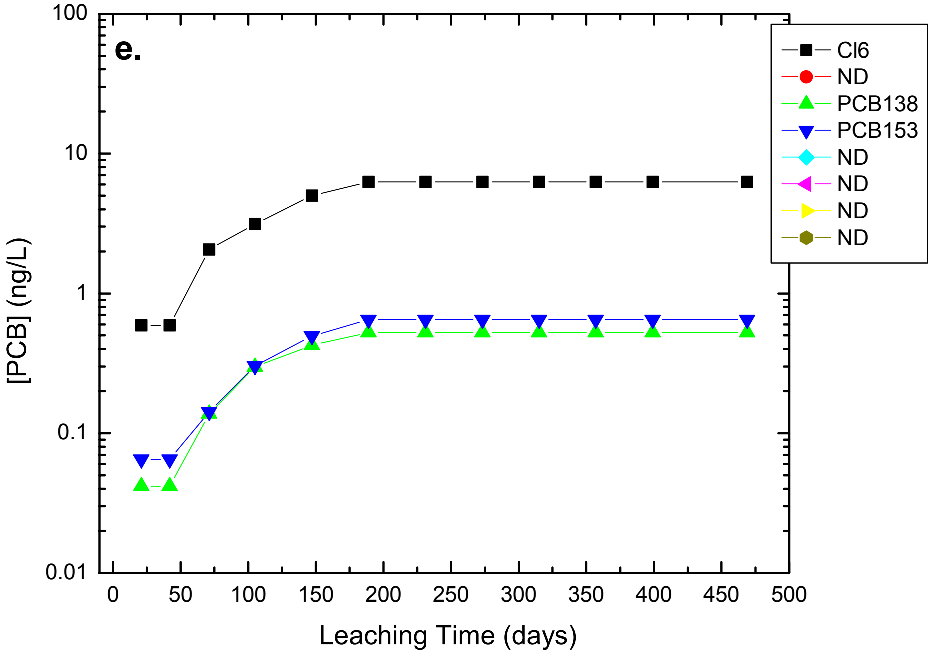
The leaching behavior for the AP subsample (1.223 g), containing 0.52 mg (0.043 wt%) at 25^{o}C/~1 bar for nearly 500 days and exposed to a total volume of 13.89 L of seawater leachate is shown in Figure 44(a) for tPCBs and detected homologues Cl3-Cl7. Each of these homologue curves is again plotted with corresponding target congeners in Figure 44(b-f). This sample leached the least number of different homologue groups out of all leached solids, but this does not necessarily translate into a lower leach rate overall. The leach rate is dependent upon the change in concentration over a change in time, not the simply the diversity of PCB congeners or homologues that leach out over time. This will be discussed in detail within the Leach Rate Calculations (**<u>RESULTS AND DISCUSSION</u>** section) in this report.




b.
1
0.1
0.01
1E-3
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl3
ND
PCB28


c.
100
10
1
0.1
0.01
1E-3
[PCB] (ng/L)
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
ND
ND


d.
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
ND
PCB118
ND
ND


e.
[PCB] (ng/L)
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Leaching Time (days)
Cl6
ND
PCB138
PCB153
ND
ND
ND
ND

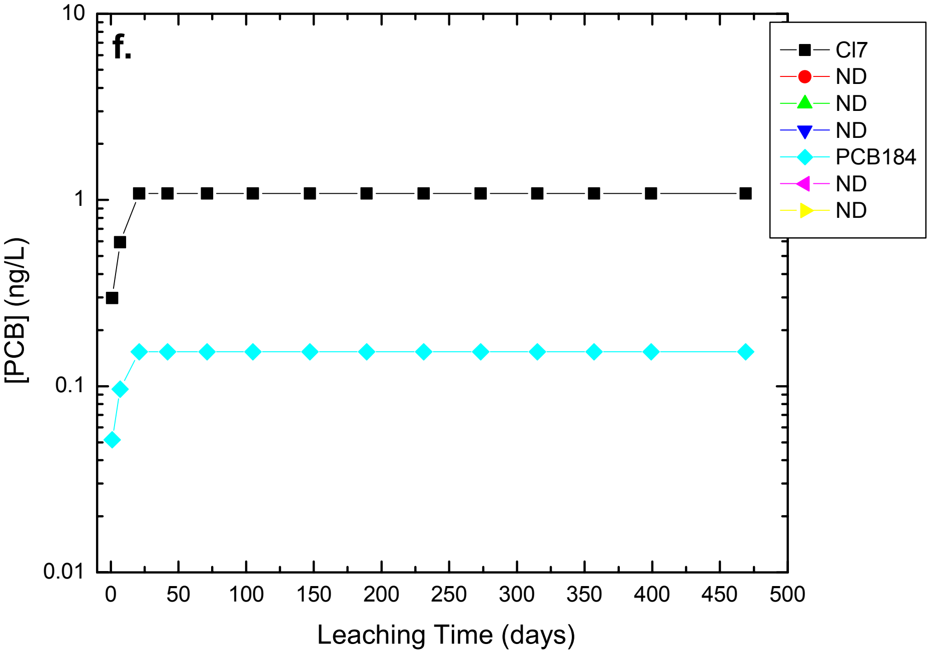


Figure 44 (a-f). Experimental PCB concentration vs. leaching time for AP containing 0.52 mg (0.043 wt%) tPCBs exposed to a total volume of 13.89 L of seawater leachate, Plot a) shows tPCBs concentration and contributing homologue group concentrations vs. leaching time, where the sum of the homologue curves is equal to the upper tPCB curve. Plots (b-f) are homologue group concentrations and target congener concentrations within homologue groups Cl3-Cl7 vs. leaching time.

Total released homologue and congener distributions are shown in Figure 45, compared with the initial PCB signatures for AP solid. The detected homologues and congeners are normalized and plotted as percent of measured tPCBs in each matrix (leachate vs. solid). In both matrices the percent contribution of some analytes to tPCBs was < 0.1%. Such a low level in the solid can still be significant if the analyte leaches into seawater, as shown in the leachate PCB signatures. The most significant levels of release from AP were from homologue groups Cl3-Cl7.

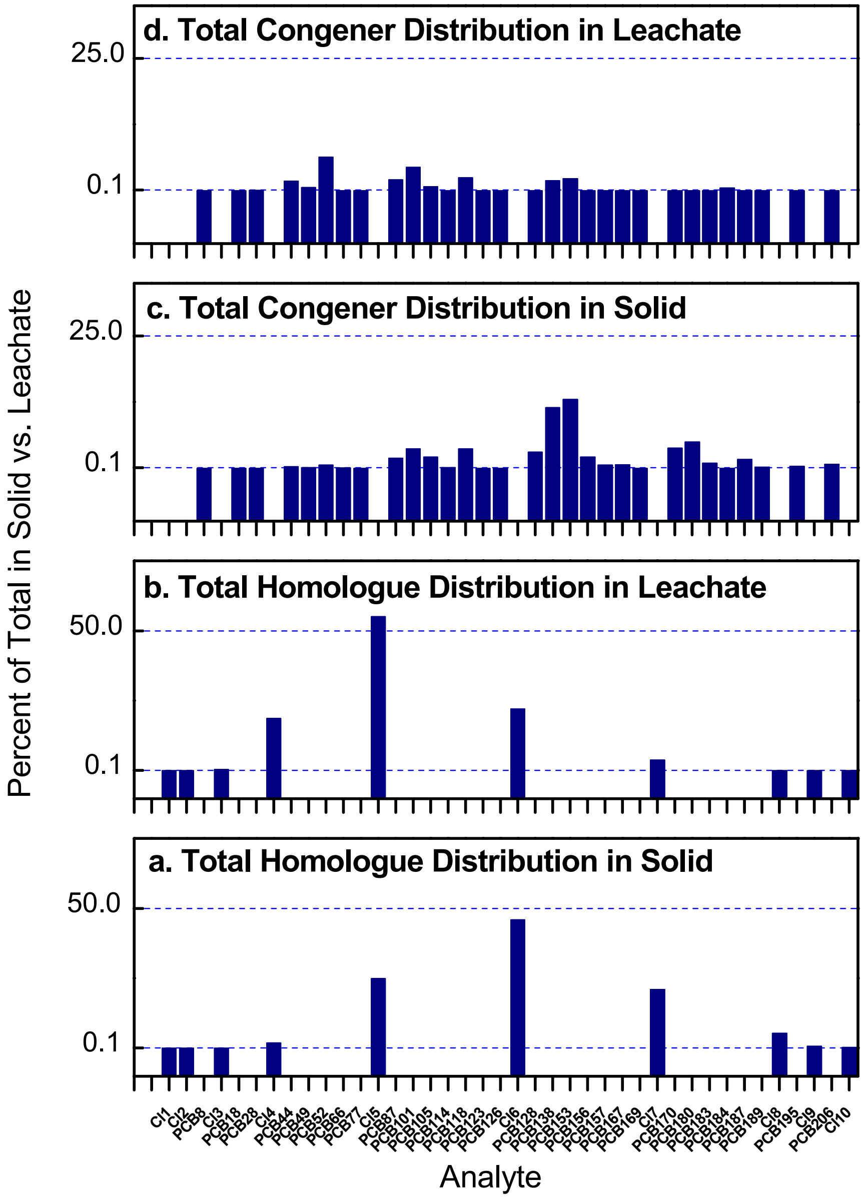


Figure 45 (a-d). Experimental homologue and congener PCB signatures for AP solid (a & c) compared with total homologue and congener distributions of PCBs leached from AP into seawater (b & d). The leachate distributions correspond to all PCBs released over the entire experiment and are derived from the cumulative leachate concentration endpoint for analytes plotted in **Figure 44**. Solid distributions correspond to the initial PCB content in AP solid, derived from the post-leaching mass balance performed at the end of the experiment. Analytes present at levels below 0.1% are plotted on an offset linear scale to indicate their presence, but this scale is not conducive to observing the degree of experimental variance at these very low sub-percentage levels. The experimental values showing the experimental variance can be found in the mass balance tables included in APPENDIX C.

Normalized fingerprints are shown below for specific AP leachate samples at key intervals across the entire leaching experiment (exposure time). Figure 46homologue group fingerprints correspond to a) the maximum leach rate, broadest homologue and congener distributions, and a single detection of the trichlorobiphenyl group, b) the final detection of the hexachlorobiphenyl group, c) increase of the tetrachlorobiphenyl group with a concurrent decrease in pentachlorobiphenyl group, and

d) the final empirical leach rate, characterized by the narrowest homologue and congener distributions (entirely tetrachlorobiphenyl). The corresponding target congener fingerprints are depicted in Figure 47(a-d), where a) illustrates the single detection of PCB 28 and the final detection of PCB 184 in the leaching experiment.

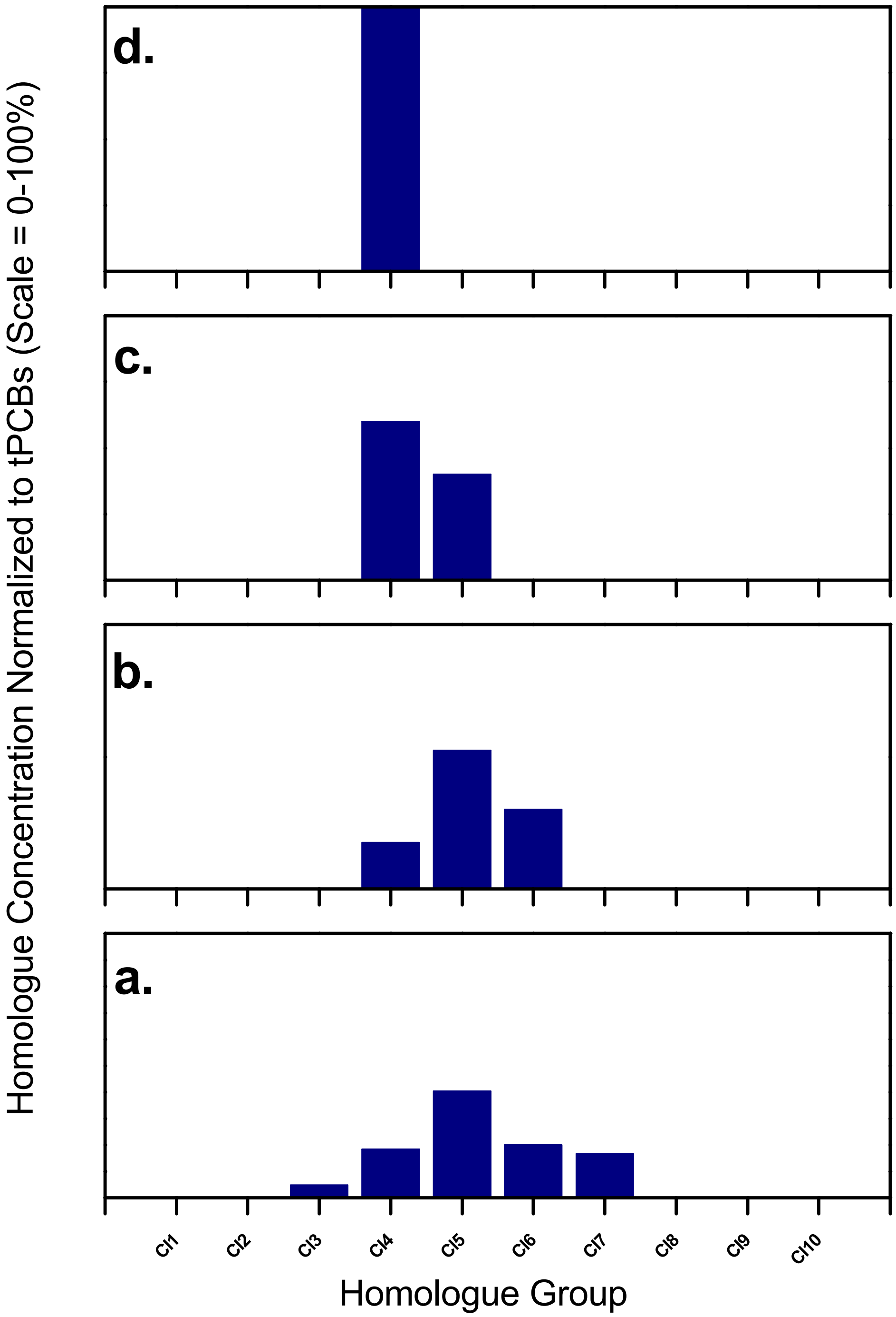


Figure 46 (a-d). Homologue fingerprints during the AP leaching experiment, normalized as percent of total, for leaching intervals a) 7 to 21 days, b) 147 to 189 days, c) 273 to 315 days, d) 399 to 469 days.

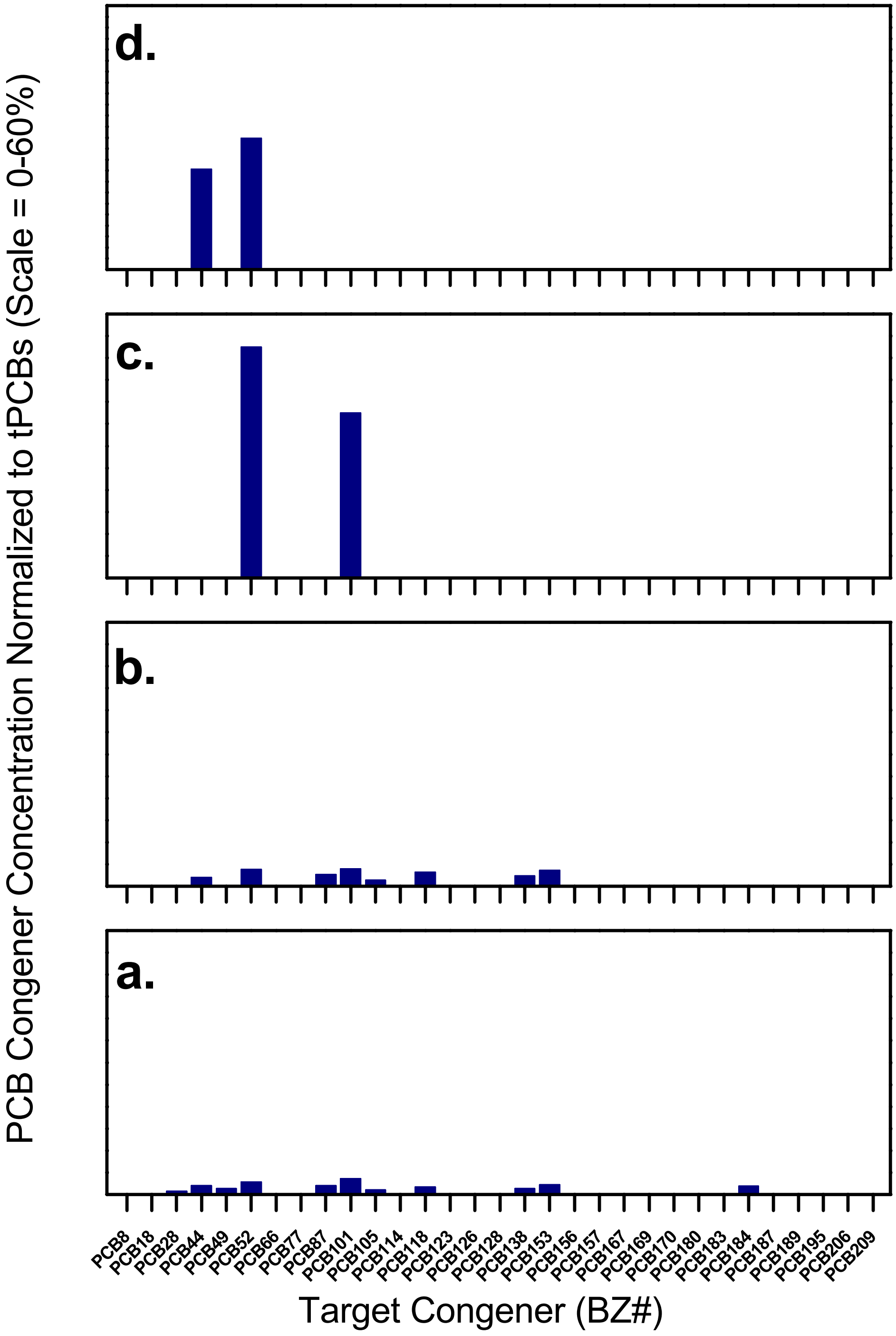


Figure 47 (a-d). Congener fingerprints during the AP leaching experiment, normalized as percent of total, for leaching intervals a) 7 to 21 days, b) 147 to 189 days, c) 273 to 315 days, d) 399 to 469 days.

RESULTS AND DISCUSSION

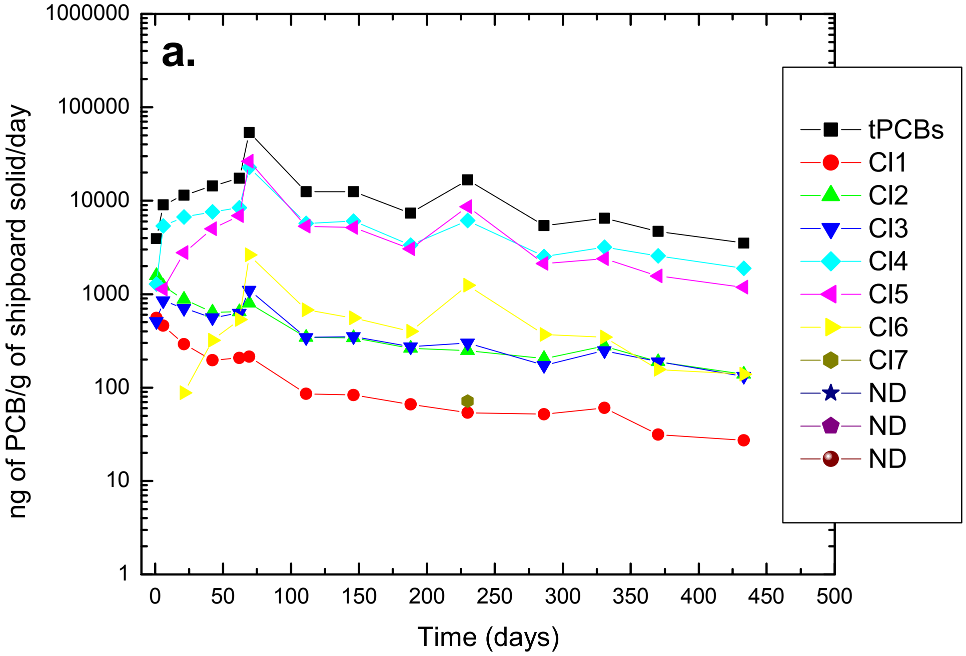
Average Leach Rate Calculations

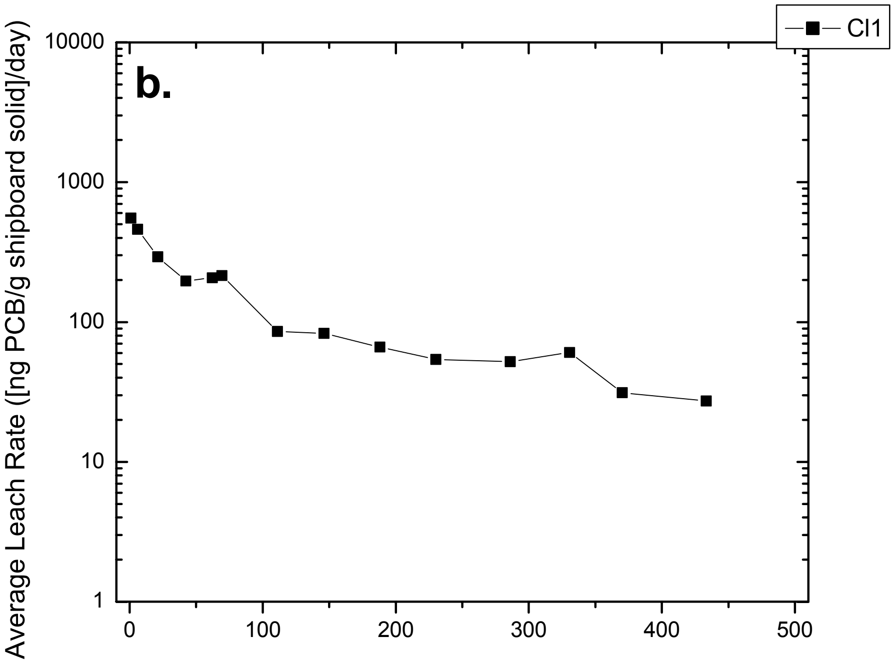
Average leach rates were calculated using the concentration versus time data from the **EMPIRICAL DATA AND OBSERVATIONS** section above. The average leach rate for any given analyte was calculated by the change in analyte concentration divided by the time over which the concentration change occurred, as was shown in Equation 1 and Equation 2. The average leach rates for the leaching experiments in this study were determined from the concentration change in seawater leachate samples divided by the corresponding incremental exposure time (sampling interval) associated with the solid, which is the difference in time between adjacent analyte data points on the concentration versus time curves. The average leach rates calculated for each sampling interval across the entire leaching experiment or exposure time were then plotted as a function of absolute exposure/leaching time. For purposes of evaluating average leach rate dynamics as a function of time, each experimental concentration vs. time plot above was converted into an average leach rate vs. time plot, shown in the sections below. These average leach rate curves can be related to the slopes between adjacent points on the respective concentration vs. time curves and plotting them as a function of time. Leach rates for all analytes for all leaching experiments, first achieved some maximum value over a period of days to months, and then slowly decreased over the remainder of the leaching series (experiment). In some instances, erratic leaching behavior was observed; typically evidenced very early in the leaching process by extreme variations (increases and decreases up to ~ an order of magnitude) in leach rate. Unstable behavior can be attributed to physical and chemical conditioning processes that a shipboard solid might undergo upon seawater exposure. These might include changes in surface wetting properties, rinsing of outer solid surfaces, solid degradation and/or decomposition processes, and other processes that act to change the accessibility of seawater to the PCBs in the solid. Generally, a curve that first exhibited unstable behavior was followed by an average leach rate curve that was considered indicative of the stabilized leaching condition. However, it is outside the scope of these studies to specifically correlate the observed unstable average rates to any changes in solid-specific properties. These curves were, instead, qualitatively evaluated relative to a practical leaching model, for which the leach rate is expected to exhibit some amount of variance upon initial seawater exposure and then achieve a stabilized release condition. The model describes a leach rate increase up to some maximum over a period of time that may or may not be observable within the experimental timeframe. This should be followed by a constant or decreasing rate with time, as PCBs are slowly depleted at different rates from the seawater accessible solid interface (SASA). After this maximum or plateau in rate, leaching eventually becomes limited by PCB availability, i.e. becomes diffusion-limited (limited by transport from the innermost regions of the solid to the leaching surface, as illustrated in Figure 3).

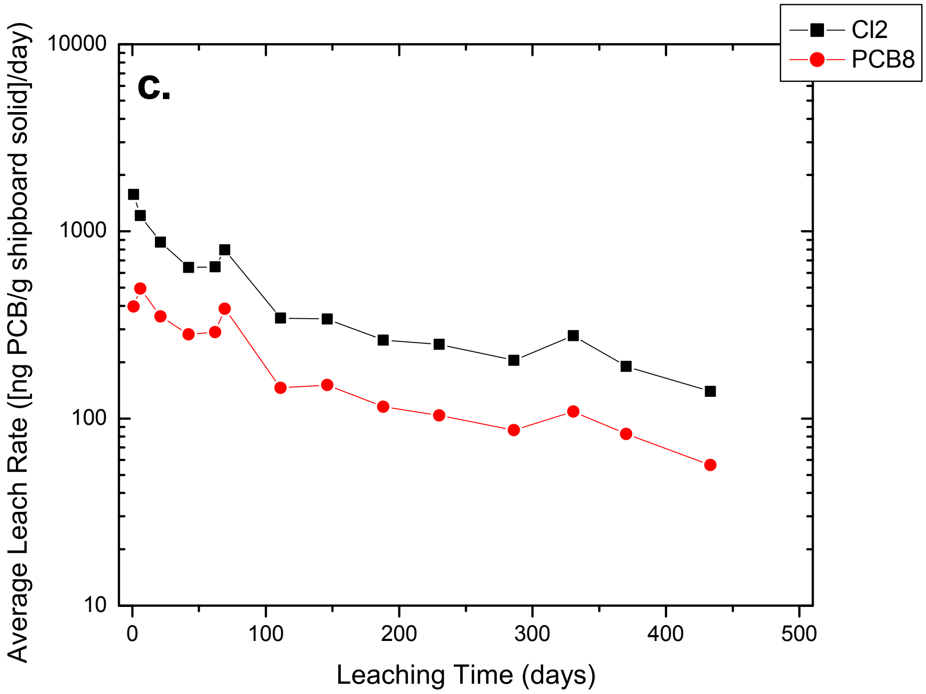
The conventions previously followed in the **EMPIRICAL DATA AND OBSERVATIONS** section apply for all plots of average PCB leach rate versus leaching time below, i.e. for each shipboard solid leaching experiment, the tPCB leach rate is plotted with the contributing homologue leach rates. Correspondingly, each homologue leach rate is then plotted with that homologue group's contributing target congener leach rates. The data presented here can be found in Appendix D with the cumulative concentration curve data plotted in previous sections, and are empirically derived leach rates with no adjustment made to very low or near MDL analyte concentrations evaluated as part of the respective uncertainty analyses and evaluation in the Data Quality Analysis section. If a homologue group or a target congener was not detected, a rate could not be calculated (represented as zero in Appendix D) for that leaching interval, and it is therefore not plotted as part of the curve. These are identified by discontinuities in the plotted leach rate curves.

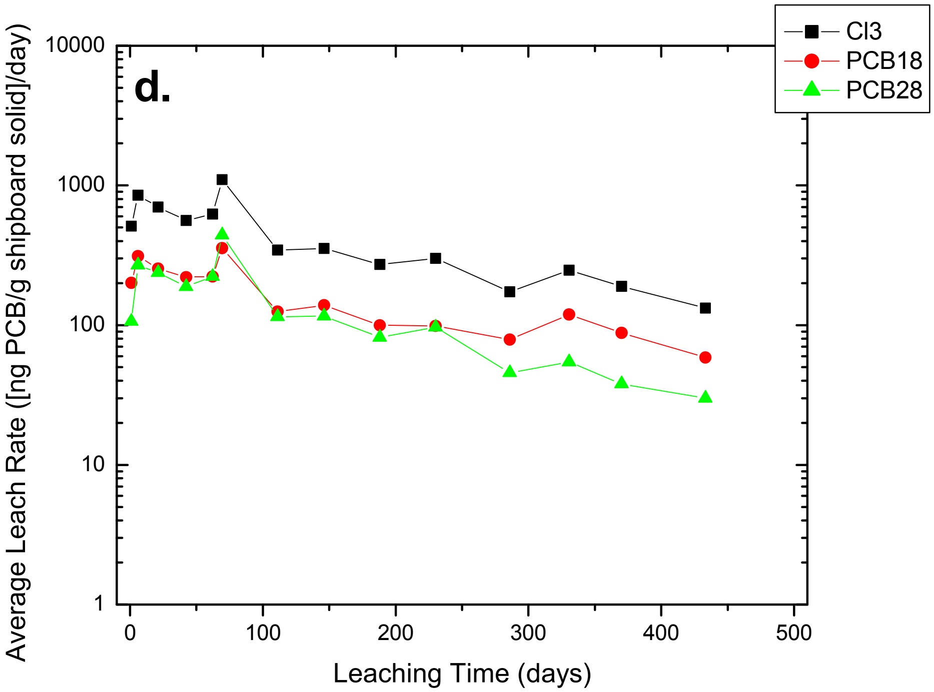
Aroclor 1254 (A1254) Analytical Control Dissolution Rate Behavior

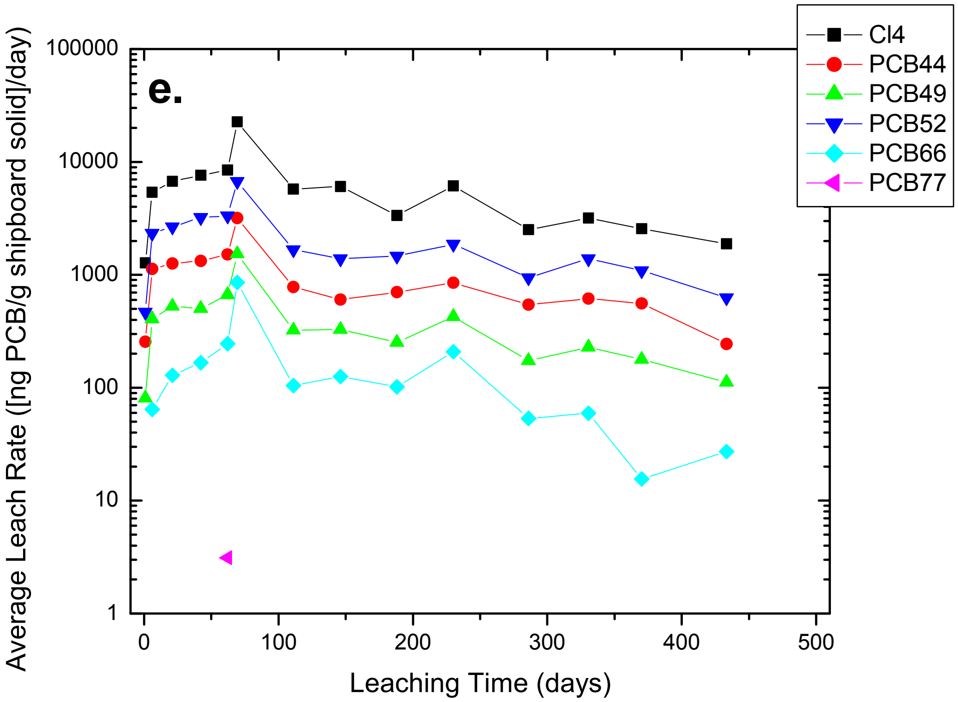
The plots in Figure 48(a-h) below illustrate the dissolution rate behavior for the Aroclor 1254 positive analytical control. These curves are most useful for establishing an upper limit as a seawater PCB solvation capacity for A1254 as a reference point for the shipboard solid leach rate curves that follow, for which A1254 is present in the solid. PCB leaching from shipboard solids relies partially upon PCB dissolution, with the shipboard solid matrix exerting an inhibitory influence on the solubility component of the leaching mechanism. One might expect a very different physical process for placing a solid such as neat A1254 into seawater, considering the absence of shipboard solid matrix. However, the Aroclor is itself a solid matrix, and can behave somewhat analogous to a shipboard solid matrix, albeit the matrix is comprised only of a mixture of different PCB congeners that is itself dissolving. Each A1254 PCB congener resides in (and is released from) this solid matrix and as a result, only PCB-PCB interactions in the A1254 solid control the release in concert with individual PCB solubilities. In contrast, the interaction between PCBs and a shipboard solid matrix likely dominates during shipboard solid leaching if the PCBs are dispersed homogeneously throughout the solid. If PCBs arephase-separated in a shipboard solid, with domains of PCBs dispersed in a PCB matrix similar to an Aroclor, PCB-PCB interactions would be increased relative to PCB-shipboard solid interactions, and a combination of these behaviors would dictate the observed leach rate behavior. It is also possible that PCBs could be selectively phase-separated, that is some regions of the shipboard solid could be rich in a particular PCB congener or congeners even though the bulk composition is closely matched with a particular Aroclor. Even a very small congener-rich phase could effect the observed leaching, particularly if the phase is present at the interface (SASA). It is outside the scope of this investigation to determine the interfacial compositions or relative magnitudes of PCB-PCB and various PCB-shipboard solid interactions at the molecular level, however, although the cohesive (PCB-PCB) interaction is likely stronger, the release is likely greatly enhanced because the Aroclor matrix itself is dissolving and influencing (increasing) the dissolution. This dynamic dissolution behavior of the PCB matrix is a fundamental difference between a neat Aroclor’s release behavior and release from PCBs homogeneously dispersed in inert shipboard solid matrices. For this reason, the neat Aroclor analytical control behavior can only be considered an analytical control or measure of A1254 PCBs solvation capacity in seawater under the leaching conditions of the study, and is only representative of the dissolution component of those PCBs uninhibited by the solid matrix at active leaching surfaces of shipboard solids, vice a leaching surrogate or leaching control. Neat Aroclor 1254 can, however, be considered a surrogate/control for the leaching behavior of highly mobile material matrices such as oils or greases that contain Aroclor 1254.

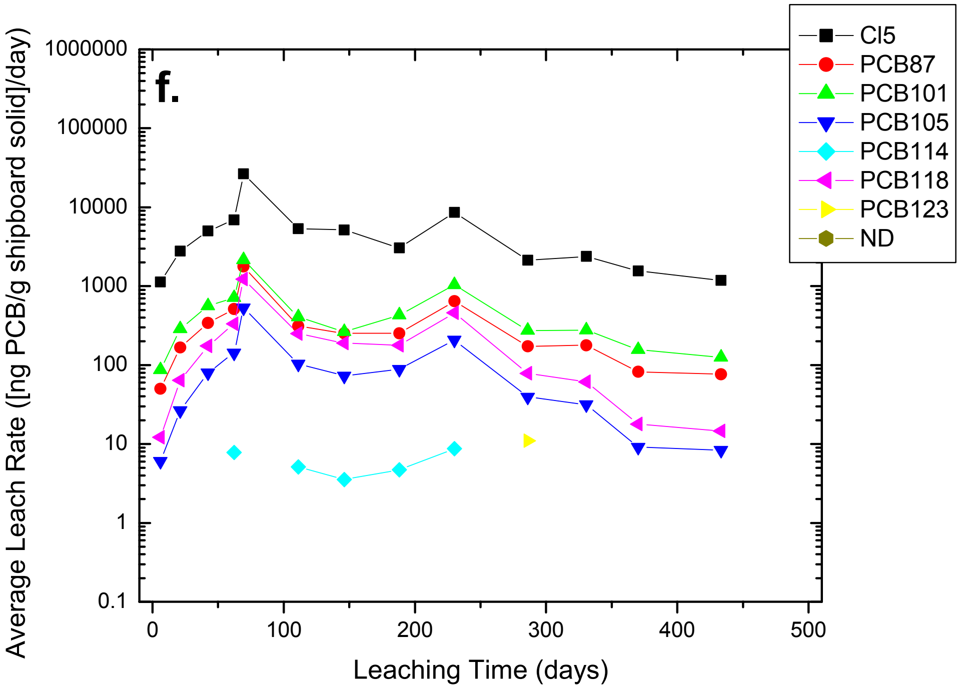

a.
ng of PCB/g of shipboard solid/day
1000000
100000
10000
1000
100
10
1
0
50
100
150
200
250
300
350
400
450
500
Time (days)
tPCBs
Cl1
Cl2
Cl3
Cl4
Cl5
Cl6
Cl7
ND
ND
ND

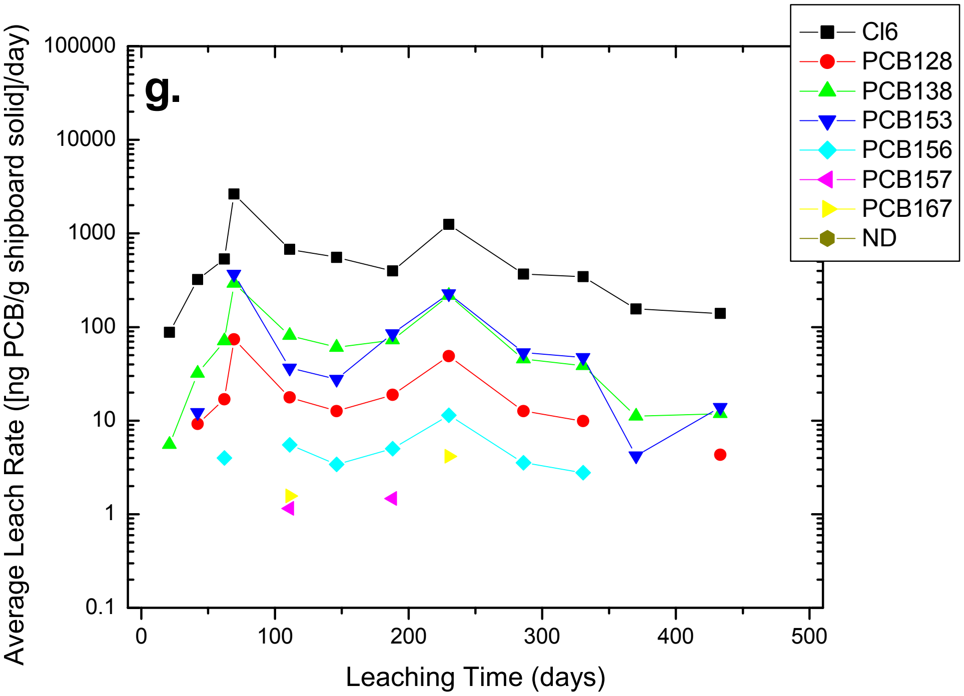

b.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10000
1000
100
10
1
0
100
200
300
400
500
Leaching Time (days)
Cl1


c.
Cl2
PCB8
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10000
1000
100
10
0
100
200
300
400
500
Leaching Time (days)


d.
Cl3
PCB18
PCB28
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10000
1000
100
10
1
0
100
200
300
400
500
Leaching Time (days)


e.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1
10
100
1000
10000
100000
0
100
200
300
400
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77


f.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
0.1
1
10
100
1000
10000
100000
1000000
0
100
200
300
400
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
PCB114
PCB118
PCB123
ND



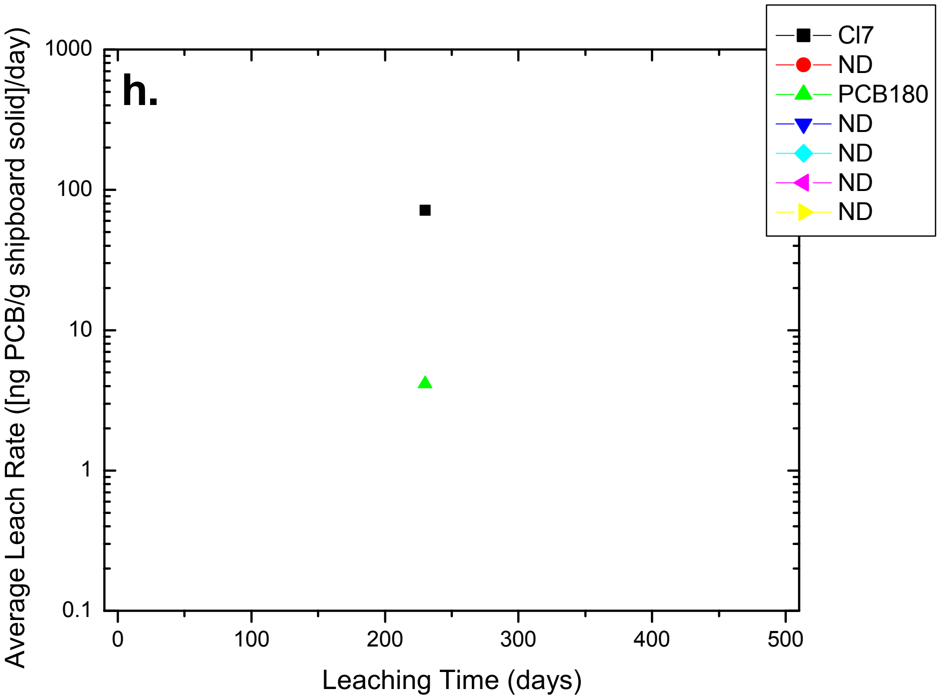


Figure 48 (a-h). Plot a) shows experimental tPCBs average dissolution rate and contributing homologue group average dissolution rates vs. time for pure Aroclor 1254. The sum of the homologue average dissolution rates is equal to the tPCBs average dissolution rate curve (solid black squares). Plots (b-h) show homologue group average dissolution rates and corresponding target congener average dissolution rates within those detected homologue groups (Cl1-Cl7) vs. time for pure Aroclor 1254. Lines connecting adjacent data points indicate detection in consecutive seawater samples (continued dissolution of that PCB congener or homologue group), whereas no line indicates a discontinuity in dissolution (analyte not detected in an adjacent seawater sample). Non-detected target congeners within detected homologue groups included PCB 126 (Cl5); PCB 169 (Cl6); and PCBs 170, 183, 184, 187, & 189 (Cl7).

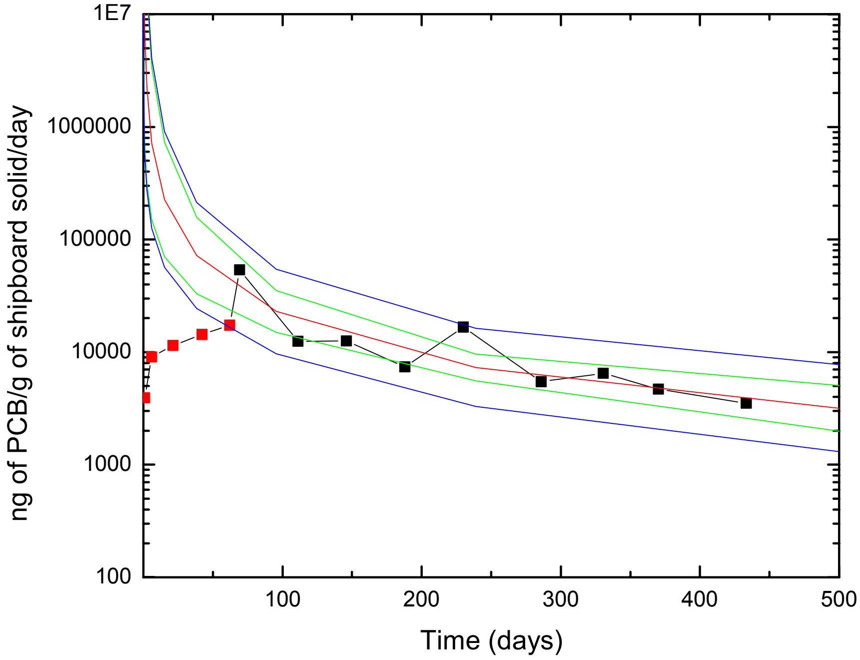
Each of the average dissolution rate curves above describe the release behavior in what would be the worst-case release scenario for a solid containing A1254 at the interface (SASA), in which neat Aroclor 1254, a complex mixture of PCB congeners, is exposed to seawater and allowed to dissolve until limited only by availability from the Aroclor itself (total dissolution). It is important to note that the process monitored above was not a "leaching" control or surrogate for understanding the shipboard solid leaching mechanism, except perhaps the PCB dissolution component. Nor was it a solubility experiment, where an excess of the neat Aroclor would be placed in a known volume of seawater and allowed to equilibrate until saturation was reached and no more solid was observed to dissolve. Such a process would perhaps take anywhere from hours to days, before being limited by the PCB concentration in seawater (true saturation limit), at which point the process would be complete. Because of how the experiments in this study were performed, the neat Aroclor solid matrix itself limits the dissolution behavior in part. For shipboard solid experiments, the experimental design called for seawater exchange at specific sample collection intervalsto avoid saturation of the seawater as indicated by tPCB screening levels for A1254 congeners, but for Aroclor dissolution experiments, saturation was a possibility during dissolution intervals (between seawater sampling/exchange points). This, in effect, results in a neat Aroclor dissolution control curve that represents the A1254 PCB seawater dissolution capacity or effective saturation condition along the A1254 curve, *under the specific experimental conditions* used in shipboard solid leaching measurements. It is for this similarity that Aroclor results are, at times, referred to as "leaching", and inadvertent reference to Aroclors "leaching" should be in the context of positive analytical controls, not "leaching" controls, or surrogates for the leaching process defined by PCBs leaching from inert solid matrices. Likewise, the term "leachate" is used generically for the seawater surrounding a sample from which PCBs dissolve.

In the A1254 average dissolution rate curves above (Figure 48a-h), there is perhaps some indication of rapid initial dissolution, as suggested by the apparent spike observed in the average rate between day 62 and day 69. Complete evaluation of this type of behavior cannot be addressed in this study because the leaching data collection interval was too long due to sampling logistics (requires real-time data collection with acquisition time shorter than the kinetics associated with PCB dissolution). However, we can consider the calculated average rates between 42 and 62 days, between 62 and 69 days, and between 69 and 111 days. These data are 390 (=7803 pptr/20 days), 1253 (=8775 pptr/7 days), and 286 (=11992 pptr/42 days), respectively. While these average dissolution rates are not many orders of magnitude apart, they are significantly different, as evidenced by the practical explanation for the observed spike; that is, it only took 7 days to change by 8775 pptr, exceeding the preceding concentration change of 7803 pptr, which took 20 days, nearly three times as long. Also, the subsequent concentration change (11992 pptr) was larger by 3217 pptr, but it took 6 times longer to reach this concentration, suggesting some type of limiting behavior by the Aroclor matrix, if indeed there was initially rapid PCB dissolution. These observations reveal (perhaps not surprisingly) that a calculated average leach rate is dictated somewhat by the time interval over which one might allow the release to occur before sampling, underscoring the fact that calculated rates in this study are not instantaneous (distinct rates corresponding to a distinct point in leaching time), but averages calculated over the leaching time-interval.

The observed Aroclor leaching behaviors in the A1254 average dissolution rate vs. time curves are valid and necessary positive analytical controls for evaluating the PCB solvation capacity of the seawater under the empirical leaching conditions, provided that a shipboard solid contains Aroclor 1254 or similar Aroclor, e.g. 1260). To this end, each of the concentration leaching curves in the Shipboard

Solid Specific Leaching Data section for shipboard solids that contained a significant amount of A1254 and/or 1260, but not A1268, were validated against the pure Aroclor 1254 *concentration vs. time curves* also found in the Shipboard Solid Specific Leaching Data section (black rubber pipe hanger liner, electrical cable, and foam rubber/Ensolite). It was confirmed that most of the shipboard solid leachate PCB concentrations were all *lower* than concentrations observed for the Aroclor analytical controls, consistent with PCB release suppressed only by the shipboard solid matrix. A similar comparison was also performed on the raw concentration data in Appendix C for all analytes in individual seawater samples across the experimental timeframes, with significant suppression of PCB concentrations by the shipboard solids observed. The average leach rates subsequently calculated and plotted below for these solids are thus below the effective saturation limit and considered valid measures of release. The pure A1254 results can also be used to estimate the worst-case leaching behavior for materials not tested in this work that might contain A1254. For example, A1254 results can be used as a proxy for mobile A1254 or 1260-containing oils and greases.[6]

Each of the analytes in the A1254 average leaching curves were extrapolated beyond the experimental time frame using standard data-treatment and curve-fitting methods described in the Leach Rate Analysis section. These results were especially useful for demonstrating that average leach rates are expected to continue decreasing beyond the average leach rates experimentally determined in this study. All regression analyses (curve-fit plots and associated ANOVA results) can be found in APPENDIX A for all analytes. Results of curve fitting for A1254 are plotted for tPCBs only in Figure 49 below to illustrate how the leach rate (predicted value with upper and lower 95th percentile confidence and prediction limits) is expected to decrease beyond the experimental time frame. These values, extrapolated to 1000 years, are tabulated below the figure. The final empirical tPCBs average value is included as a reference (3505 ng/g shipboard solid-day at 433 days).



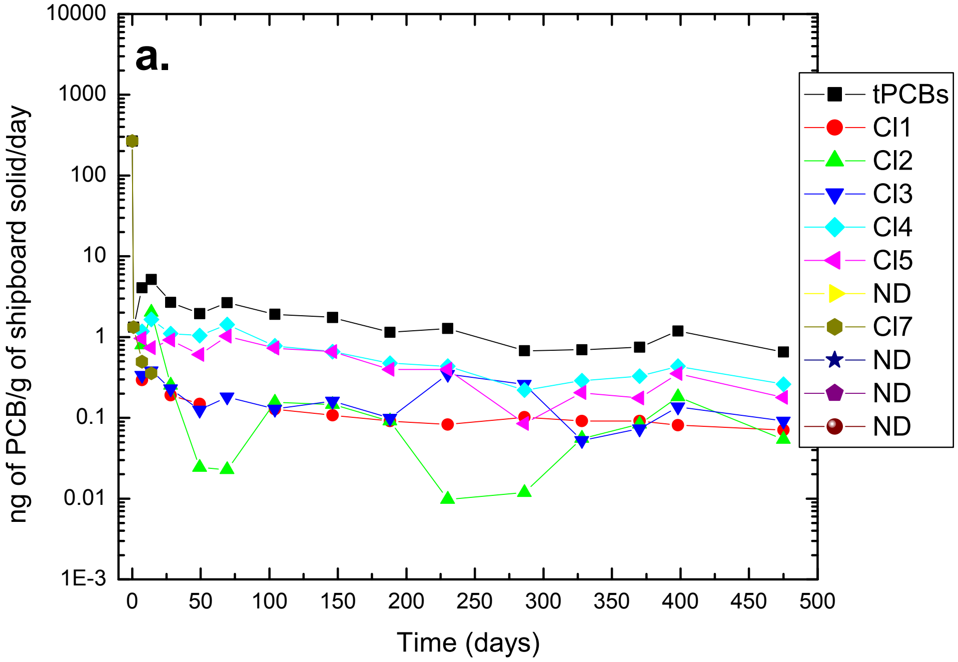
Time (days)	**Curve Fit**	**95% UCI**	**95% LCI**	**95% UPI**	**95% LPI**
433	***3505***				
597.28962	2607.38024	5021.29955	1353.91877	8178.85457	831.22052
1493.48334	850.17907	2610.14027	276.92169	3665.95851	197.16657

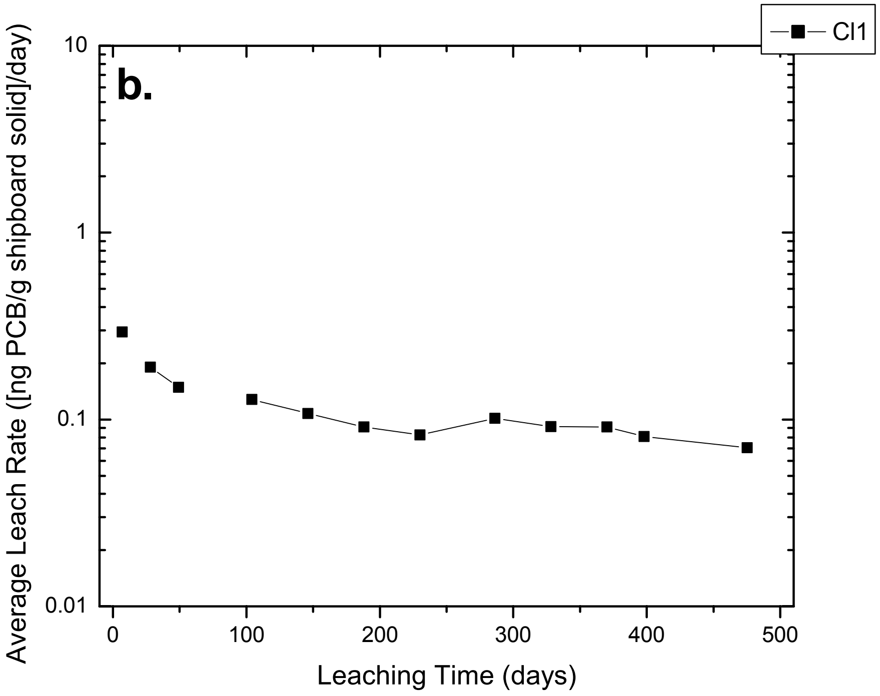
3734.35667	277.21482	1385.69414	55.45817	1784.2291	43.07074
9337.51277	90.39044	740.42725	11.03475	903.61604	9.04193
23347.83539	29.47328	396.74147	2.18952	467.26176	1.85907
58379.72389	9.61025	212.89281	0.43382	244.52286	0.3777
145974.65266	3.13358	114.33564	0.08588	128.90918	0.07617
365000	1.02175	61.43775	0.01699	68.28956	0.01529

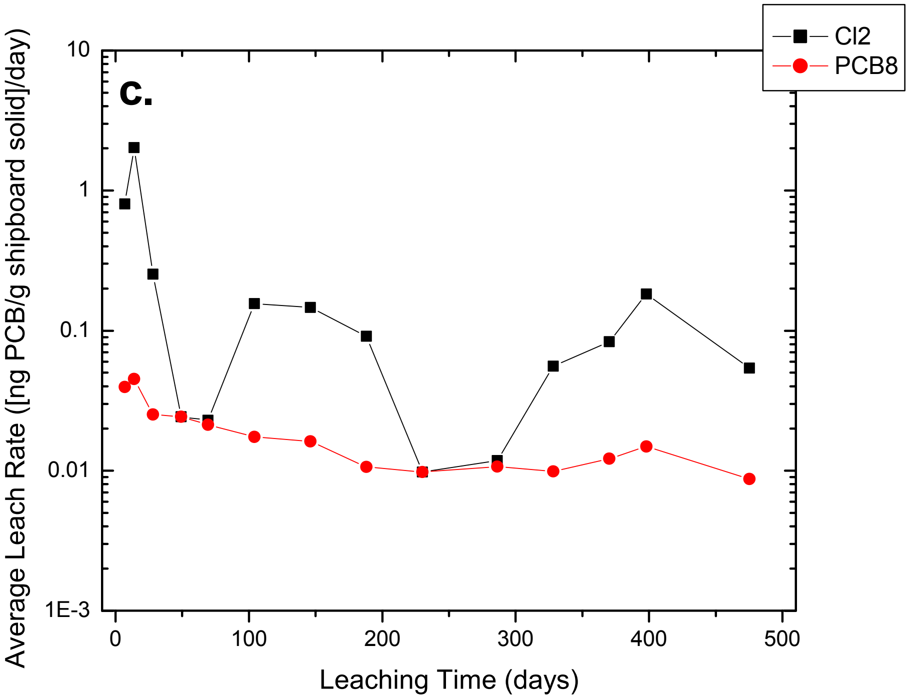
Figure 49. A1254 tPCBs average leach rate extrapolation results (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over the 1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

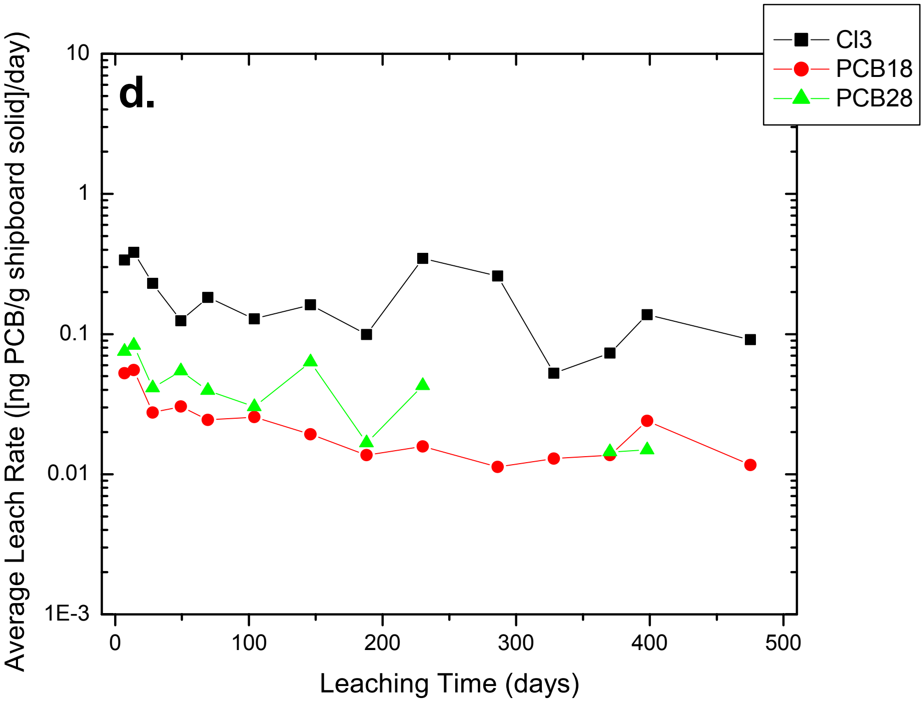
Black Rubber Pipe Hanger Liner (BRPHL) Leach Rate Behavior

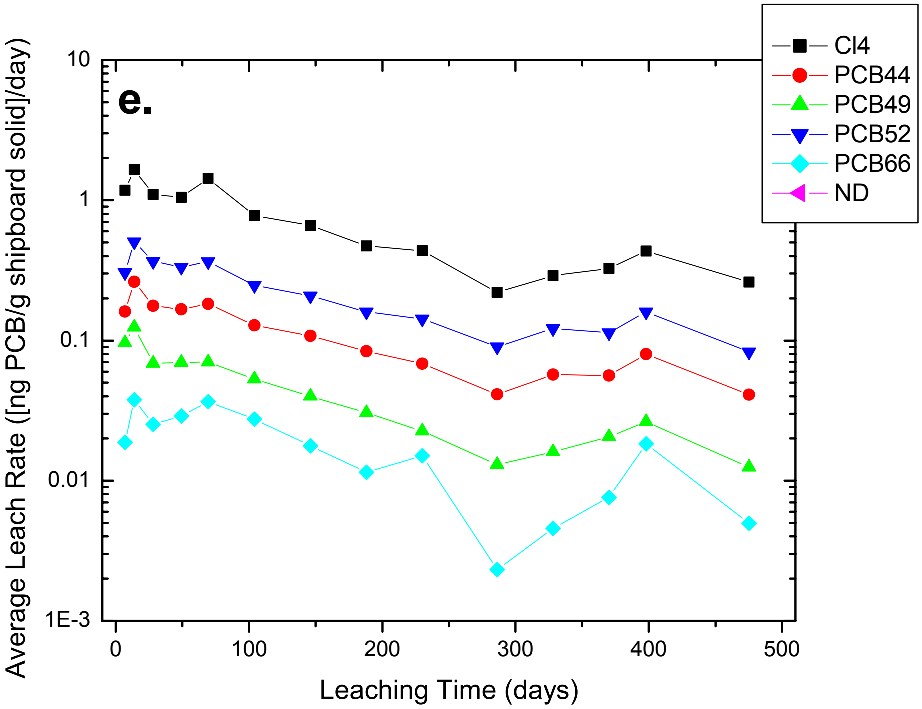
This leached sample contained 0.16 wt% tPCBs with A1254 likely to be the primary Aroclor component (nominally 97% of the PCB content) with a small amount of Aroclor 1260 identified (nominally 3% of the PCB content), as indicated in Table 10. The average leach rate curves for BRPHL are shown in Figure 50(a-g) below for detected homologues Cl1-Cl5, and for only those target congeners detected within each of these homologue groups. The average leach rate values for tPCBs lie predominantly in the 1-10 ng/g shipboard solid-day range, significantly lower (by 3 orders of magnitude) than the tPCBs average leach rate for A1254. This indicates significant suppression of PCB leaching by the BRPHL polymer matrix. Note that the Cl7 homologue and target congener PCB184 were only detected in the earliest stages of leaching, and the leaching had stopped for these analytes by the end of the first month of leaching (See Figure 50g below).

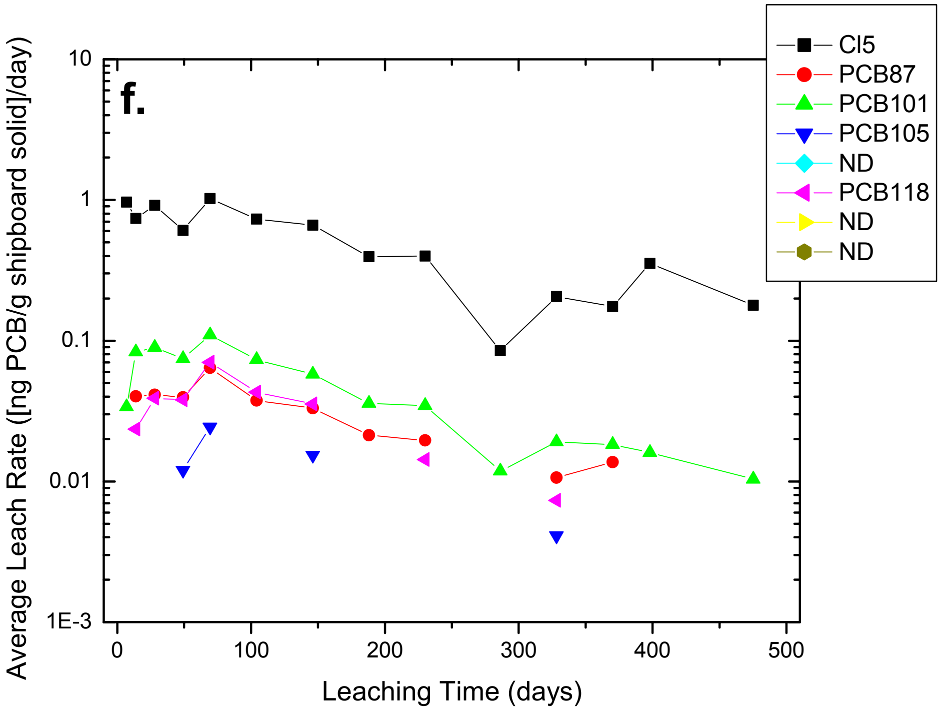



b.
Cl1
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
0
100
200
300
400
500
Leaching Time (days)


c.
Cl2
PCB8
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


d.
Cl3
PCB18
PCB28
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


e.
Cl4
PCB44
PCB49
PCB52
PCB66
ND
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)



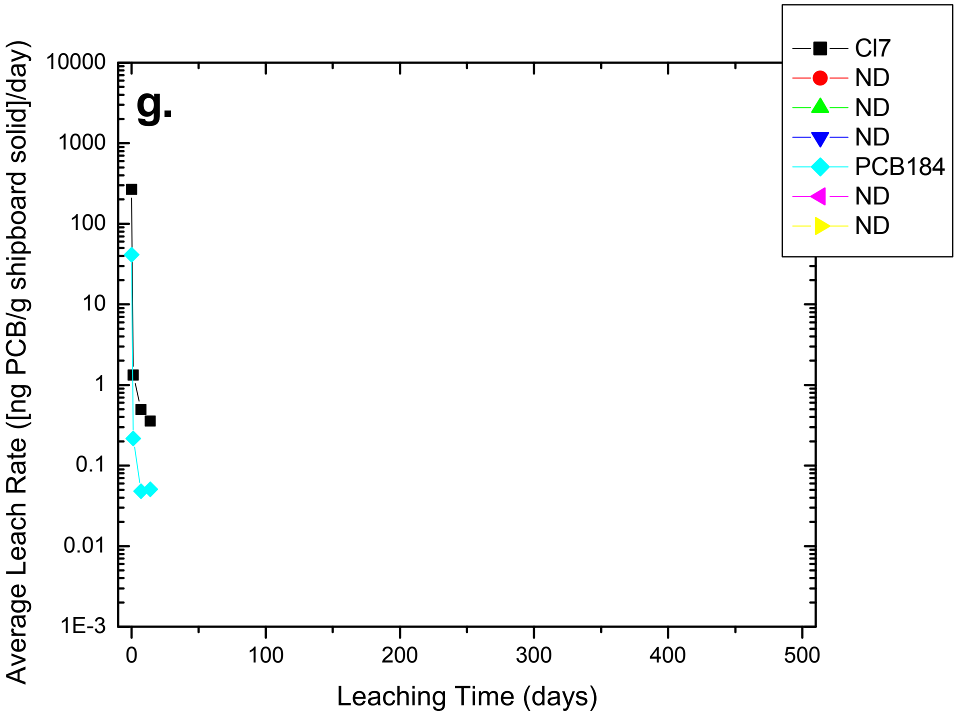
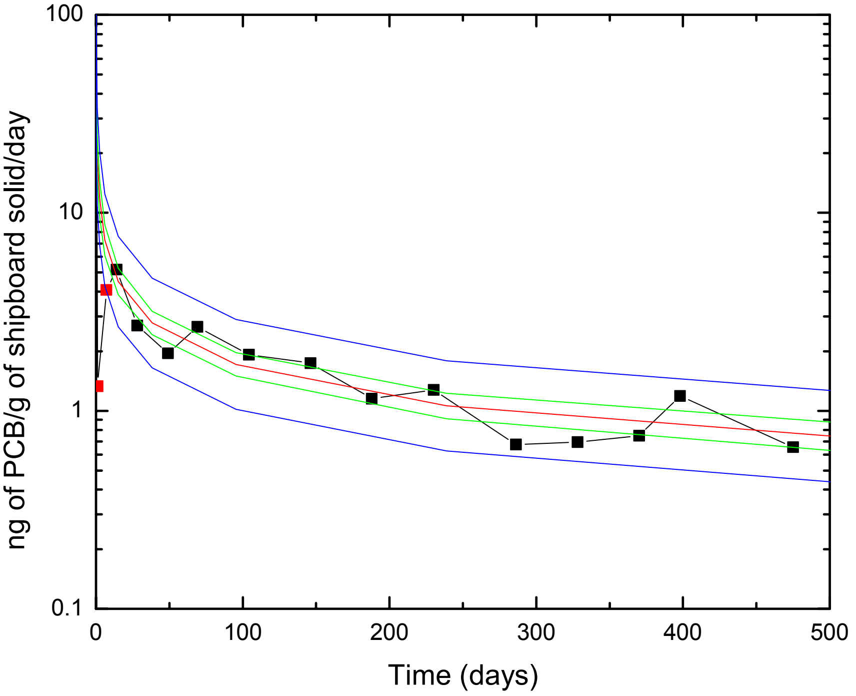


Figure 50 (a-g). Plot a) shows experimental tPCBs average leach rate and contributing homologue group average leach rates vs. leaching time for BRPHL. The sum of the homologue average leach rate curves is equal to the tPCBs average leach rate curve (solid black squares). Plots (b-g) show the detected homologue group average leach rates and corresponding target congener average leach rates within those homologue groups (Cl1-Cl5, and Cl7) vs. leaching time for BRPHL. Lines connecting adjacent data points indicate detection in consecutive leachate samples (continued leaching of that PCB congener or homologue group), whereas no line indicates a discontinuity in leaching (analyte not detected in an adjacent leachate sample). Non-detected target congeners within detected homologue groups included PCB 77 (Cl4); PCBs 114, 123, & 126 (Cl5); and PCBs 170, 180, 183, 187, & 189 (Cl7).

The above curves were extrapolated beyond the experimental time frame using standard data-treatment and curve-fitting methods as described in the Leach Rate Analysis section. These results are summarized for tPCBs only below (Figure 51), with detailed curve-fit plots and ANOVA results included in APPENDIX A for all analytes. These values, extrapolated to 1000 years, are tabulated below the figure. For reference purposes, the final experimental data point corresponds to a tPCBs average leach rate of 0.66 ng/g shipboard solid-day at 475 days.

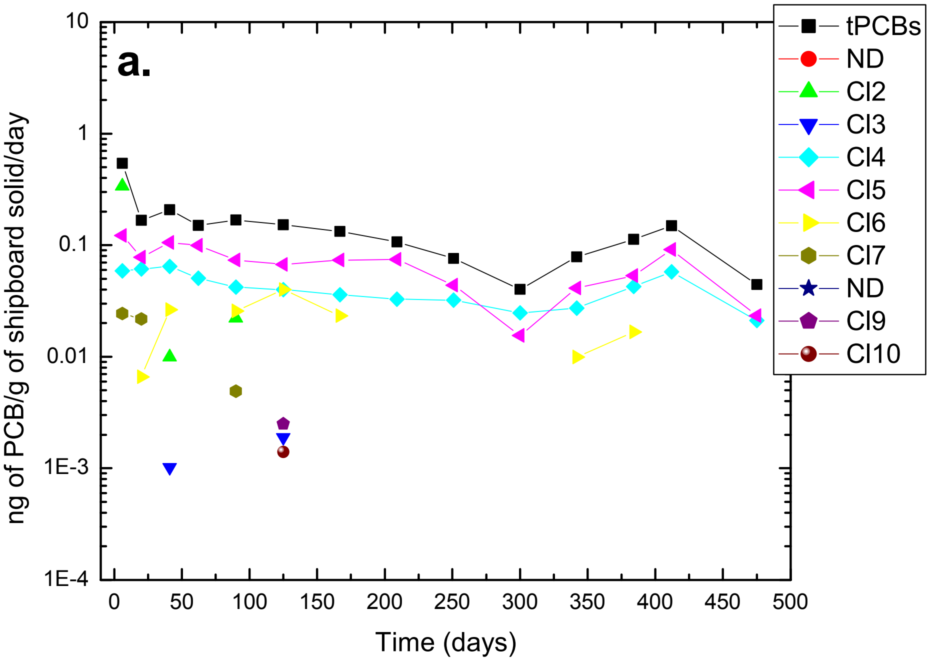


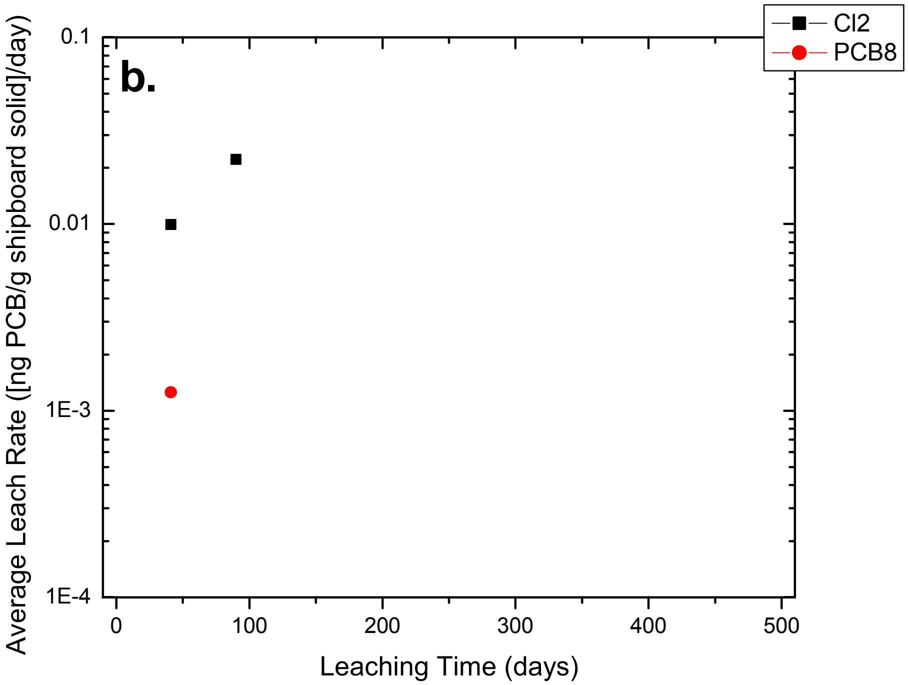
Time (days)	Curve Fit	95% UCI	95% LCI	95% UPI	95% LPI
475	***0.66***				
597.28962	0.6539	0.77635	0.55077	1.11353	0.38399
1493.48334	0.40379	0.49434	0.32983	0.69499	0.2346
3734.35667	0.24935	0.31617	0.19665	0.43524	0.14285
9337.51277	0.15397	0.20278	0.11692	0.27342	0.08671
23347.83539	0.09508	0.13028	0.06939	0.17225	0.05248
58379.72389	0.05871	0.0838	0.04114	0.1088	0.03169
145974.65266	0.03626	0.05395	0.02437	0.06888	0.01908
365000	0.02239	0.03475	0.01443	0.0437	0.01147

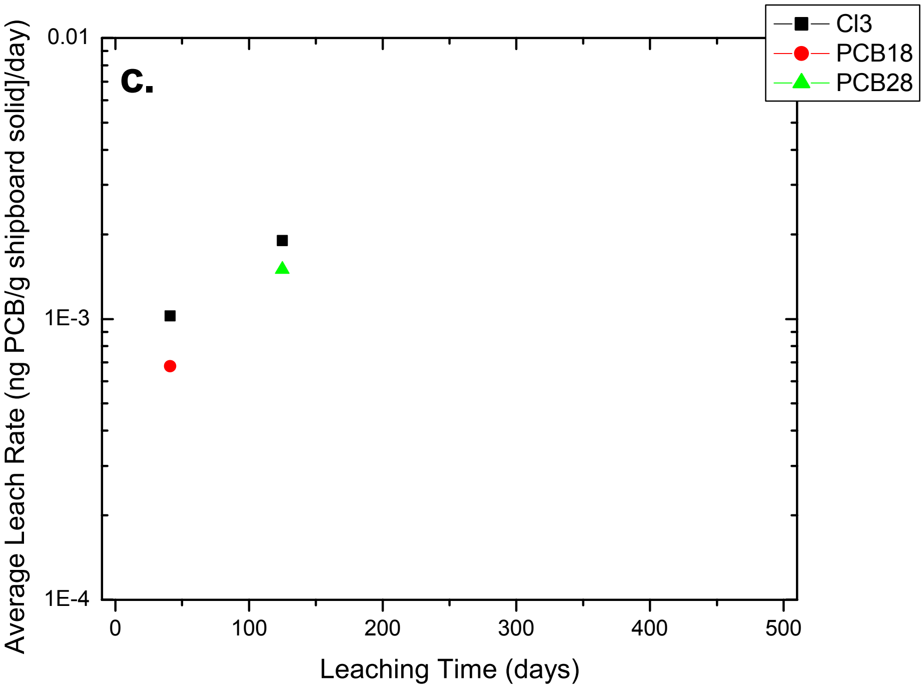
Figure 51. Extrapolation results for BRPHL tPCBs average leach rate (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over the 1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

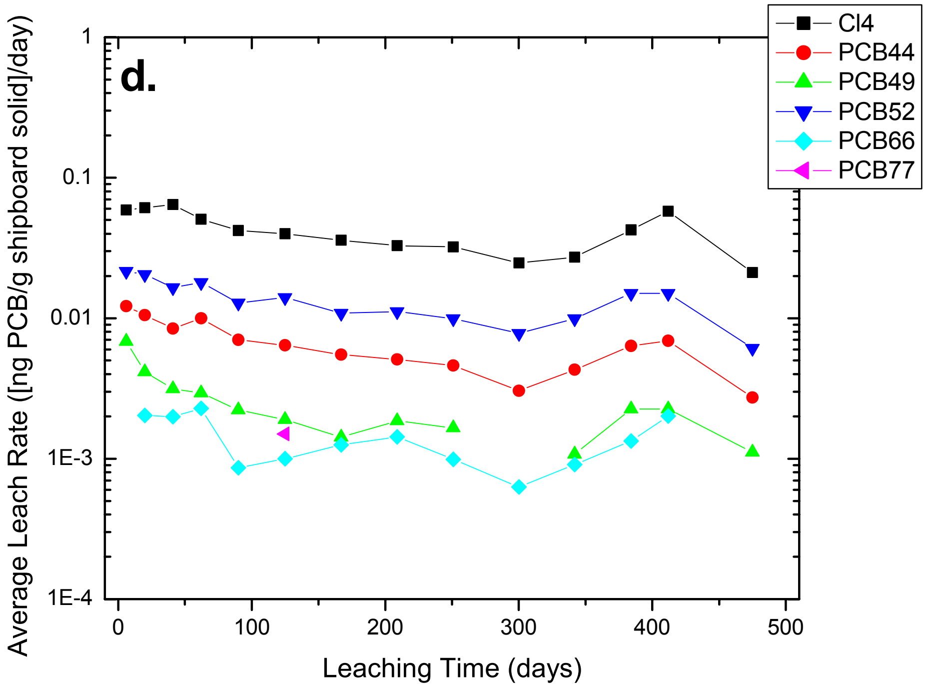
Electrical Cable (EC) Leach Rate Behavior

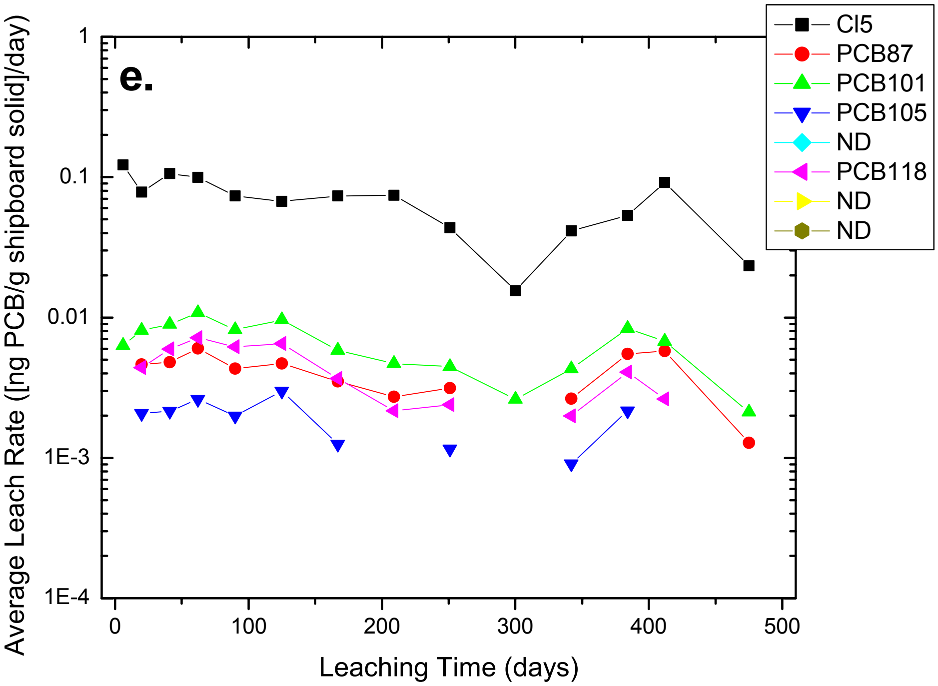
The tPCB content for this shipboard solid sample was 0.12 wt%, with the likely primary component identified in Table 10 as (nominally) 91% Aroclor 1254, with a possible Aroclor 1260 component (nominally 8%), and an even smaller amount of Aroclor 1242 possible (nominally 1%). The average leach rate curves for EC are plotted below in Figure 52(a-i), with average leach rate curves for tPCBs, homologue groups Cl2-Cl7, Cl9-Cl10, and each of these homologue groups' target congeners. The average leach rates for EC are generally below 0.2 ng/g shipboard solid-day, 4 orders of magnitude below the A1254 average leach rates, signifying substantial leaching suppression by the EC solid matrix. Most of the leaching occurred in homologue groups Cl4-Cl6 across the entire leaching timeframe, whereas many of the remaining detected homologue groups and corresponding target congeners were detected only sporadically.

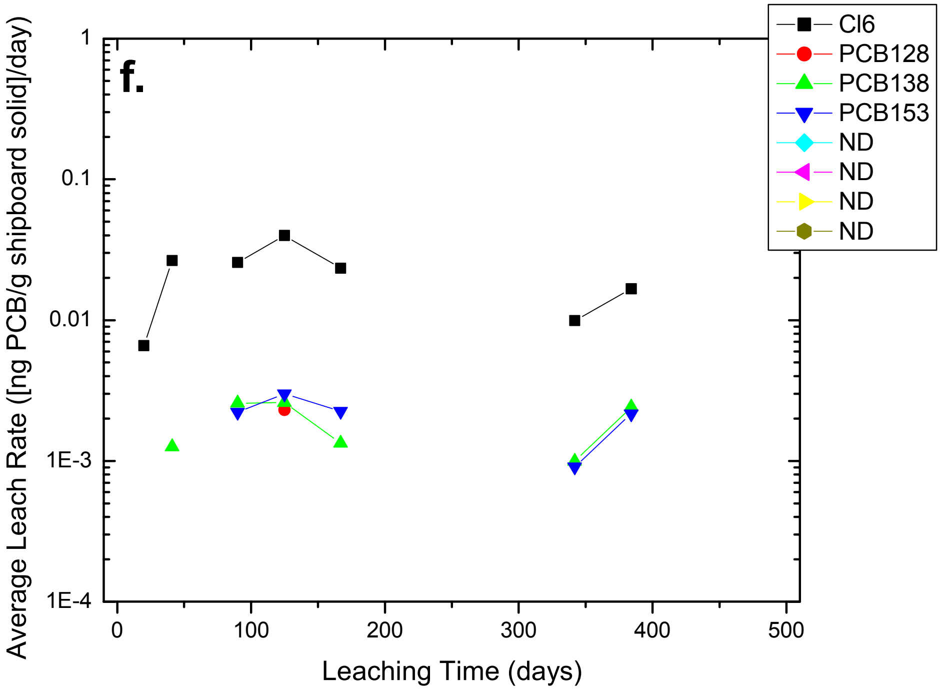


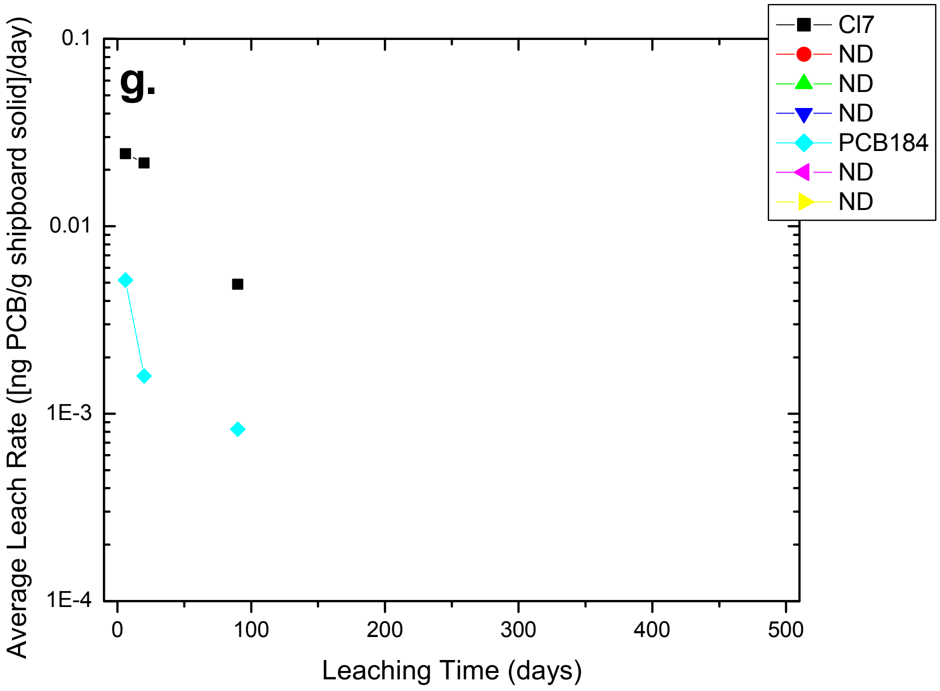

b.
■ Cl2
● PCB8
Average Leach Rate ([ng PCB/g shipboard solid]/day)
0.1
0.01
1E-3
1E-4
0
100
200
300
400
500
Leaching Time (days)

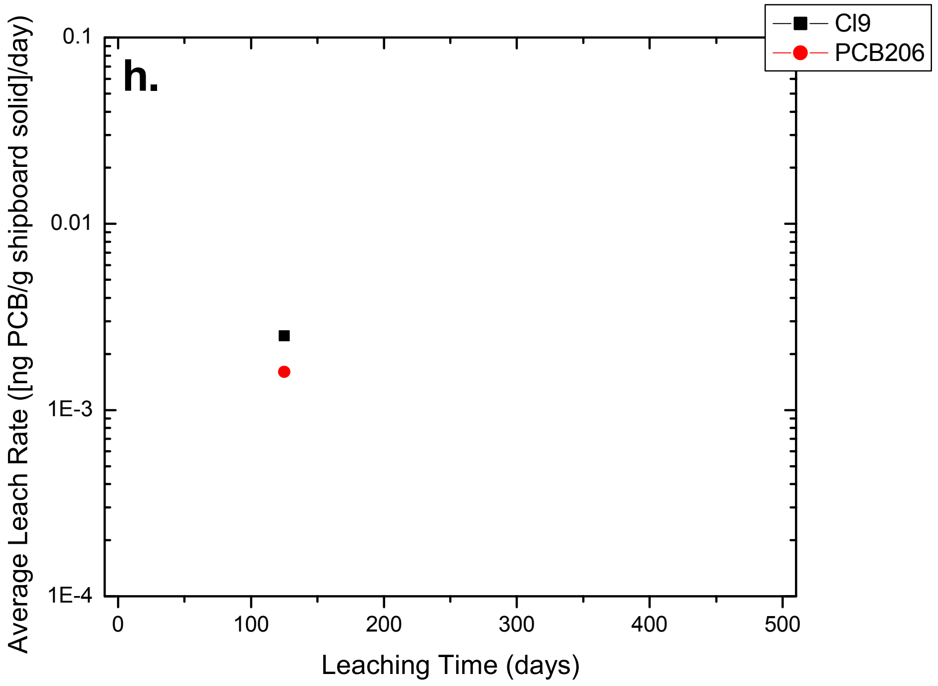

c.
■ Cl3
● PCB18
▲ PCB28
Average Leach Rate (ng PCB/g shipboard solid]/day)
0.01
1E-3
1E-4
0
100
200
300
400
500
Leaching Time (days)


d.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1
0.1
0.01
1E-3
1E-4
0
100
200
300
400
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77


e.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1
0.1
0.01
1E-3
1E-4
0
100
200
300
400
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
ND
PCB118
ND
ND


f.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1
0.1
0.01
1E-3
1E-4
0
100
200
300
400
500
Leaching Time (days)
Cl6
PCB128
PCB138
PCB153
ND
ND
ND
ND


g.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
0.1
0.01
1E-3
1E-4
0
100
200
300
400
500
Leaching Time (days)
Cl7
ND
ND
ND
PCB184
ND
ND



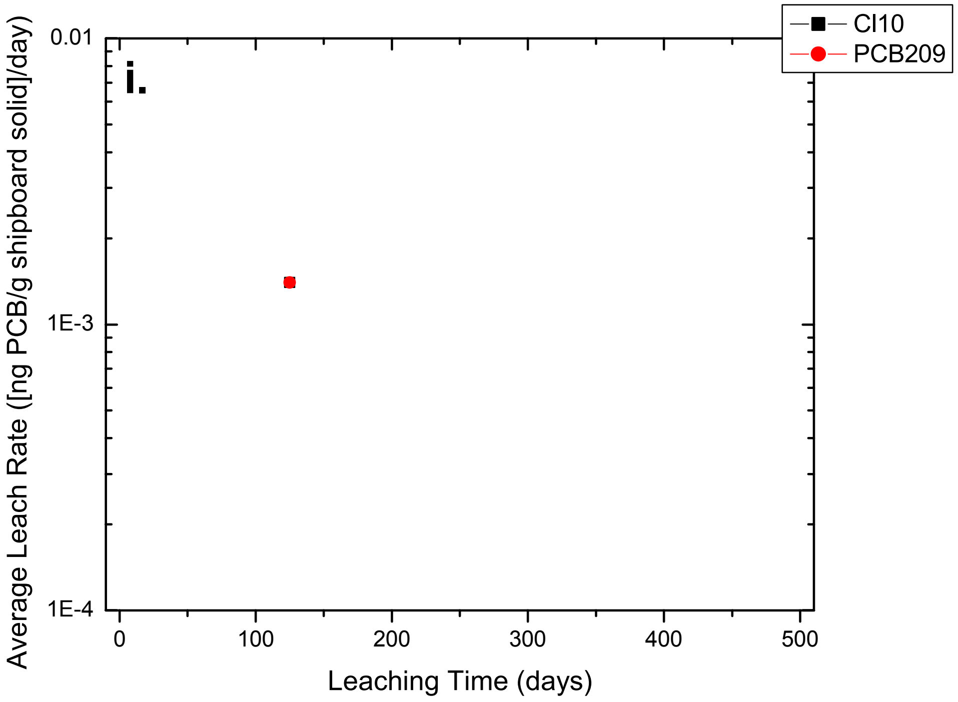
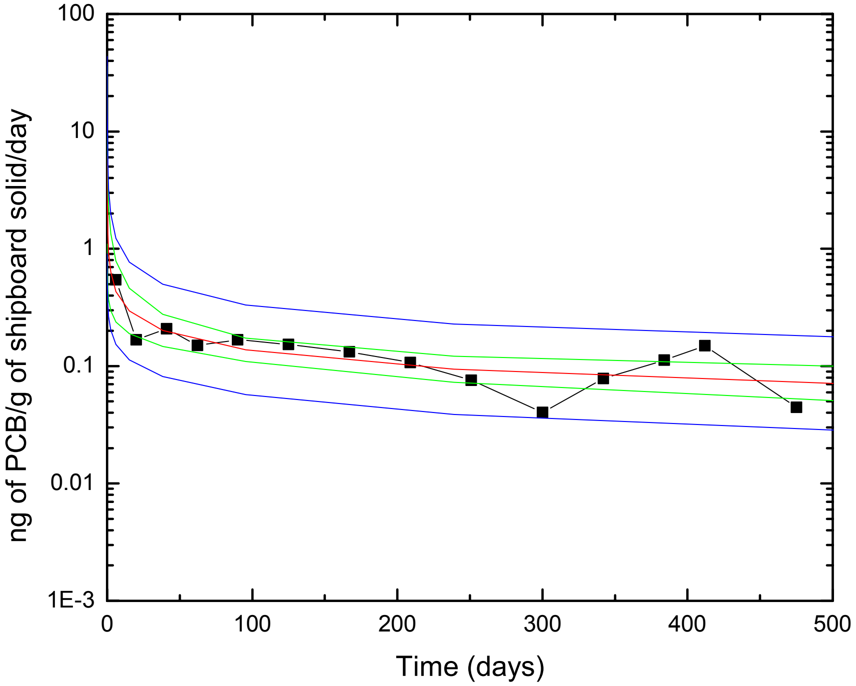


Figure 52 (a-i). Plot a) shows experimental tPCBs average leach rate and contributing homologue group average leach rates vs. leaching time for EC. The sum of the homologue average leach rate curves is equal to the tPCBs average leach rate curve (solid black squares). Plots (b-i) show homologue group average leach rates and corresponding target congener average leach rates within those detected homologue groups (Cl2-Cl7, Cl9 and Cl10) vs. leaching time for EC. Lines connecting adjacent data points indicate detection in consecutive leachate samples (continued leaching of that PCB congener or homologue group), whereas no line indicates a discontinuity in leaching (analyte not detected in an adjacent leachate sample). Non-detected target congeners within detected homologue groups included PCBs 114, 123, & 126 (Cl5); PCBs 156, 157, 167, 169

(Cl6); PCBs 170, 180, 183, 187, & 189 (Cl7). Note that Cl10 and PCB209 should be experimentally identical and are plotted here to demonstrate this concurrence.

The average leach rate curves for EC were extrapolated beyond the experimental time frame using standard data-treatment and curve-fitting methods described in the Leach Rate Analysis section. These results are summarized below for tPCBs (Figure 53), with detailed curve-fit plots and ANOVA results for all analytes included in APPENDIX A. These values, extrapolated to 1000 years, are tabulated below the figure. For reference purposes, the final experimental data point corresponds to a tPCBs average leach rate of 0.044 ng/g shipboard solid-day at 475 days.

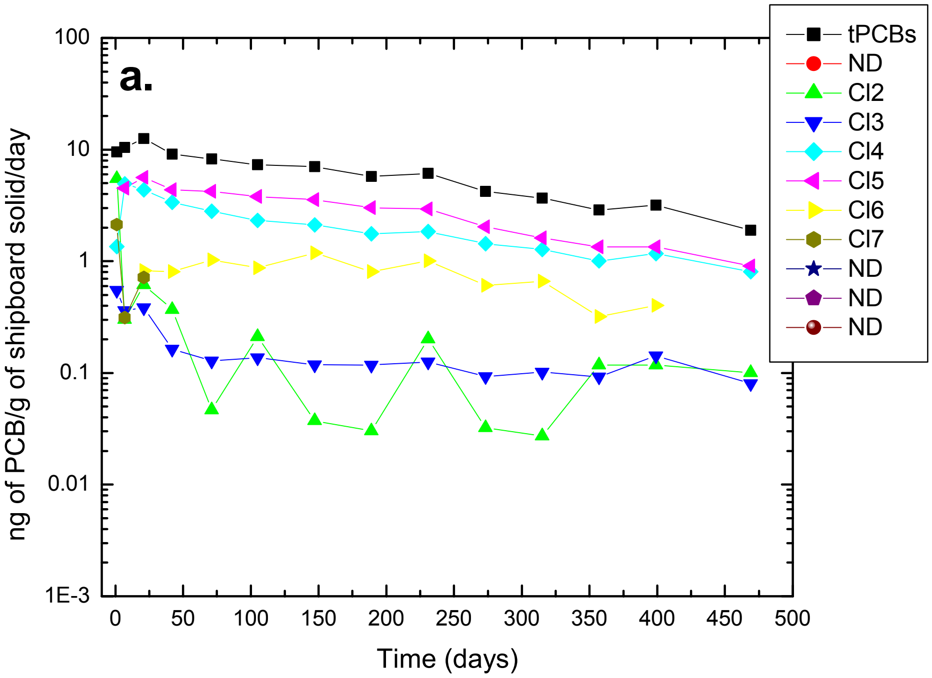


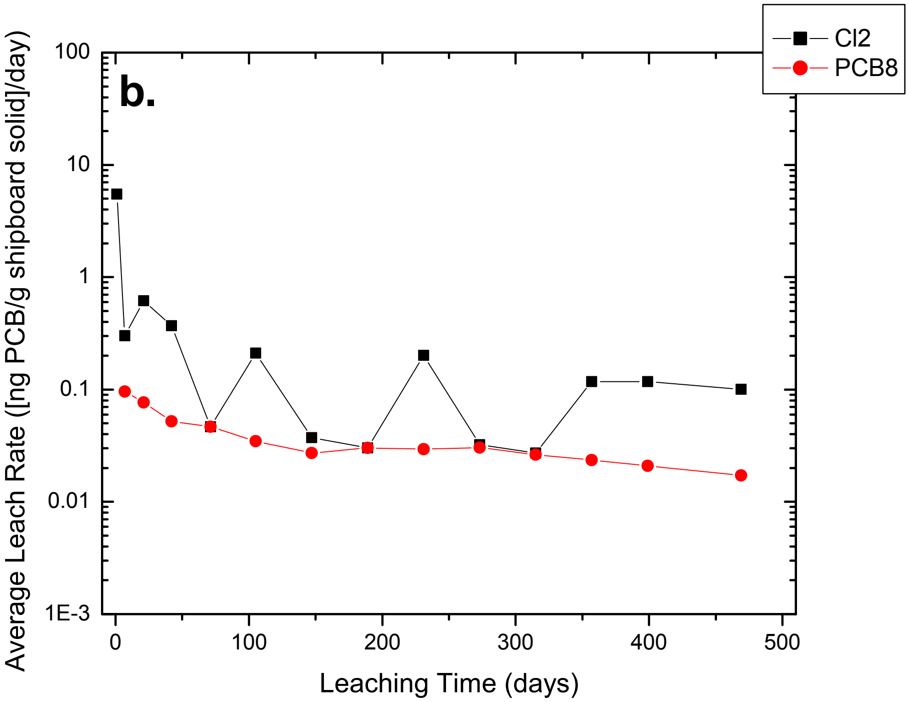
Time (days)	Curve Fit	95% UCI	95% LCI	95% UPI	95% LPI
475	*0.044*				
597.28962	0.06429	0.09263	0.04462	0.16202	0.02551
1493.48334	0.0439	0.07293	0.02642	0.11805	0.01632
3734.35667	0.02997	0.05811	0.01546	0.08797	0.01021
9337.51277	0.02047	0.04655	0.009	0.06671	0.00628
23347.83539	0.01397	0.03739	0.00522	0.05127	0.00381
58379.72389	0.00954	0.03008	0.00303	0.0398	0.00229
145974.65266	0.00651	0.02423	0.00175	0.03112	0.00136
365000	0.00445	0.01952	0.00101	0.02448	8.08216E-4

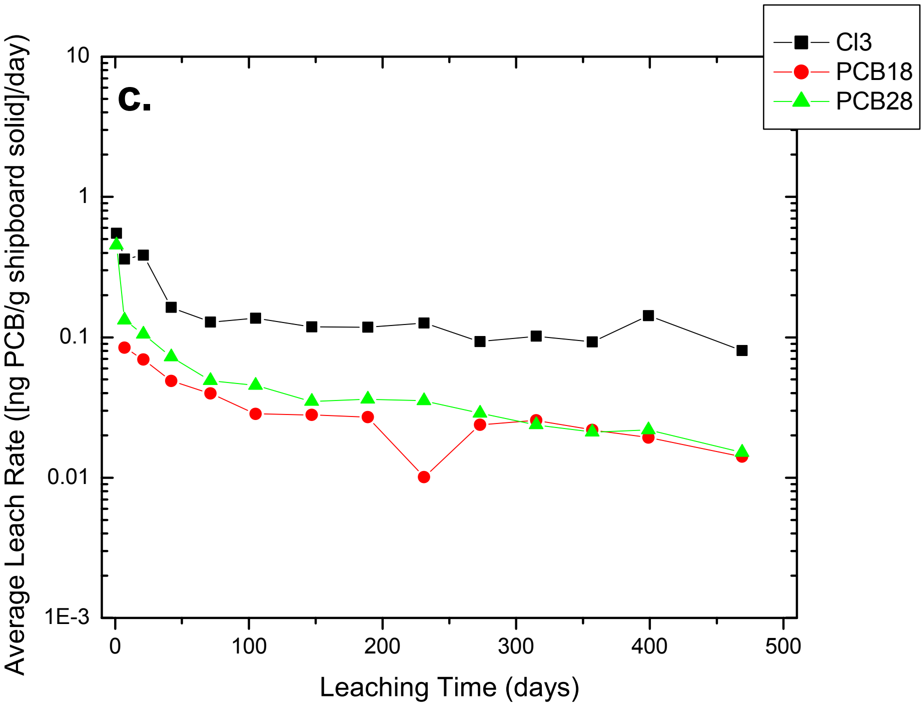
Figure 53. Extrapolation results for EC tPCBs average leach rate (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over the 1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

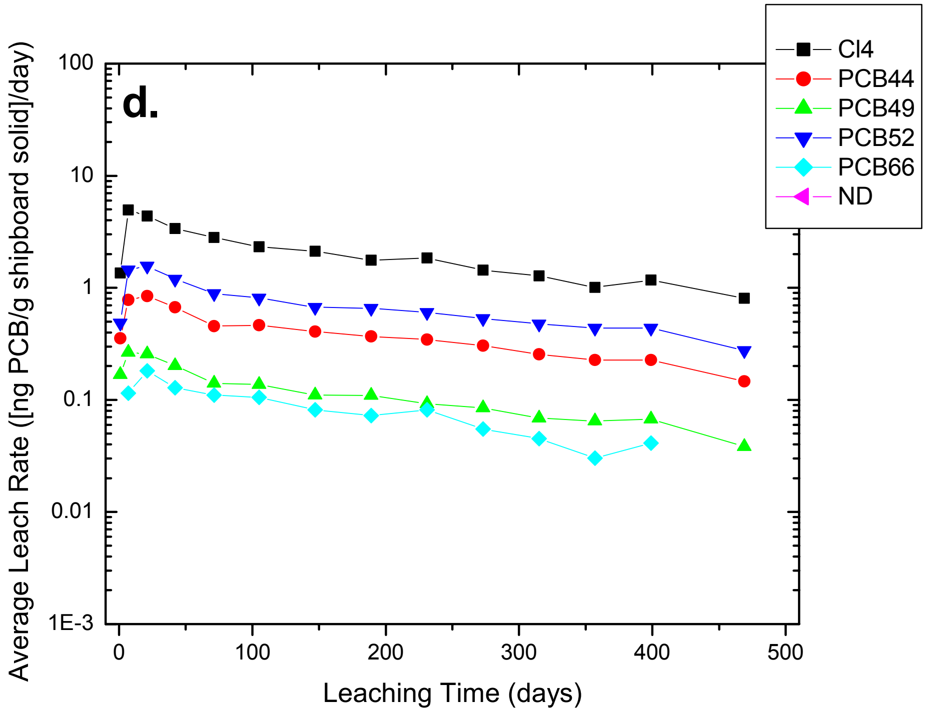
Foam Rubber/Ensolite (FRE) Leach Rate Behavior

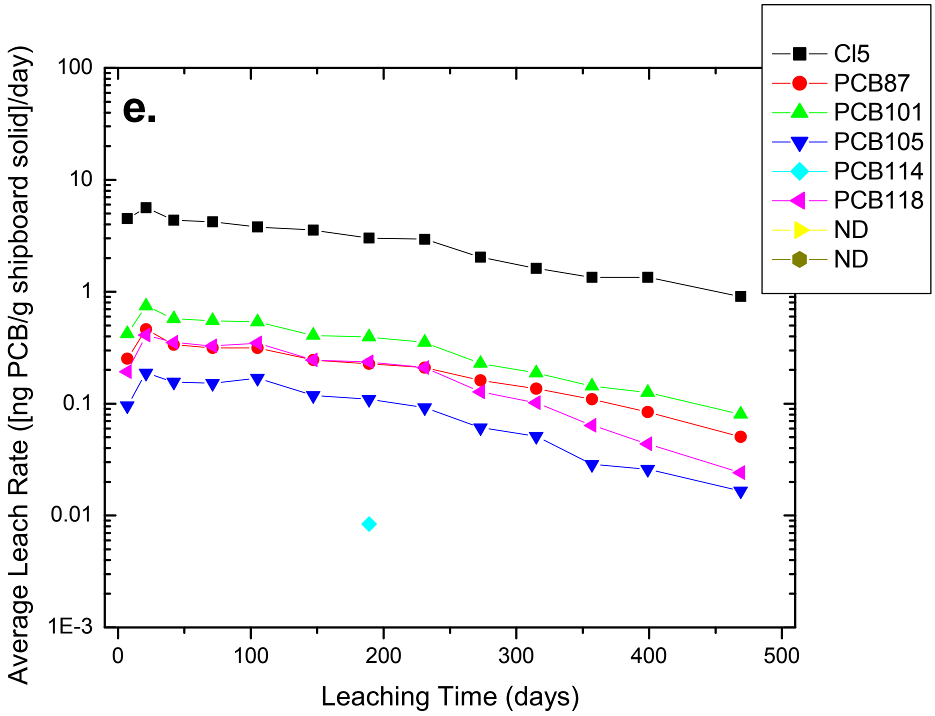
This shipboard solid sample contained 0.89 wt% tPCBs, likely comprised primarily of Aroclor 1254 (nominally 93%) and possibly Aroclor 1260 (nominally 7%) per Table 10. Average leach rate curves are plotted in Figure 54(a-g) below for tPCBs and all detected analytes (homologues Cl2-Cl7 and corresponding target congeners) across the entire leaching timeframe. All homologue groups were present (leached) throughout, with the exception of analytes Cl7 homologue group and congeners, which appeared early in the leaching and then stopped within the first month (see Figure 54g below). This behavior is qualitatively very similar to the leaching behavior exhibited by BRPHL and EC for these same target analytes, (the release for EC is 1-2 orders of magnitude lower).

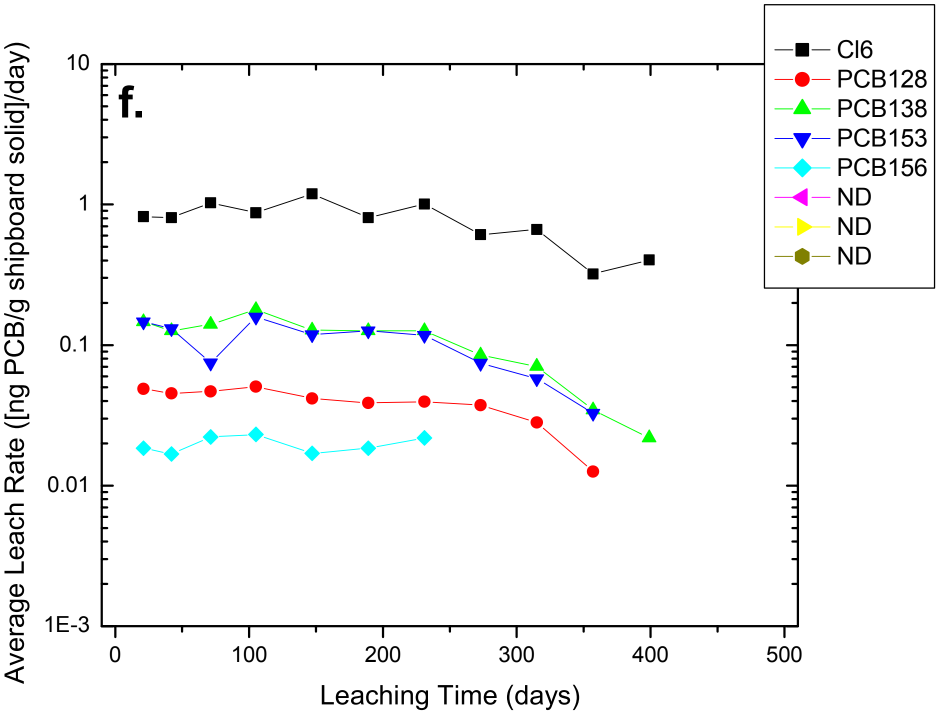



b.
Cl2
PCB8
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


c.
Cl3
PCB18
PCB28
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


d.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
PCB66
ND


e.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
PCB114
PCB118
ND
ND



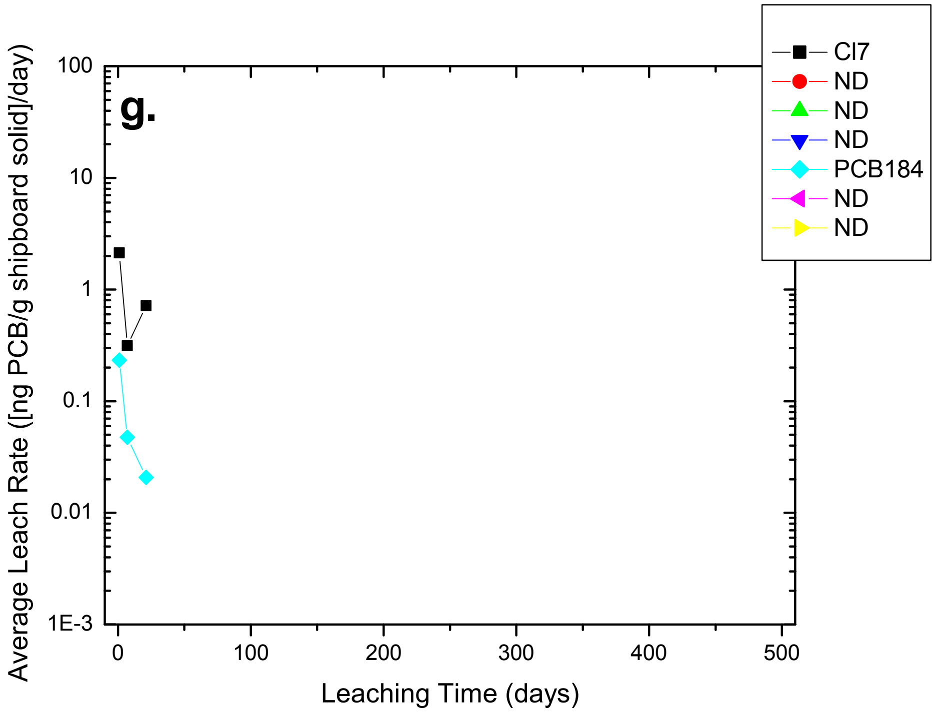
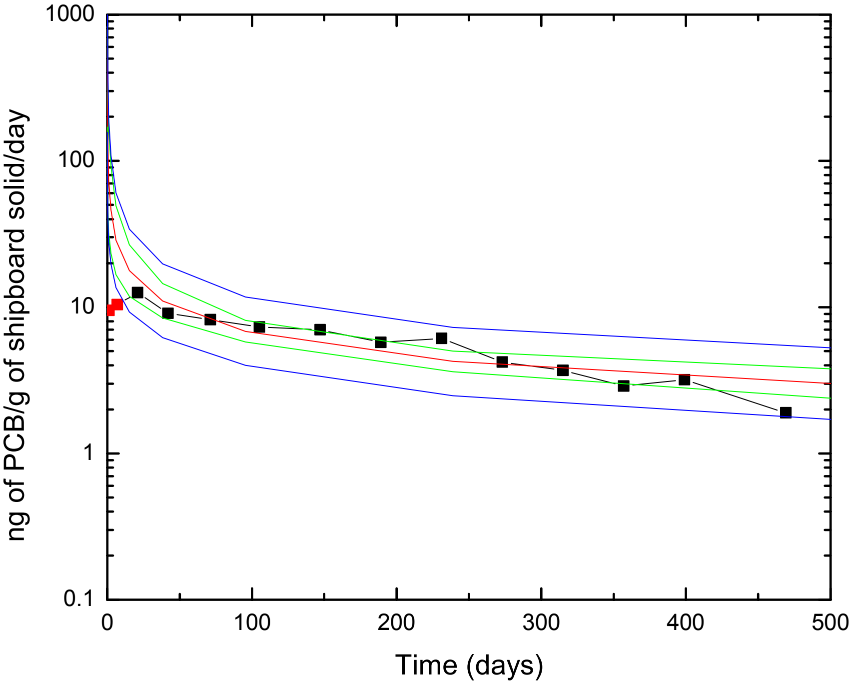


Figure 54 (a-g). Plot a) shows experimental tPCBs average leach rate and contributing homologue group average leach rates vs. leaching time for FRE. The sum of the homologue average leach rate curves is equal to the upper tPCBs average leach rate curve (solid black squares). Plots (b-g) show homologue group average leach rates and target congener average leach rates within those detected homologue groups (Cl2-Cl7) vs. leaching time for FRE. Lines connecting adjacent data points indicate detection in consecutive leachate samples (continued leaching of that PCB congener or homologue group), whereas no line indicates a discontinuity in leaching (analyte not detected in an adjacent leachate sample). Non-detected target congeners within detected homologue groups included PCB 77 (Cl4); PCBs 123 & 126 (Cl5) (note that PCB 114 only appeared once); PCBs 157, 167, 169 (Cl6); PCBs 170, 180, 183, 187, & 189 (Cl7).

The average leach rate curves for FRE were extrapolated beyond the experimental time frame using standard data-treatment and curve-fitting methods described in the Leach Rate Analysis section. All curve-fit plots and associated ANOVA results can be found in APPENDIX A for all homologue and target congener analytes. The results for tPCBs average leach rates are included in Figure 55 below to illustrate how the (predicted) rate behaves beyond the experimental time frame. These values, extrapolated to 1000 years, are tabulated below the figure. The final empirical tPCBs average value is included as a reference (1.89 ng/g shipboard solid-day at 469 days).



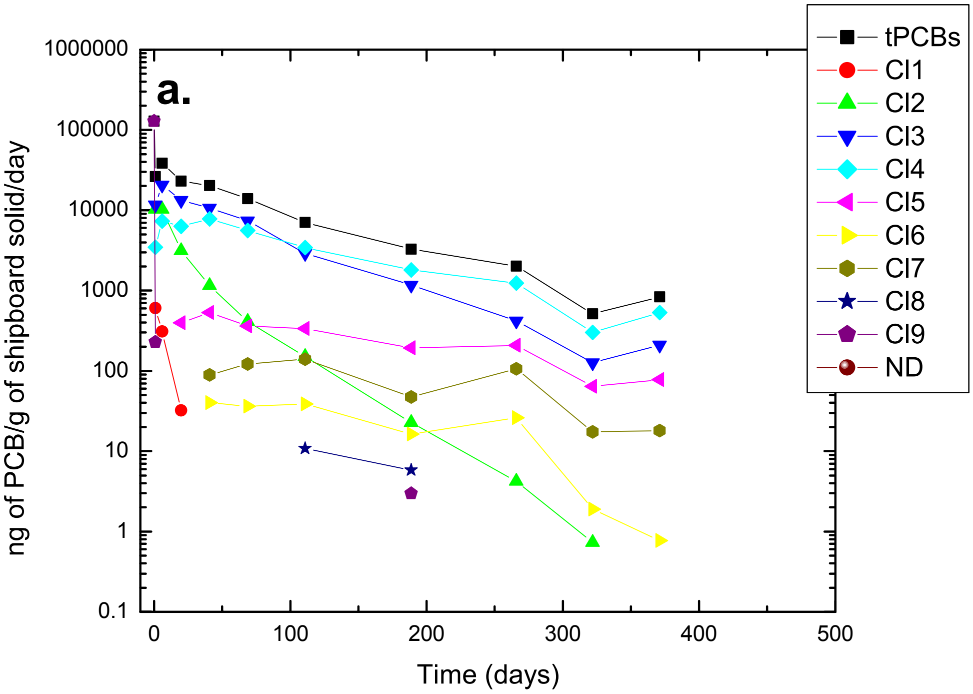
Time (days)	Curve Fit	95% UCI	95% LCI	95% UPI	95% LPI
469	***1.89***				
597.28962	2.63945	3.42056	2.03671	4.69037	1.48532
1493.48334	1.63852	2.41713	1.11072	3.11933	0.86069
3734.35667	1.01717	1.72362	0.60026	2.12314	0.48731
9337.51277	0.63144	1.23335	0.32328	1.46784	0.27163
23347.83539	0.39199	0.88399	0.17382	1.02539	0.14985
58379.72389	0.24334	0.63417	0.09337	0.72135	0.08209
145974.65266	0.15106	0.45519	0.05013	0.50992	0.04475
365000	0.09378	0.32685	0.02691	0.36171	0.02431

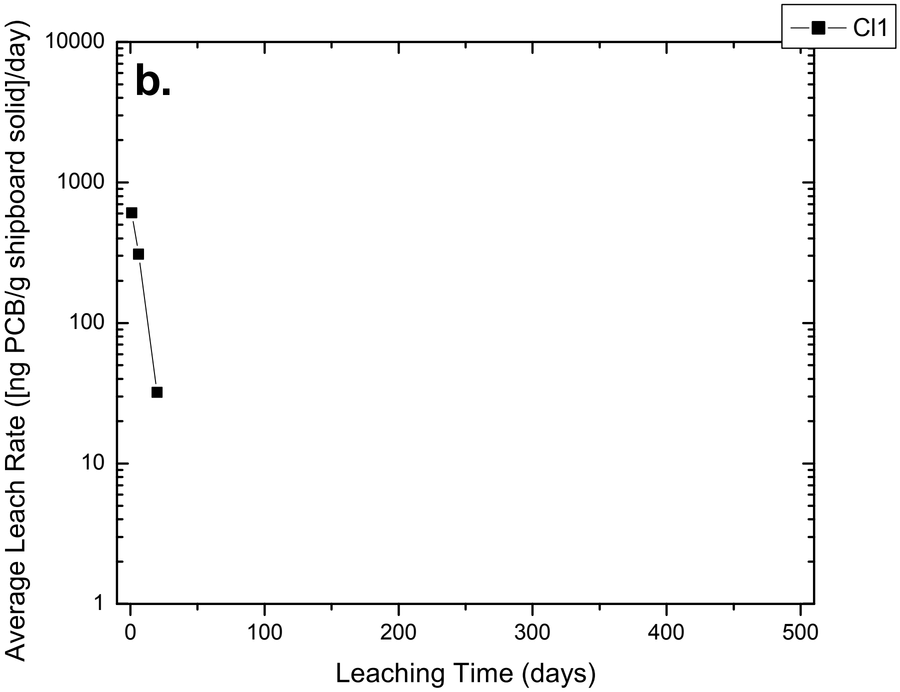
Figure 55. Extrapolation results for FRE tPCBs average leach rate extrapolation results (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over the

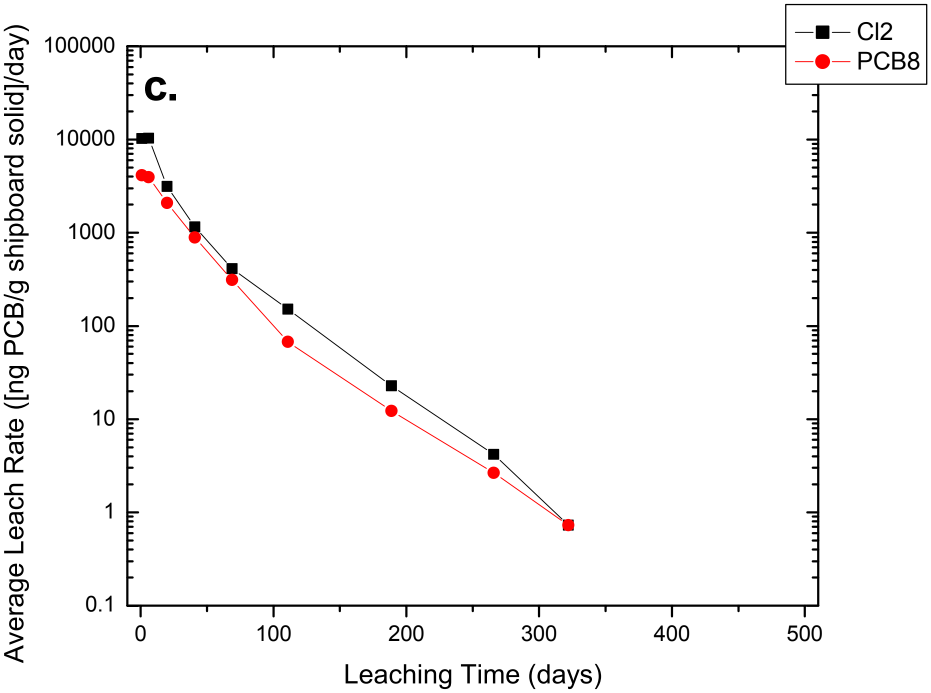
1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

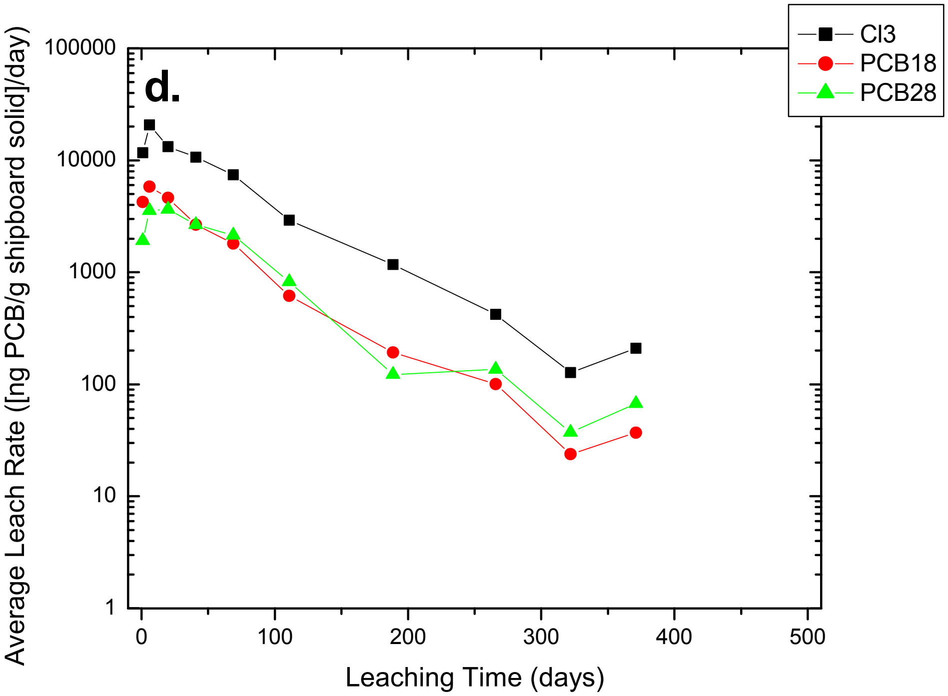
Aroclor 1268 (A1268) Analytical Control Dissolution Rate Behavior

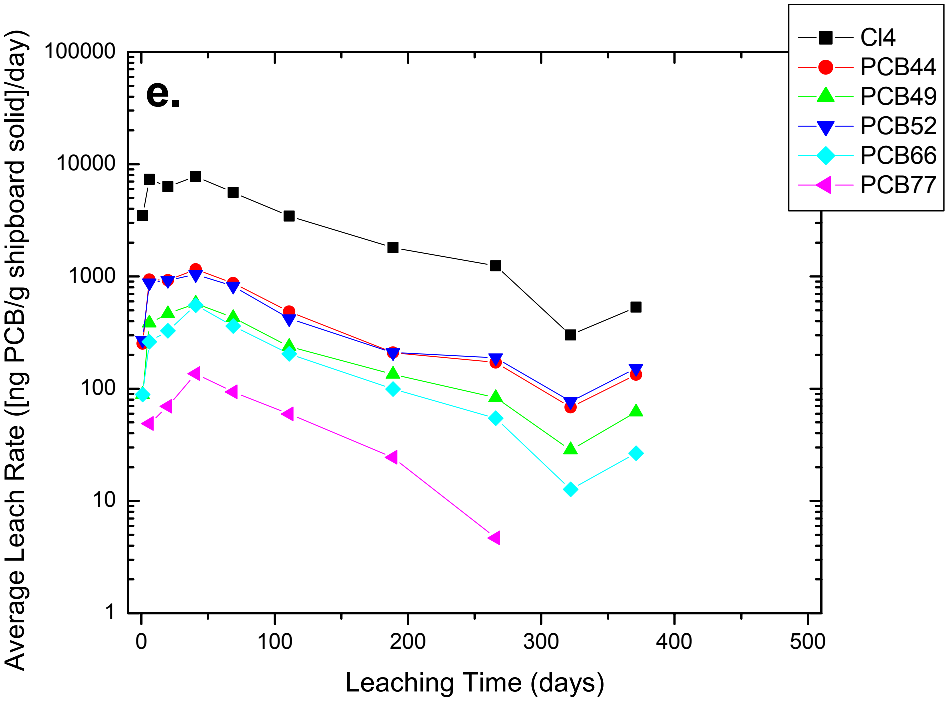
The A1268 plots below in Figure 56(a-j) represent the positive control plots that establish a reference or upper limit dissolution rate component for solids that contain a significant amount of A1268 in the shipboard solid matrix. As observed for A1254, leaching of individual congeners comprise a fundamental dissolution behavior, and the mechanism for pure A1268 dissolution is effected similarly, in that it is a pure PCB mixture and does not possess a shipboard solid matrix. Also, as with the A1254 control, each PCB congener in A1268 exists in (and is released from) a matrix comprised of a mixture of PCB congeners, resulting in only PCB-PCB interactions (cohesion) in the solid contributing to the release mechanism. This is in contrast with a shipboard solid, where the PCB-shipboard solid matrix interaction is the primary interaction during leaching and the PCB-PCB interaction in the solid, if PCBs are homogeneously dispersed in a matrix without phase-separated domains, is a much less significant contributor to the release behavior/mechanism. As mentioned previously, it is also possible that PCBs could be selectively phase-separated in some regions of the shipboard solid, rich in a particular PCB congener or congeners, in spite of the bulk composition closely matching the fingerprint for a particular Aroclor. A very small congener-rich phase present at the interface (SASA) could significantly effect the observed leaching. For reasons similar to those discussed for Aroclor 1254, the neat Aroclor 1268 analytical control behavior can only be considered a measure of A1268 PCB solvation capacity in seawater under the leaching conditions of the study, and is perhaps representative of the dissolution component of those PCBs uninhibited by the solid matrix at active leaching surfaces of shipboard solids. Aroclor 1268 is not a valid a leaching surrogate or leaching control for shipboard solids, however, neat Aroclor 1268 can be considered a surrogate/control for the leaching behavior of highly mobile material matrices such as oils or greases that contain Aroclor 1268.

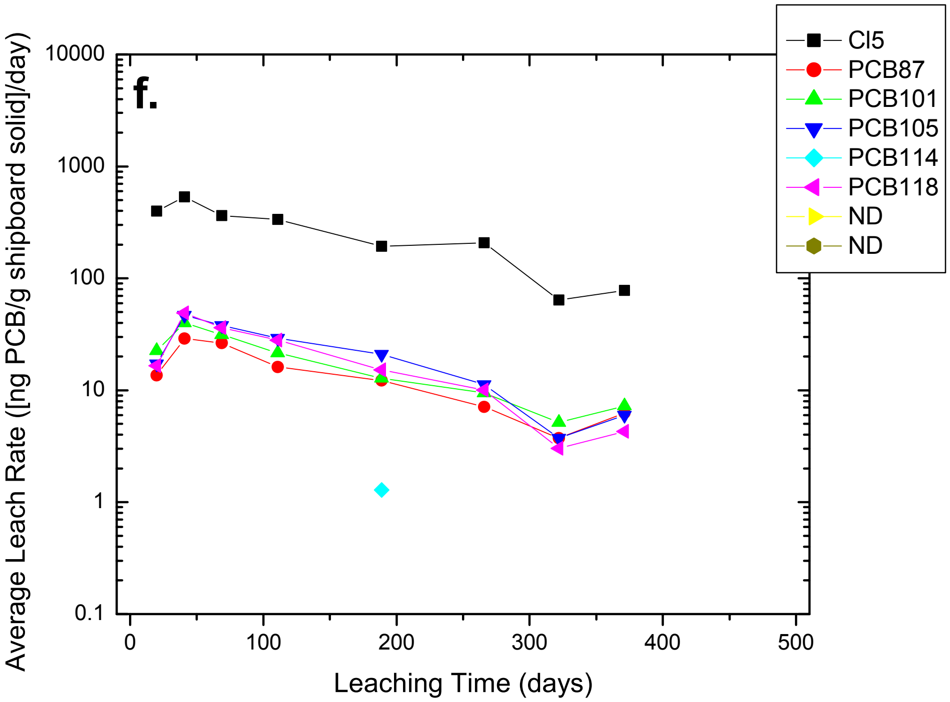


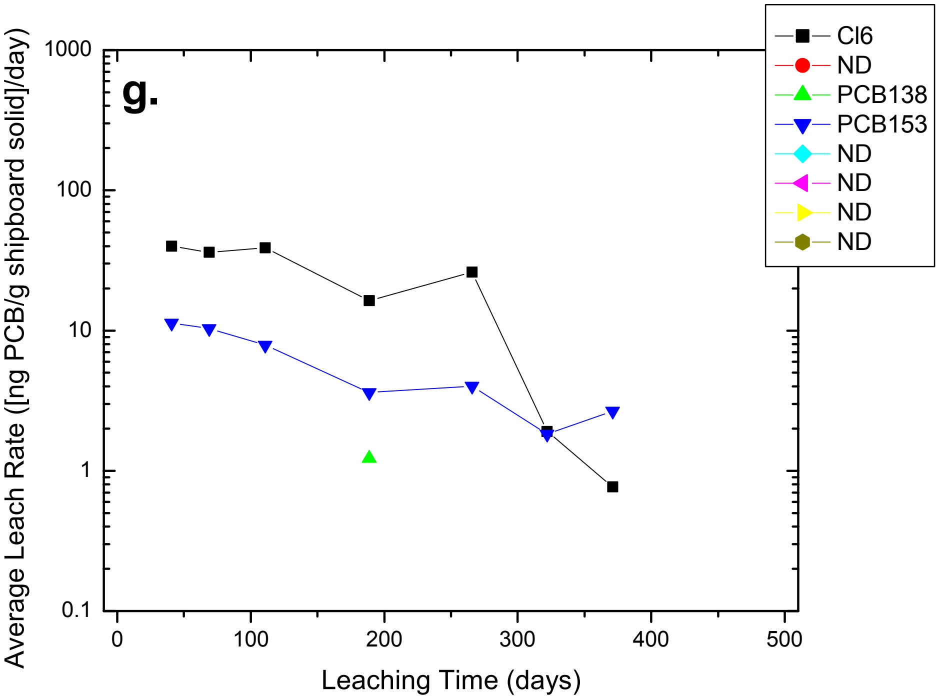

Cl1
b.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10000
1000
100
10
1
0
100
200
300
400
500
Leaching Time (days)

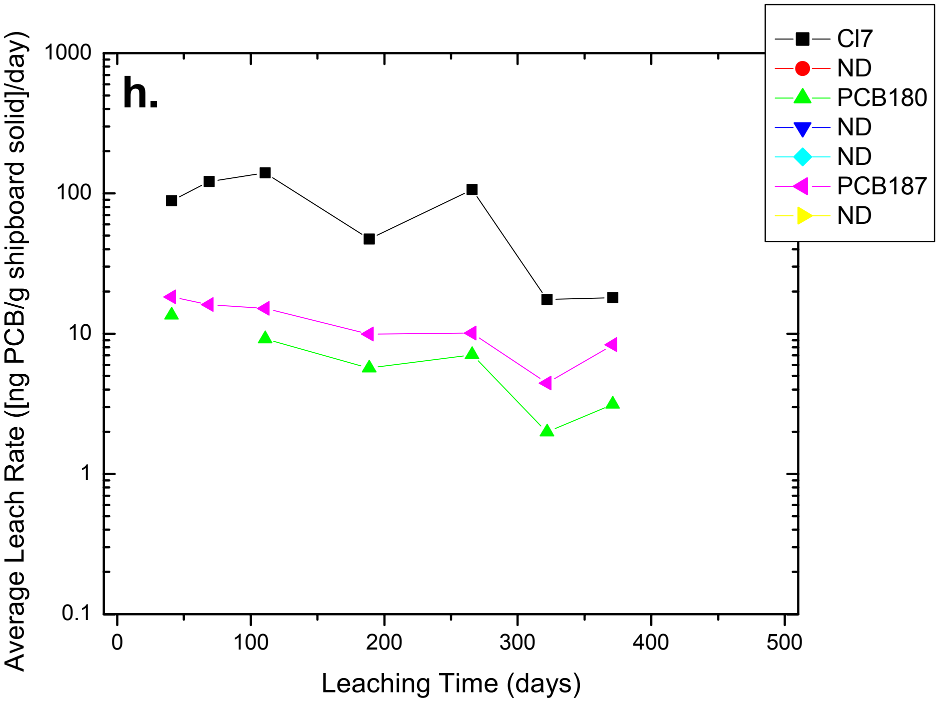

Cl2
PCB8
c.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100000
10000
1000
100
10
1
0.1
0
100
200
300
400
500
Leaching Time (days)

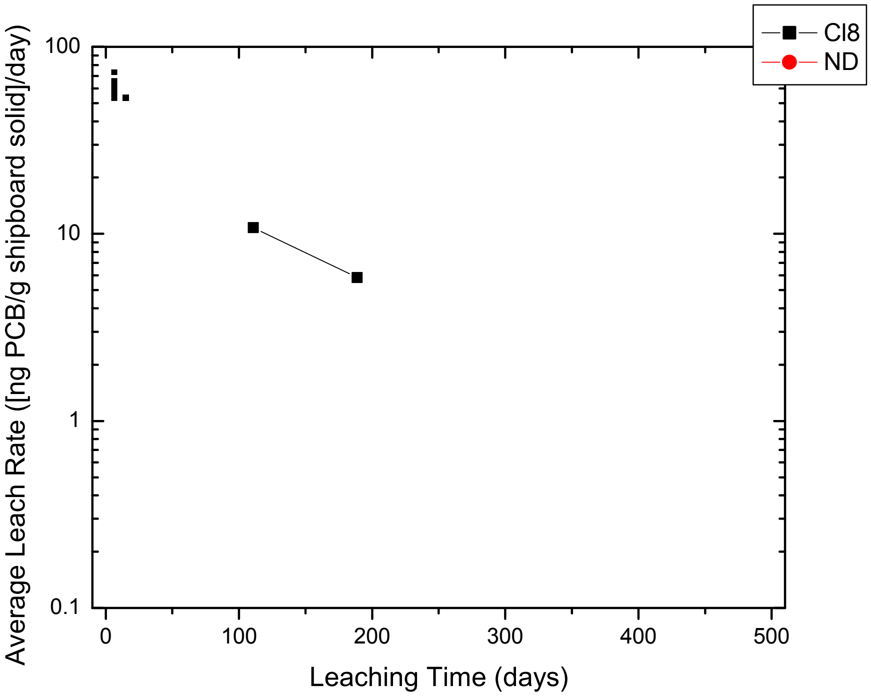

d.
Cl3
PCB18
PCB28
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100000
10000
1000
100
10
1
0
100
200
300
400
500
Leaching Time (days)


e.
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100000
10000
1000
100
10
1
0
100
200
300
400
500
Leaching Time (days)


f.
Cl5
PCB87
PCB101
PCB105
PCB114
PCB118
ND
ND
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10000
1000
100
10
1
0.1
0
100
200
300
400
500
Leaching Time (days)


g.
Cl6
ND
PCB138
PCB153
ND
ND
ND
ND
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1000
100
10
1
0.1
0
100
200
300
400
500
Leaching Time (days)


h.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1000
100
10
1
0.1
0
100
200
300
400
500
Leaching Time (days)
Cl7
ND
PCB180
ND
ND
PCB187
ND


i.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0
100
200
300
400
500
Leaching Time (days)
Cl8
ND

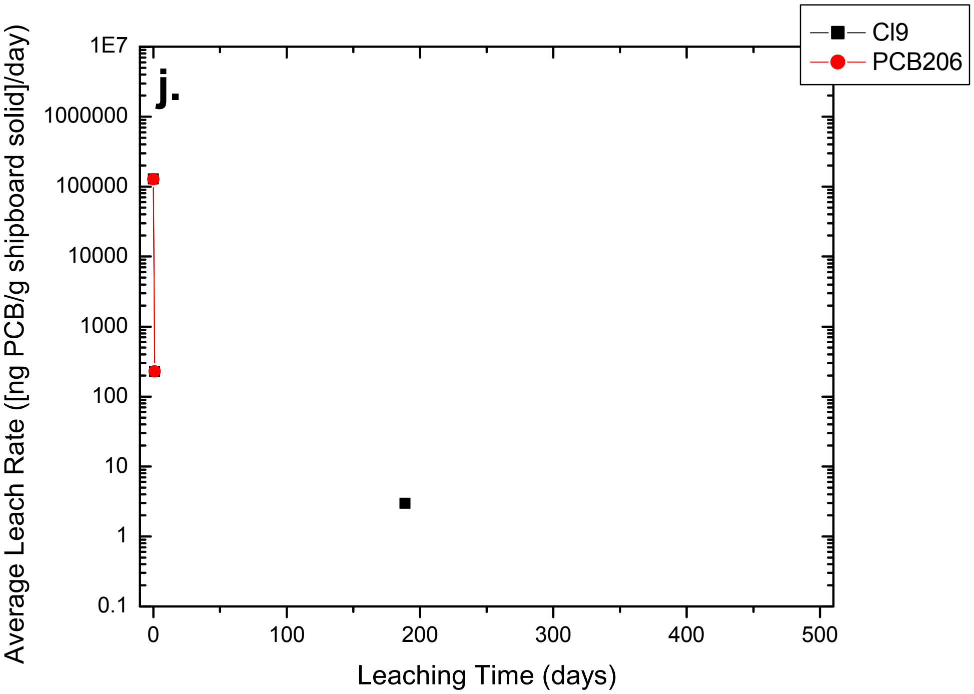
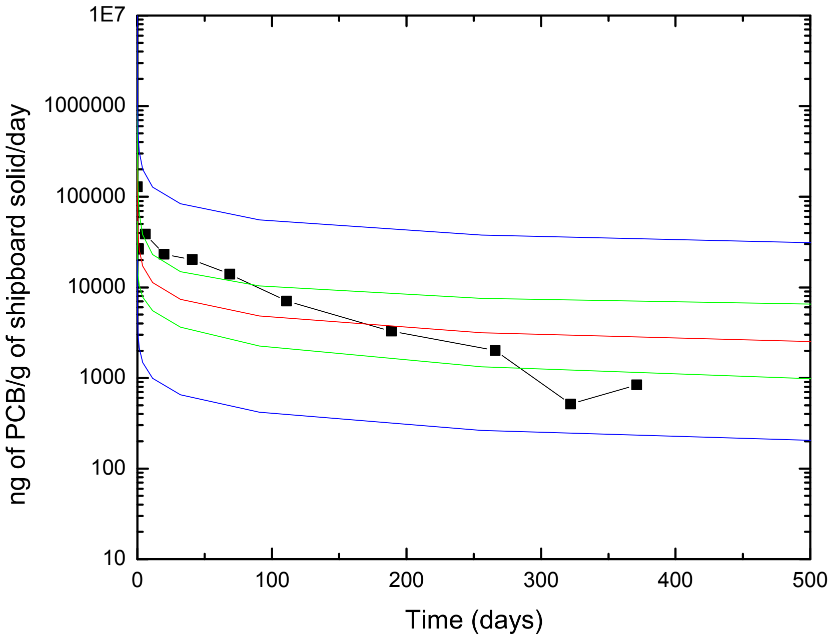


Figure 56 (a-j). Plot a) shows experimental tPCBs average leach rate and contributing homologue group average leach rates vs. leaching time for A1268. The sum of the homologue average leach rate curves is equal to the upper tPCBs average leach rate curve (solid black squares). Plots (b-j) show homologue group average leach rates and corresponding target congener average leach rates within detected homologue groups (Cl1-Cl9) vs. leaching time for A1268. Lines connecting adjacent data points indicate detection in consecutive leachate samples (continued leaching of that PCB congener or homologue group), whereas no line indicates a discontinuity in leaching (analyte not detected in an adjacent leachate sample). Non-detected target congeners within detected homologue groups included PCBs 123 & 126 (Cl5); PCBs 128, 156,157, 158, 167, & 169 (Cl6); PCBs 170, 183, 184, & 189 (Cl7); and PCB 195 (Cl8).

Each of the above A1268 average dissolution rate curves corresponds to a worst-case A1268 release scenario for a solid containing A1268 at the interface (SASA). As indicated for the pure A1254 experiment, this type of leaching experiment was not a "leaching" control/surrogate or a solubility experiment, where an excess of the pure Aroclor in a known volume of seawater would equilibrate until saturation was reached, leaving undissolved solid. A solubility experiment is limited by PCB saturation in the seawater. In this study, the pure Aroclor solid matrix itself limited the dissolution behavior in part. This was a feature of the experimental design; the seawater leachate was exchanged at similar sample collection intervals selected to avoid A1254 or A1268 saturation in shipboard solid leaching experiments, but in the case of neat Aroclor this did not preclude the possibility of saturation between leachate exchange/sampling points. Effectively, this means that a pure Aroclor positive control curve represents the seawater A1268 PCB dissolution capacity or effective saturation condition for Aroclor 1268 *under the experimental leaching conditions* used in the shipboard solid leaching determinations. It is for this similarity that Aroclor results are occasionally referred to as "leaching", and such inadvertent reference to Aroclors "leaching" should be in the context of positive analytical controls. This is not intended to imply that Aroclor results are suitable for use as "leaching" controls, or surrogates for the leaching process defined by PCBs leaching from inert solid matrices.

Each of the *concentration vs. time* leaching curves in the Shipboard Solid Specific Leaching Data section for shipboard solids likely to contain A1268 only or A1268 with A1254 and/or A1260 (felt gasket–inner, felt gasket–outer, bulkhead insulation, and aluminized paint), were evaluated against the pure Aroclor 1268 *concentration vs. time* curves, also presented in the Shipboard Solid Specific Leaching Data section. Bulkhead insulation and aluminized paint results were also evaluated against A1254 because this Aroclor is possibly present in significant amounts in addition to A1268. It was confirmed that most of the shipboard solid leachate PCB concentrations were *lower*, consistent with PCB release being suppressed by the shipboard solid matrix itself. This type of comparison was also performed on the raw concentration data in Appendix C for all analytes in individual seawater samples across the experimental timeframes, with similar significant suppression of PCB concentrations by the shipboard solids observed. As a result, the average leach rates subsequently calculated and plotted below for these solids are considered valid leaching behaviors, and occur well below the effective minimum saturation limit. The A1268 leaching results can also be used to estimate the worst-case leaching behavior for mobile materials containing A1268, but not tested in this work, e.g. oils and greases that contain A1268 can be approximated by A1268 results.

The average leach rate curve data were fit in the decreasing portion of the curves and extrapolated beyond the final experimental data point. Details for the curve fitting and extrapolation can be found in APPENDIX A, however, the results for tPCBs only have been included in Figure 57 below. These values, extrapolated to 1000 years, are tabulated below the figure. The final empirical tPCBs average value is included as a reference (838.0 ng/g shipboard solid-day at 371 days).



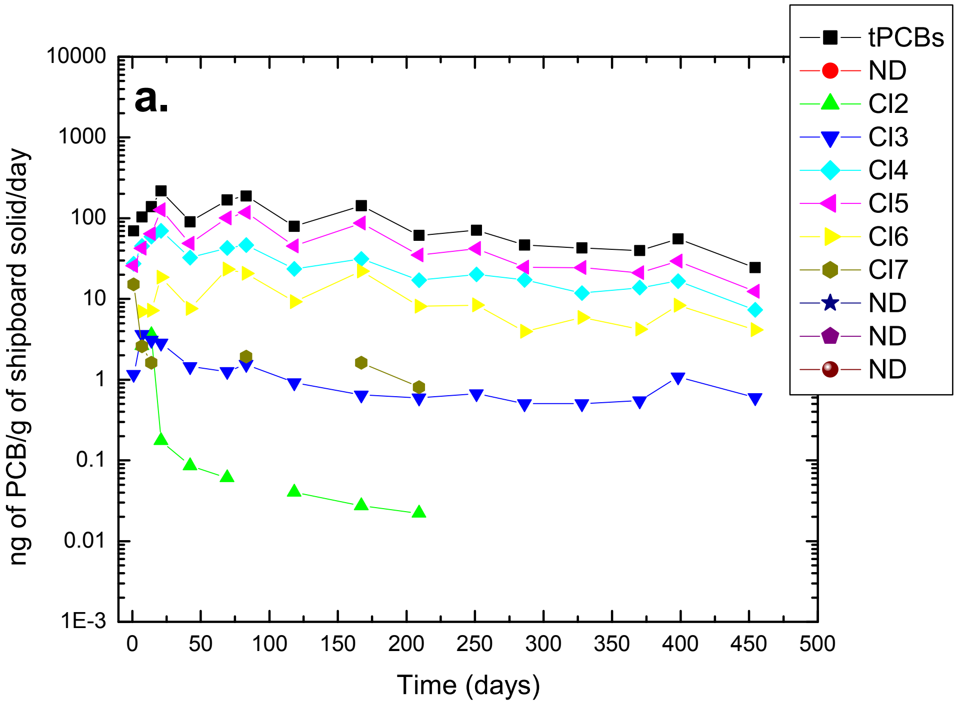
Time (days)	**Curve Fit**	**95% UCI**	**95% LCI**	**95% UPI**	**95% LPI**
371	***838.0***				
721.79008	2065.44554	5727.09147	744.89211	26146.73518	163.15862
2037.31367	1351.77061	4447.29738	410.87511	18415.72424	99.22411
5750.49054	884.69231	3504.30547	223.34825	13183.5445	59.36799
16231.24697	579.00392	2787.45135	120.26956	9577.88476	35.00204

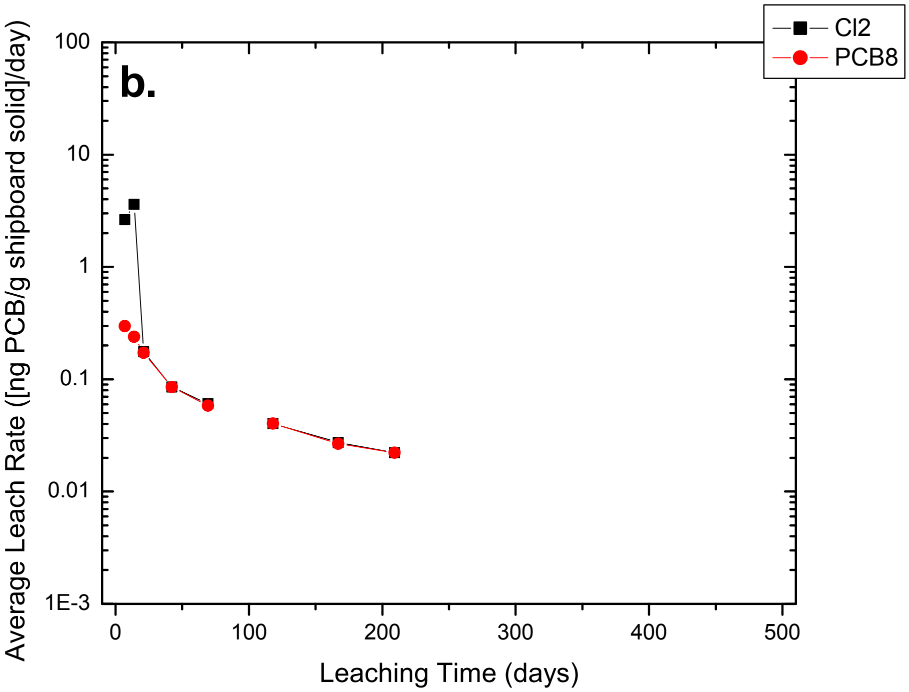
45814.07039	378.94027	2231.31173	64.35485	7050.43822	20.36692
129314.09703	248.00476	1793.99938	34.28449	5250.64023	11.71407
365000	162.31149	1446.95433	18.20722	3950.43643	6.66889

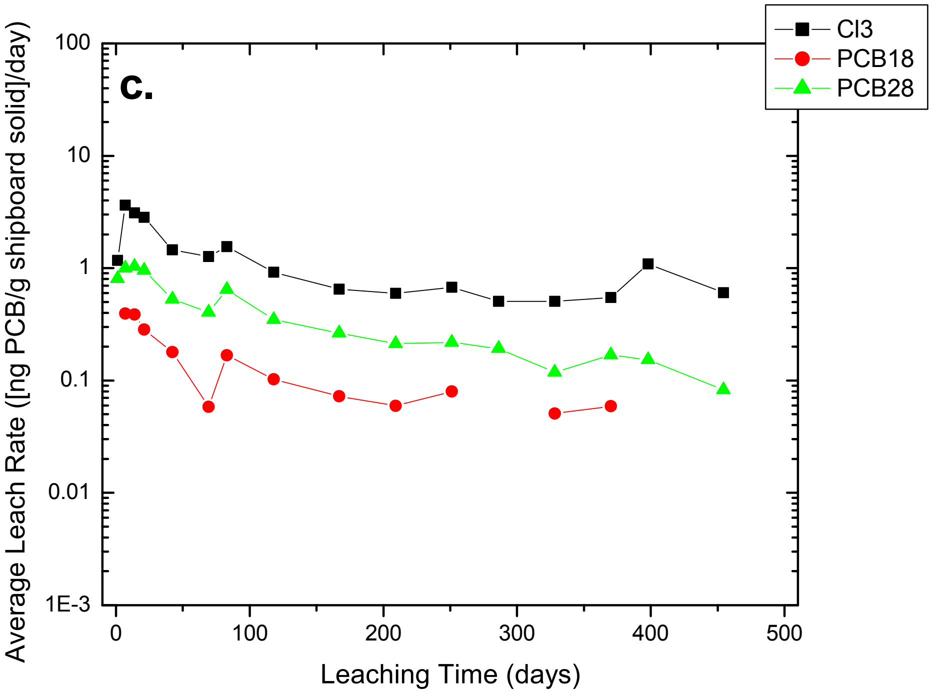
Figure 57. A1268 tPCBs average leach rate extrapolation results (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over a 1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

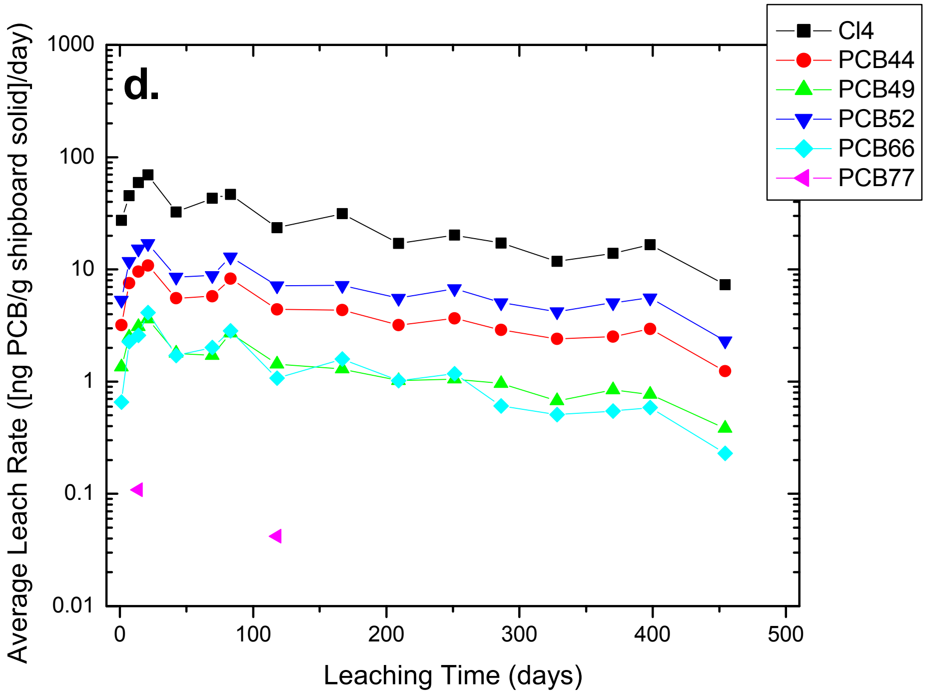
Bulkhead Insulation (BHI) Leach Rate Behavior

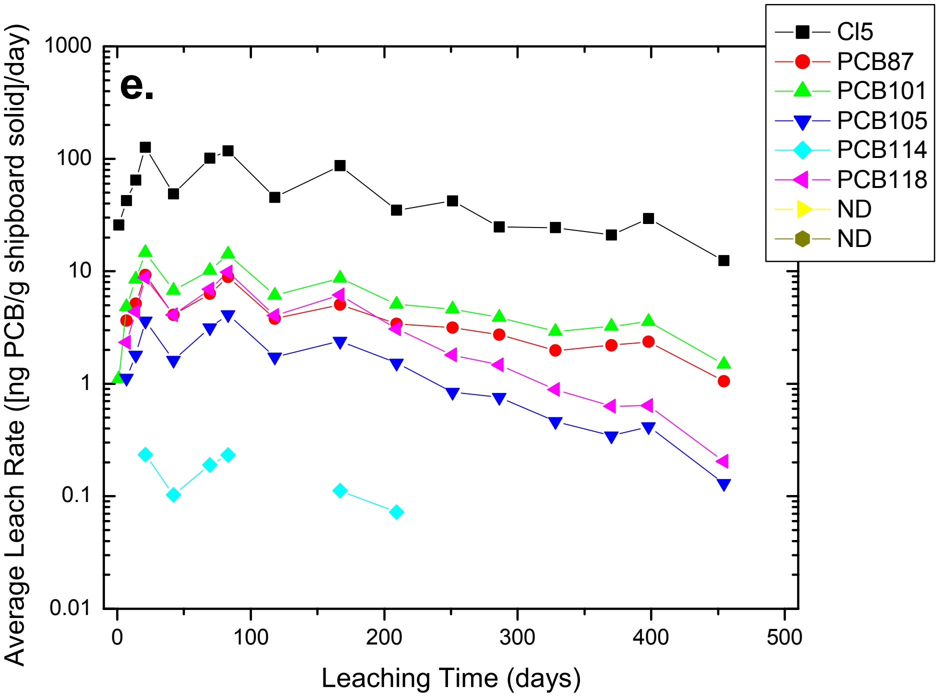
This shipboard solid contained 0.044 wt% tPCBs; nominally 15.3% A1268, 31.3% A1260, and 54.3% A1254, as indicated in Table 10. BHI exhibited the highest leach rates for all of the shipboard solids tested, however these leach rates were still ~2 orders of magnitude lower than those for either pure Aroclor. Average leach rate curves are plotted in Figure 58(a-g) below, represented by homologue groups Cl2-Cl7. Homologue groups Cl2 and Cl7, and corresponding target congeners, were observed to leach initially and then became undetectable just after 200 days of exposure.

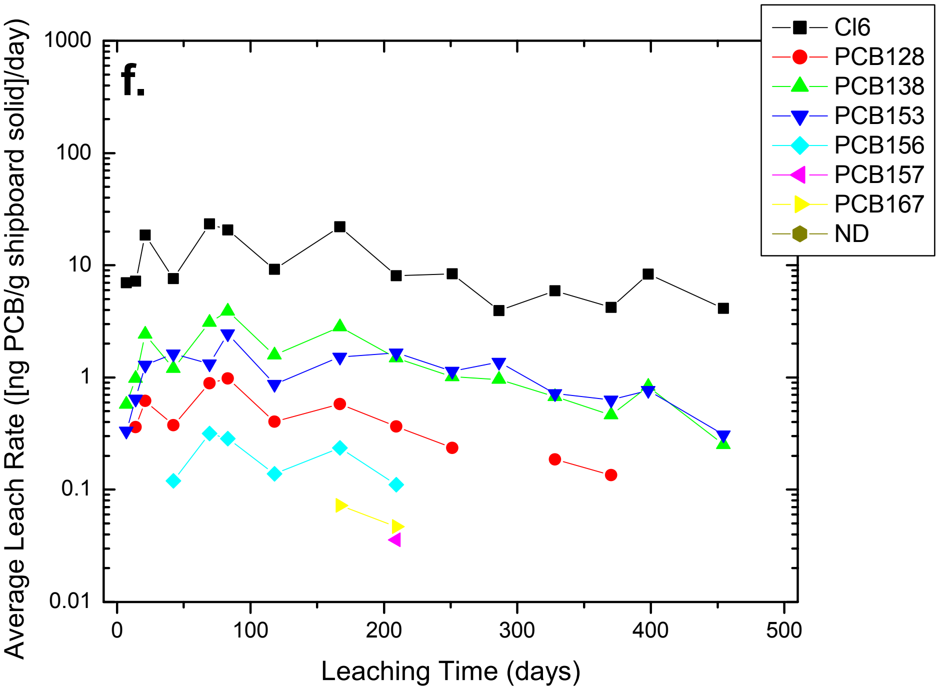



b.
Cl2
PCB8
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


c.
Cl3
PCB18
PCB28
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


d.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1000
100
10
1
0.1
0.01
0
100
200
300
400
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77


e.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1000
100
10
1
0.1
0.01
0
100
200
300
400
500
Leaching Time (days)
Cl5
PCB87
PCB101
PCB105
PCB114
PCB118
ND
ND



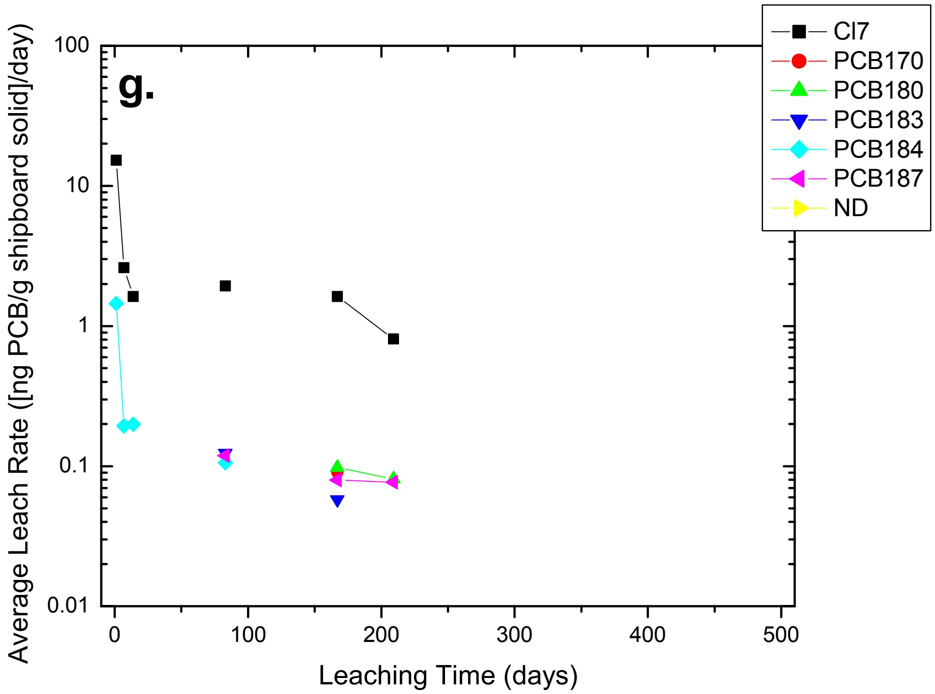
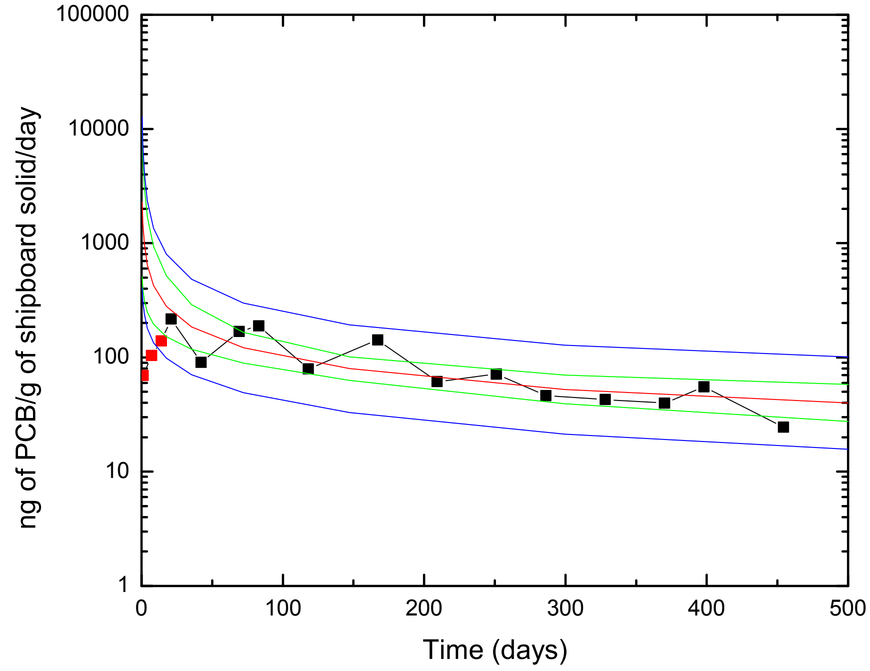


Figure 58 (a-g). Plot a) shows experimental tPCBs average leach rate and contributing homologue group average leach rates vs. leaching time for BHI. The sum of the homologue average leach rate curves is equal to the tPCBs average leach rate curve (solid black squares). Plots (b-g) show homologue group average leach rates and corresponding target congener average leach rates within detected homologue groups (Cl2-Cl7) vs. leaching time for BHI. Lines connecting adjacent data points indicate detection in consecutive leachate samples (continued leaching of that PCB congener or homologue group), whereas no line indicates a discontinuity in leaching (analyte not detected in an adjacent leachate sample). Non-detected target congeners within detected homologue groups included PCBs 123 & 126 (Cl5); PCB 169 (Cl6); and PCB 189 (Cl7).

The average leach rate curves for BHI were each extrapolated using curve fits of data in the decreasing portion of the curves. Details for the curve-fitting and extrapolation can be found in APPENDIX A, using standard methods of data-treatment and curve-fitting described in the Leach Rate Analysis section. The results for tPCBs only have been included in Figure 59 below. These values, extrapolated to 1000 years, are tabulated below the figure. The final empirical tPCBs average value is included as a reference (24.5 ng/g shipboard solid-day at 454 days).

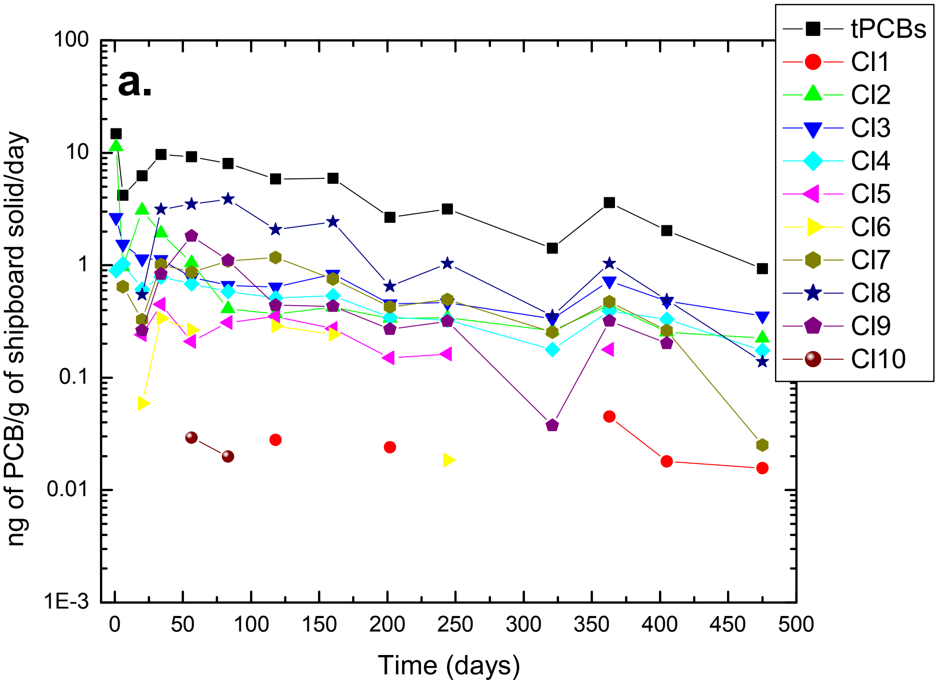


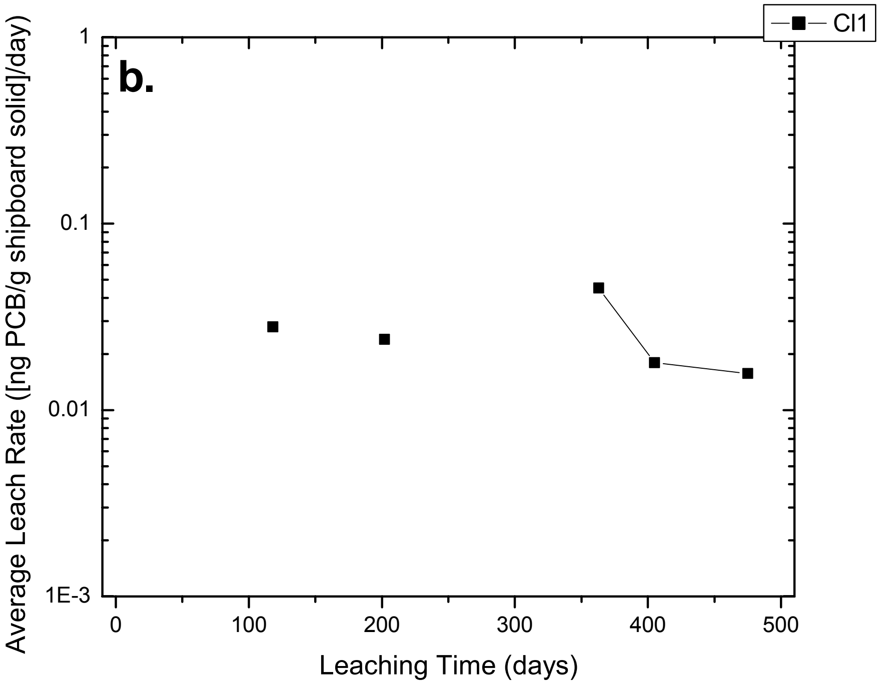
Time (days)	Curve Fit	95% UCI	95% LCI	95% UPI	95% LPI
454	***24.5***				
609.43782	34.4489	52.56691	22.57554	88.96799	13.3388
1240.296	22.64329	40.59459	12.63022	63.47185	8.07789
2524.1856	14.88345	31.66899	6.99477	46.37752	4.77639
5137.09059	9.78291	24.81893	3.85614	34.49882	2.77416
10454.73826	6.43031	19.49721	2.12076	26.00223	1.59021
21276.93684	4.22665	15.33808	1.16472	19.78835	0.90278
43301.70973	2.77818	12.07688	0.6391	15.16757	0.50887
88125.3763	1.8261	9.51476	0.35047	11.6885	0.28529
179348.15959	1.2003	7.49934	0.19211	9.04453	0.15929
365000	0.78896	5.91264	0.10527	7.02099	0.08866

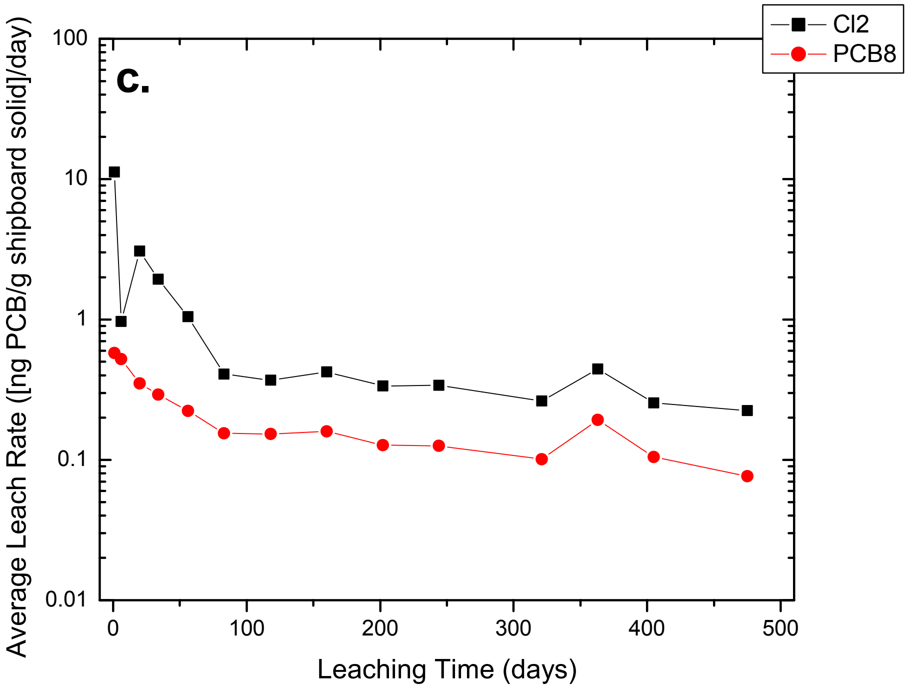
Figure 59. BHI tPCBs average leach rate extrapolation results (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over a 1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

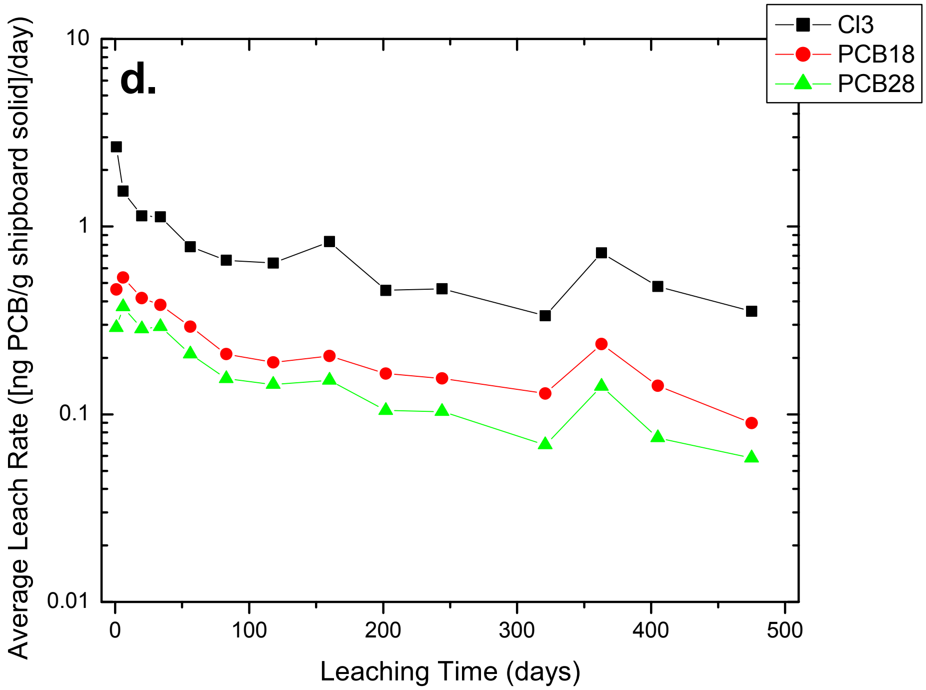
Felt Gasket/Inner (FGI) Leach Rate Behavior

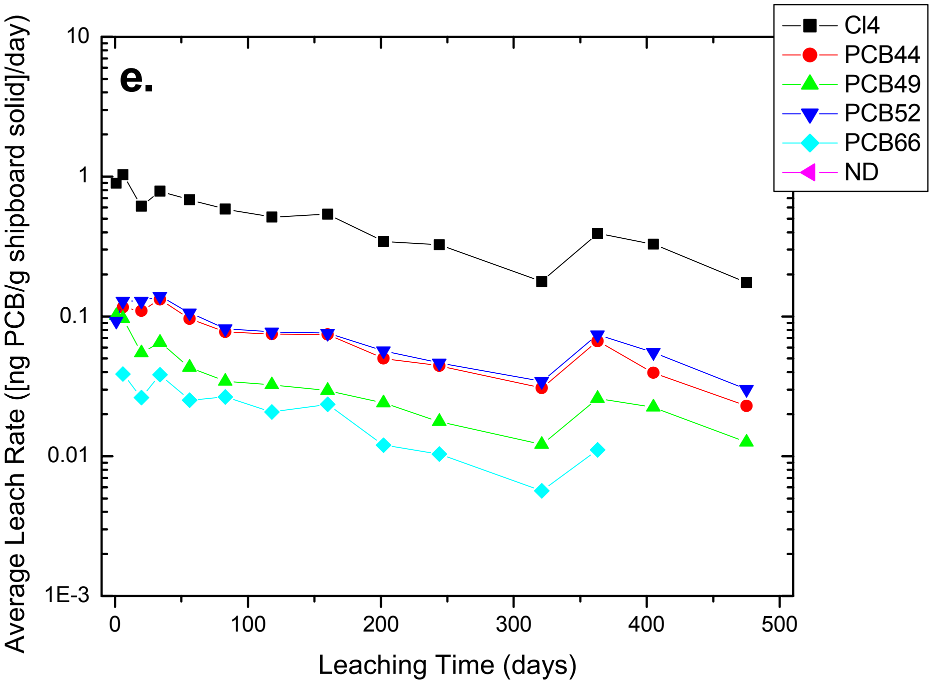
This shipboard solid contained 23.03 wt% tPCBs corresponding nominally to A1268 only, as indicated in Table 10. This shipboard solid exhibited the highest PCB concentration in any solid tested, yet did not exhibit the highest average leach rate out of all shipboard solids tested. A surface-area-normalized leach rate would perhaps correlate with PCB content in the solid, but this was not within the scope of this work, considering that the seawater accessible surface area is very likely changing as a function of exposure time. As with other solids, FGI leach rates were still lower (by ~4 orders of magnitude) than those for the pure Aroclor 1268 control. Average leach rate curves are plotted in Figure 60(a-k) below, represented by all homologue groups Cl1-Cl10, the only shipboard solid to exhibit leaching for all homologue groups. Homologue groups Cl5 and Cl6 leached throughout the first half of the experiment; both became undetecable at ~250 days of exposure, and Cl5 reappeared once more beyond that leaching time (near 350 days). Homologue group Cl10 was detected only twice prior to ~75 days. The remaining homologue groups leached consistently throughout the entire leaching series.

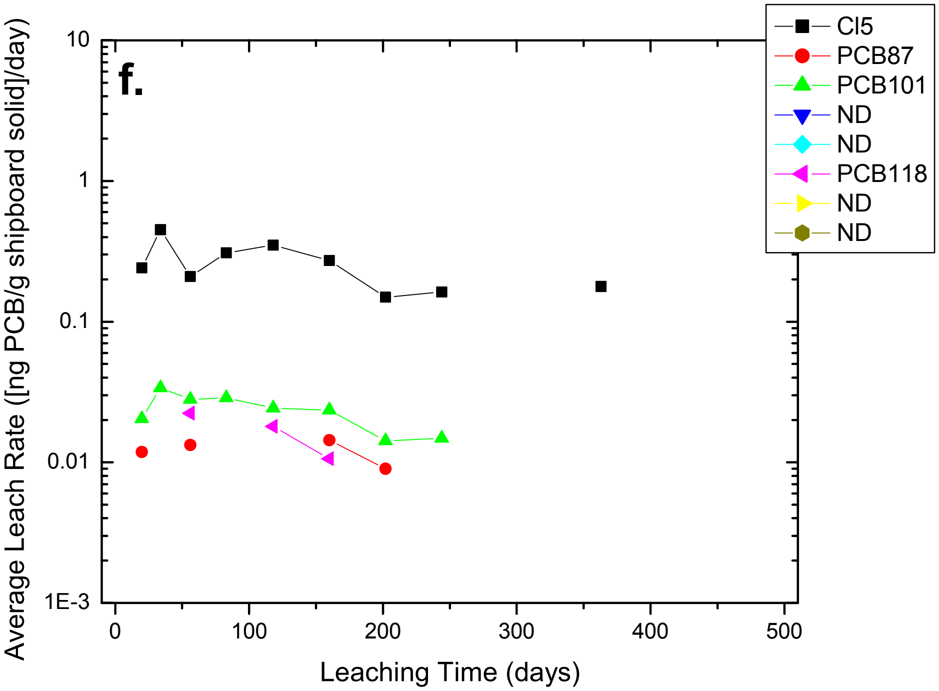


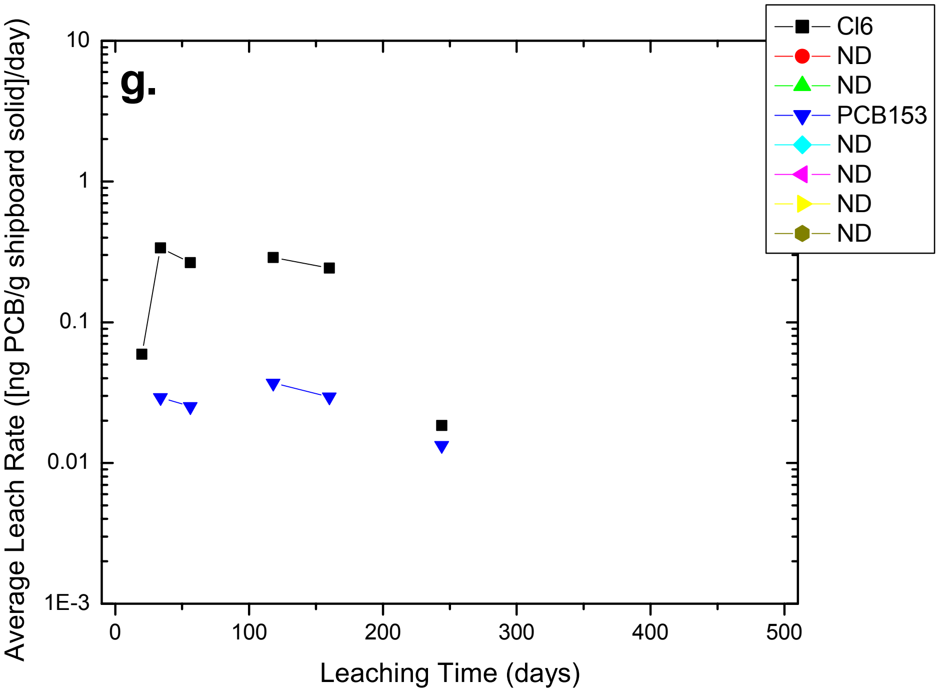

b.
—■— Cl1
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)

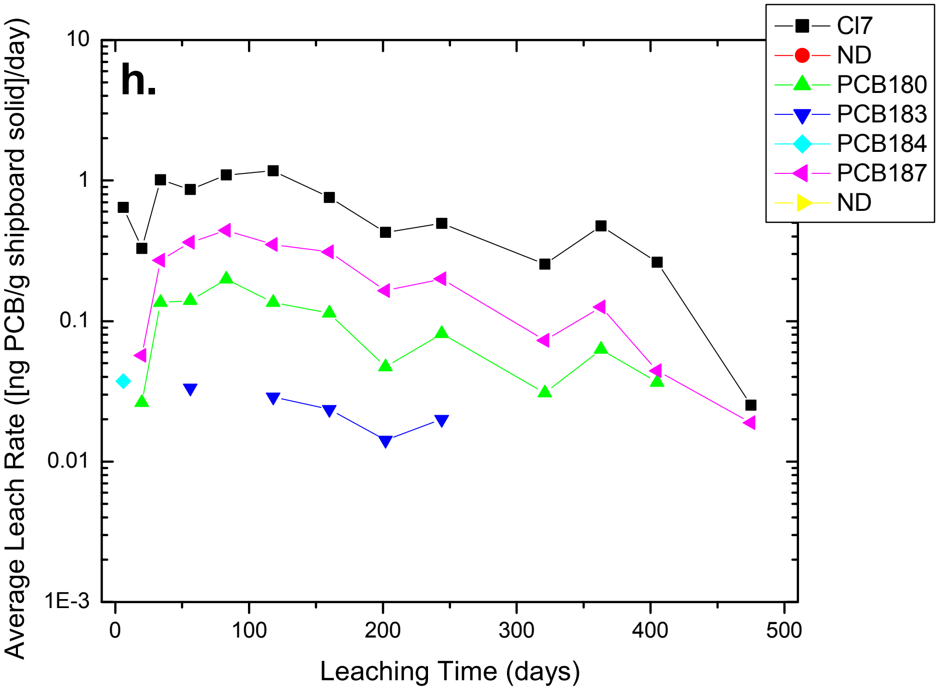

c.
—■— Cl2
—●— PCB8
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
0
100
200
300
400
500
Leaching Time (days)

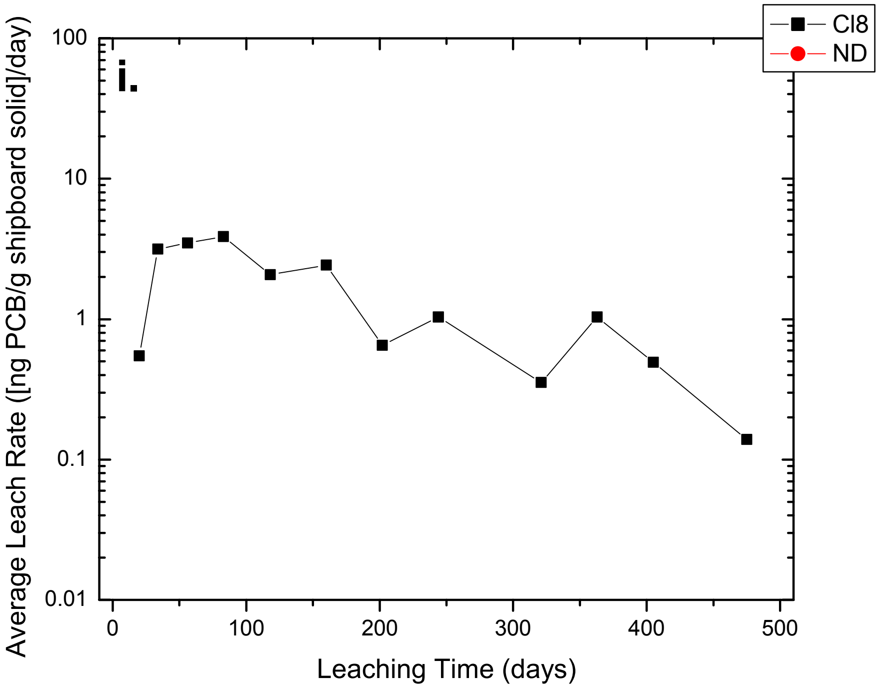

d.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
0
100
200
300
400
500
Leaching Time (days)
Cl3
PCB18
PCB28

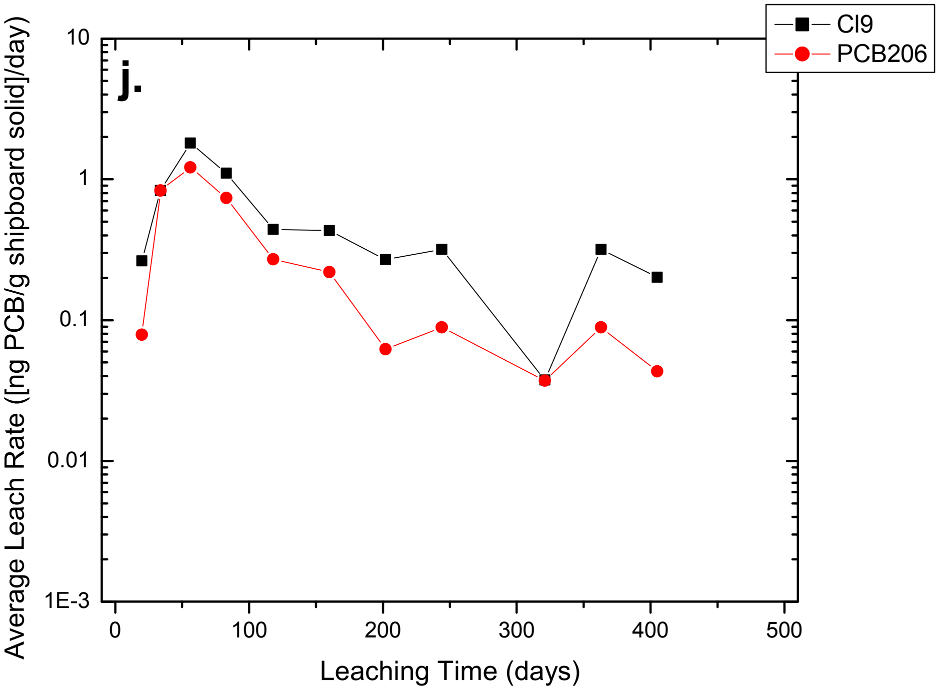

e.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
PCB66
ND


f.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)
Cl5
PCB87
PCB101
ND
ND
PCB118
ND
ND


g.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)
Cl6
ND
ND
PCB153
ND
ND
ND
ND


h.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)
Cl7
ND
PCB180
PCB183
PCB184
PCB187
ND


i.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
0
100
200
300
400
500
Leaching Time (days)
Cl8
ND



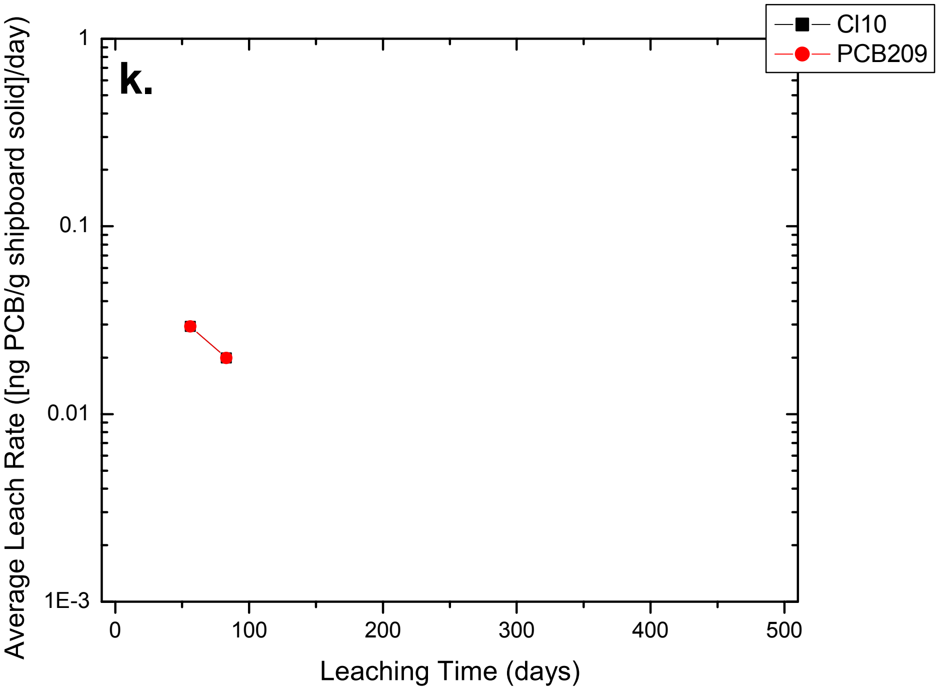
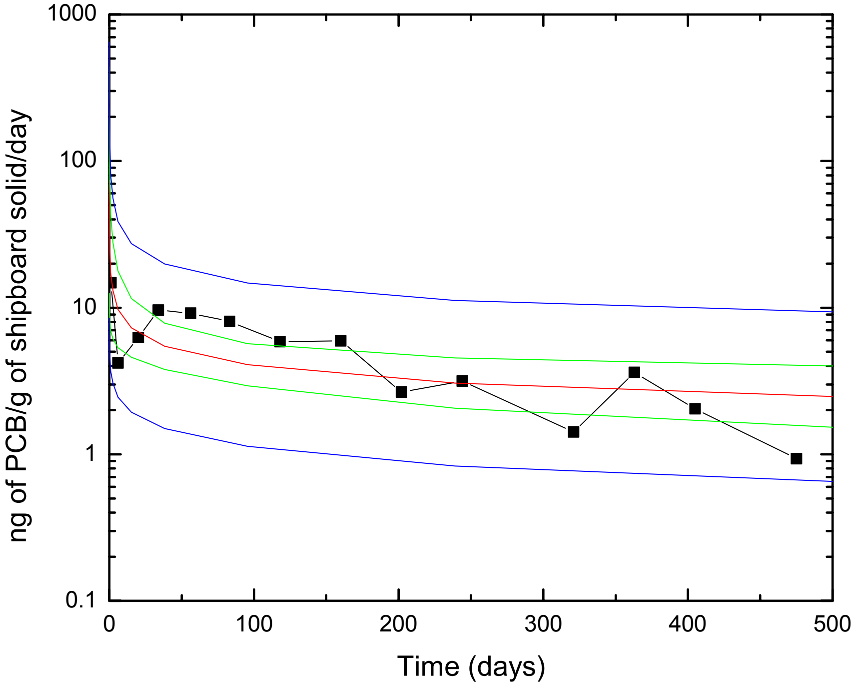


Figure 60 (a-k). Plot a) shows experimental tPCBs average leach rate and contributing homologue group average leach rates vs. leaching time for FGI. The sum of the homologue average leach rate curves is represented by the tPCBs average leach rate curve (solid black squares). Plots (b-k) show homologue group average leach rates and corresponding target congener average leach rates within detected homologue groups Cl1-Cl10 vs. leaching time for FGI. Lines connecting adjacent data points indicate detection in consecutive leachate samples (continued leaching of that PCB congener or homologue group), whereas no line indicates a discontinuity in leaching (analyte not detected in an adjacent leachate sample). Non-detected target congeners within detected homologue groups included PCB 77 (Cl4); PCBs 105, 114, 123 & 126 (Cl5); PCBs 128, 138, 156,157, 158, 167, & 169 (Cl6); PCBs 170 & 189 (Cl7); and PCB 195 (Cl8).

The average leach rate curves for FGI described above were extrapolated using curve fitting for the decreasing portion of the curves. Curve fits and extrapolation details are included in APPENDIX A, using the data-treatment and curve-fitting approach described in the Leach Rate Analysis section of this report. Figure 61 below summarizes the results for tPCBs only. These values, extrapolated to 1000 years, are tabulated below the figure. The final empirical tPCBs average value is included as a reference (0.93 ng/g shipboard solid-day at 475 days).

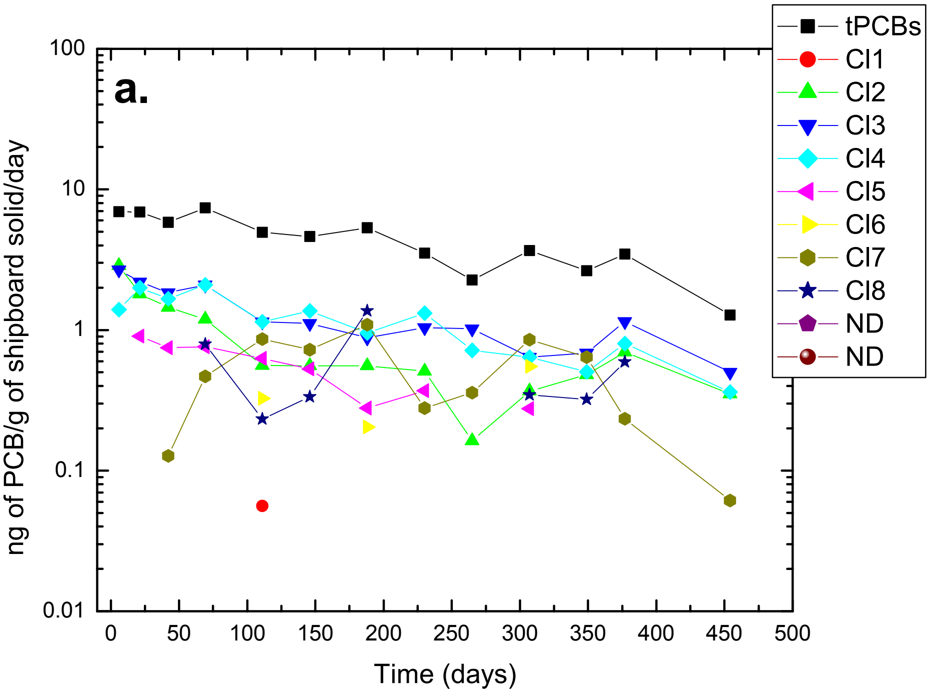


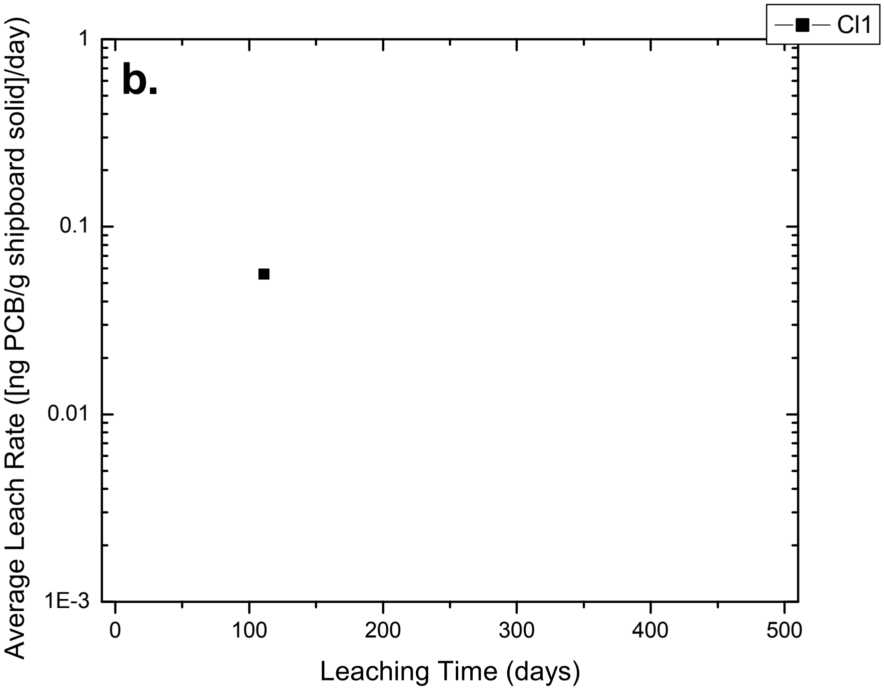
Time (days)	Curve Fit	95% UCI	95% LCI	95% UPI	95% LPI
475	*0.93*				
597.28962	2.28678	3.81706	1.37	8.74794	0.59778
1493.48334	1.71146	3.30541	0.88616	6.96722	0.42041
3734.35667	1.28089	2.89931	0.56588	5.65456	0.29015
9337.51277	0.95863	2.56001	0.35898	4.66301	0.19708
23347.83539	0.71746	2.26897	0.22686	3.89647	0.1321
58379.72389	0.53696	2.01571	0.14304	3.29132	0.0876
145974.65266	0.40187	1.79346	0.09005	2.80468	0.05758
365000	0.30076	1.5974	0.05663	2.40713	0.03758

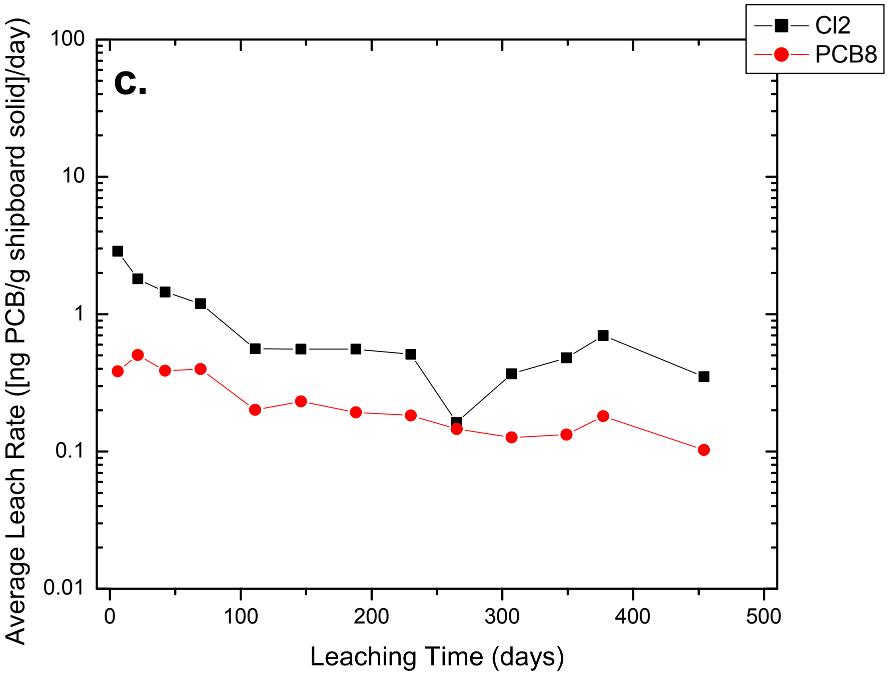
Figure 61. FGI tPCBs average leach rate extrapolation results (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over a 1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

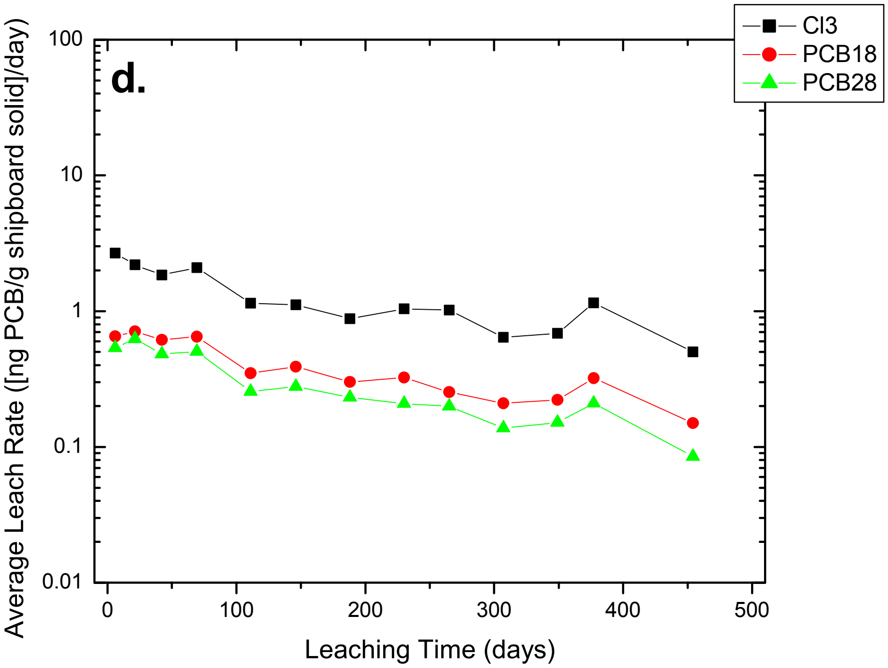
Felt Gasket/Outer (FGO) Leach Rate Behavior

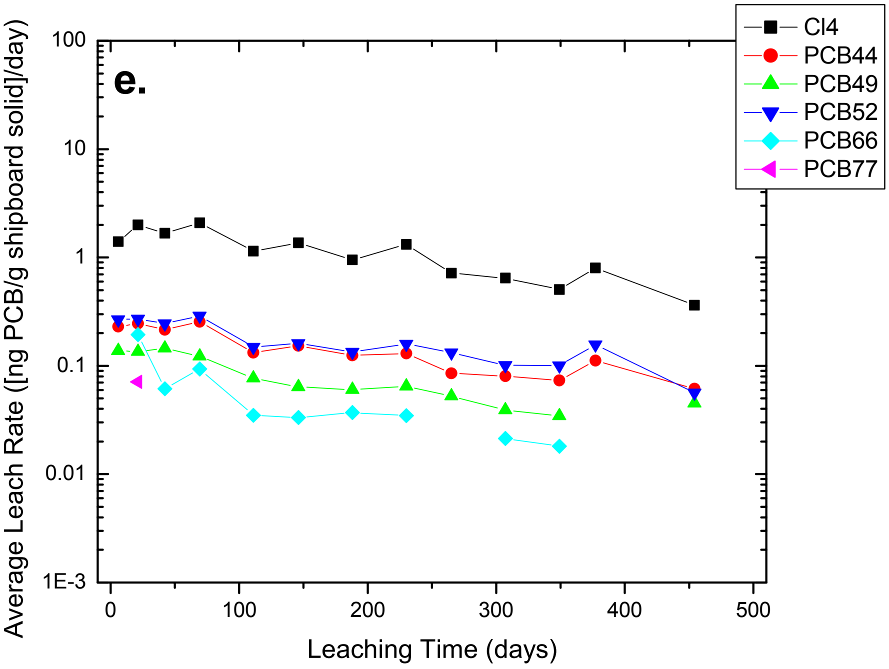
This shipboard solid contained 11.74 wt% tPCBs as Aroclor 1268 (Table 10), similar to FGI. However, its leaching behavior was somewhat different as shown below in Figure 62(a-i). Homologue groups Cl1-Cl8 represent the leaching behavior, with only a single Cl1 detection observed at just after 100 days of leaching. Homologue groups Cl5 and Cl8 consistently appeared early in the leaching but later appeared only sporadically, Cl6 was only sporadically detected throughout, whereas the other detected homologue groups consistently leached throughout. Again, as observed for FGI, this solid contained a high level of PCBs (second highest concentration), but leached at ~4.5 orders of magnitude less than the A1268 control.

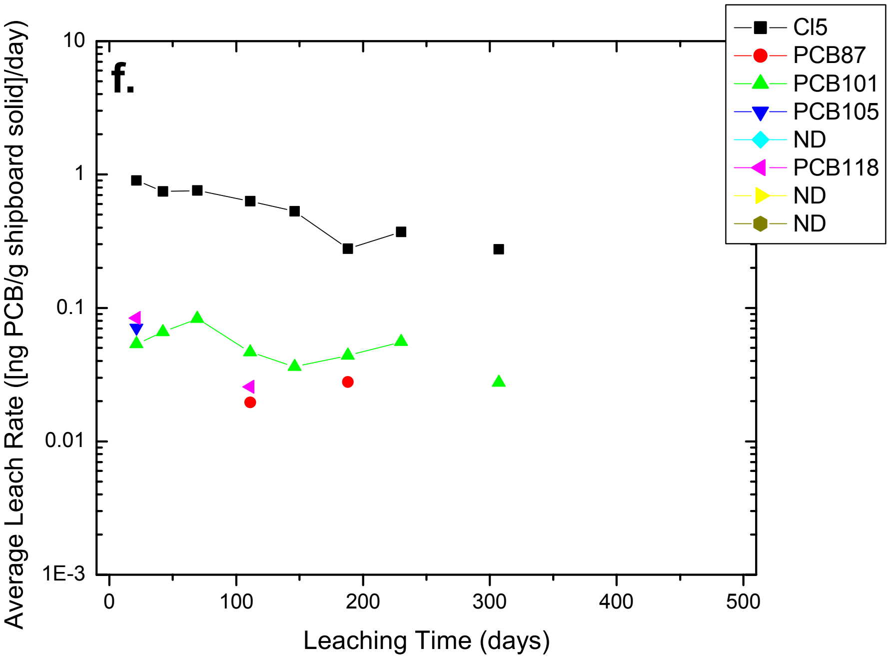


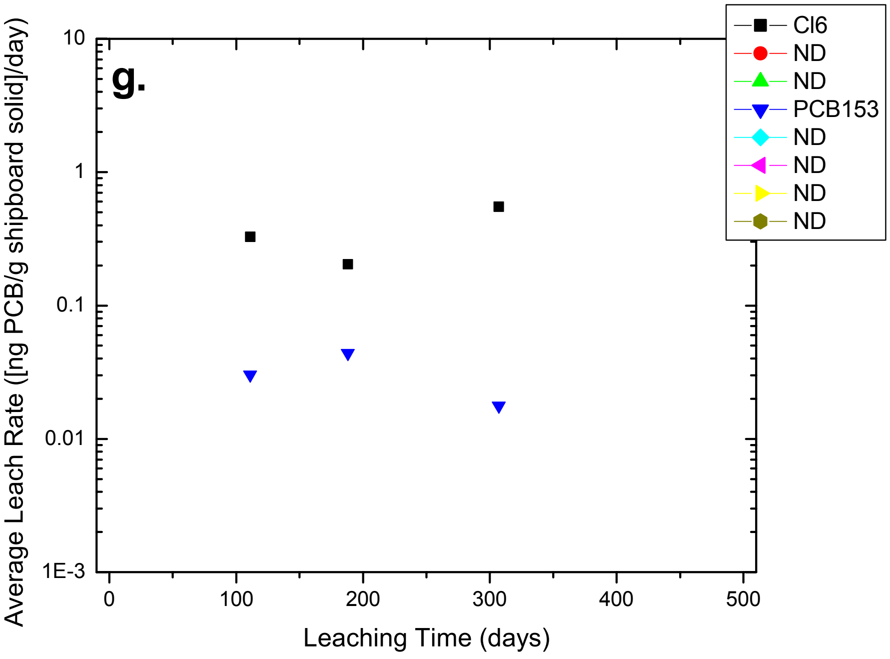

b.
Cl1
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)

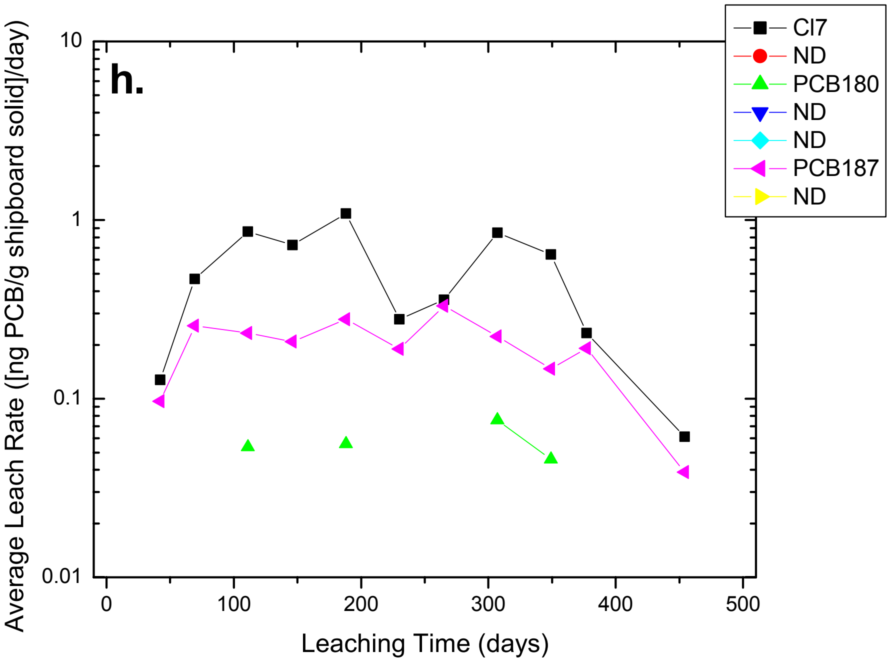

c.
Cl2
PCB8
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
0
100
200
300
400
500
Leaching Time (days)


d.
Cl3
PCB18
PCB28
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
0
100
200
300
400
500
Leaching Time (days)


e.
Cl4
PCB44
PCB49
PCB52
PCB66
PCB77
Average Leach Rate ([ng PCB/g shipboard solid]/day)
100
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


f.
Cl5
PCB87
PCB101
PCB105
ND
PCB118
ND
ND
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


g.
Cl6
ND
ND
PCB153
ND
ND
ND
ND
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)



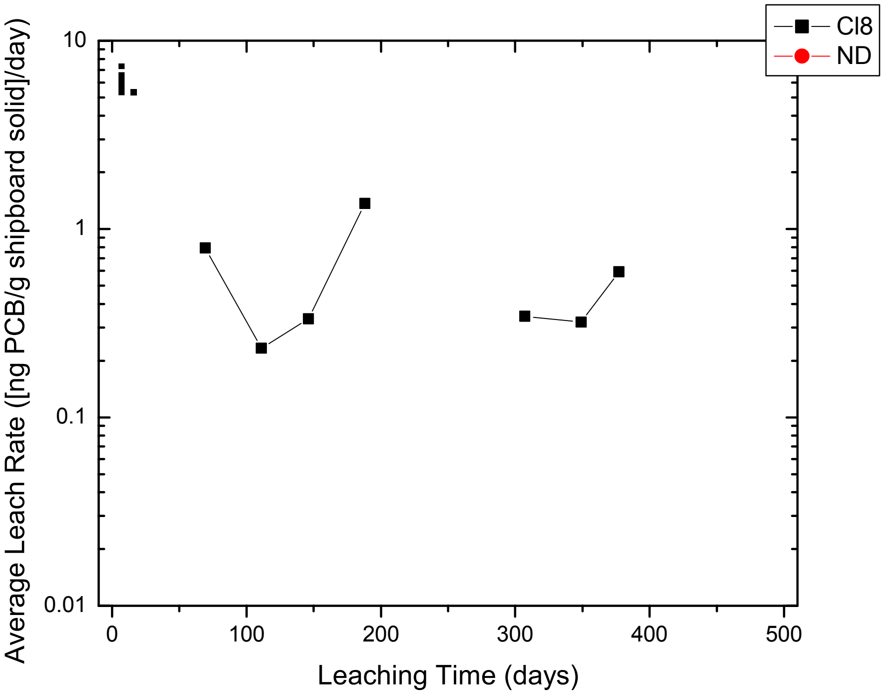
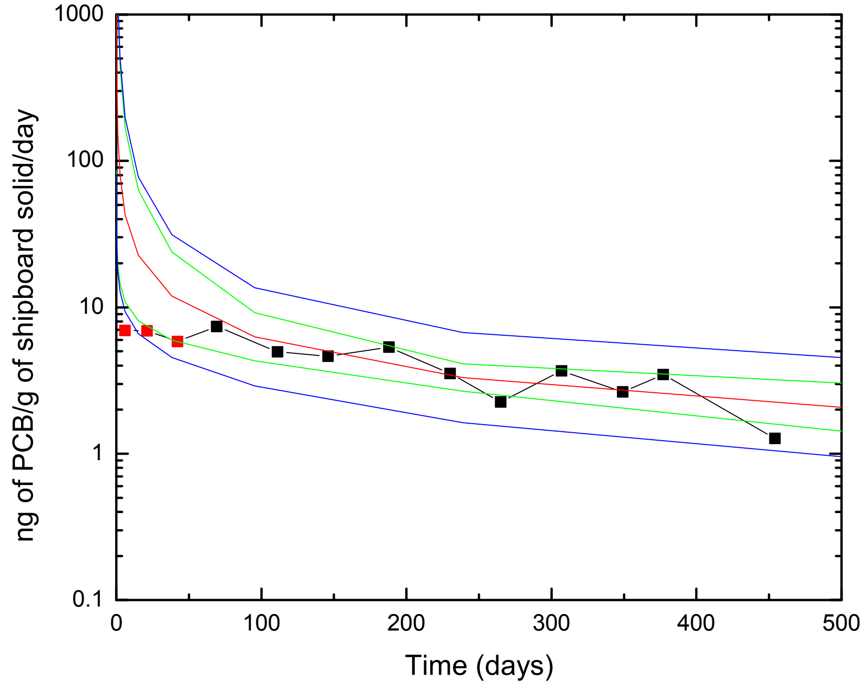


Figure 62 (a-i). Plot a) shows experimental tPCBs average leach rate and contributing homologue group average leach rates vs. leaching time for FGO. The sum of the homologue average leach rate curves is represented by the tPCBs average leach rate curve (solid black squares). Plots (b-i) show homologue group average leach rates and corresponding target congener average leach rates within detected homologue groups Cl1-Cl8 vs. leaching time for FGO. Lines connecting adjacent data points indicate detection in consecutive leachate samples (continued leaching of that PCB congener or homologue group), whereas no line indicates a discontinuity in leaching (analyte not detected in an adjacent leachate sample). Non-detected target congeners within detected homologue groups included PCBs 114, 123 & 126 (Cl5); PCBs 128, 138, 156,157, 158, 167, & 169 (Cl6); PCBs 170, 183, 184, & 189 (Cl7); and PCB 195 (Cl8).

The average leach rate curves for FGO above were extrapolated from curve fits of the tail or decreasing portion of the curves. The results of curve fitting and extrapolation, using the standard methods of data-treatment and curve-fitting described in the Leach Rate Analysis section, are included in APPENDIX A. Figure 63 below summarizes the extrapolation results for tPCBs only. These values, extrapolated to 1000 years, are tabulated below the figure and includes the final empirical average leach rate for reference purposes (1.27 ng/g shipboard solid-day at 454 days).

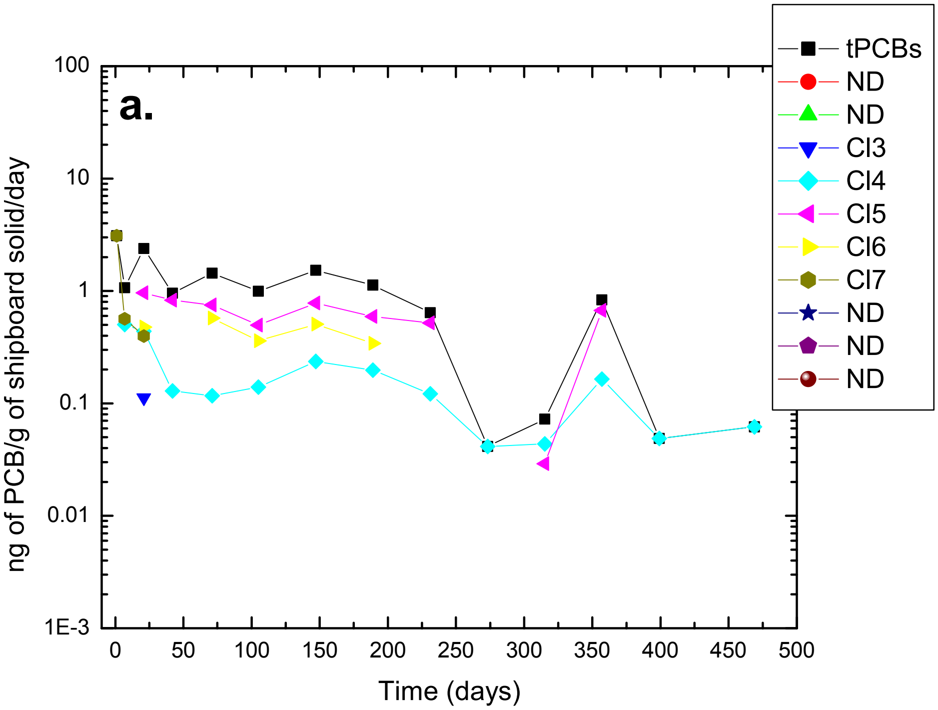


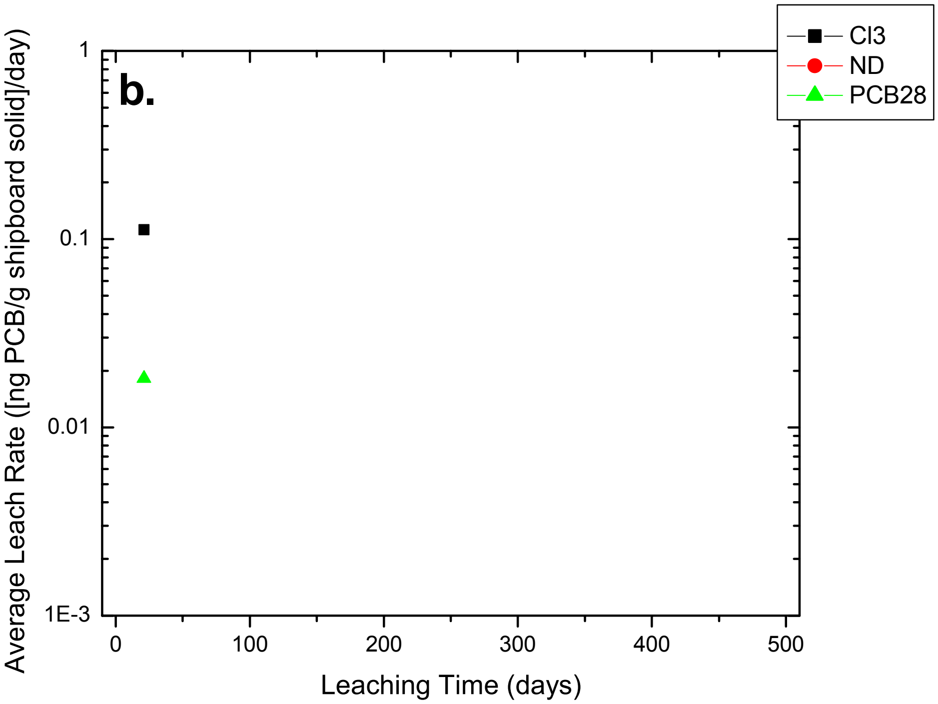
Time (days)	Curve Fit	95% UCI	95% LCI	95% UPI	95% LPI
454	***1.27***				
597.28962	1.74724	2.70788	1.1274	3.90491	0.7818
1493.48334	0.92149	1.97122	0.43077	2.54622	0.33349
3734.35667	0.48599	1.45706	0.1621	1.76294	0.13397
9337.51277	0.25631	1.08195	0.06072	1.25714	0.05226
23347.83539	0.13518	0.80498	0.0227	0.91051	0.02007
58379.72389	0.07129	0.59951	0.00848	0.66537	0.00764
145974.65266	0.0376	0.44674	0.00316	0.48893	0.00289
365000	0.01983	0.33303	0.00118	0.36058	0.00109

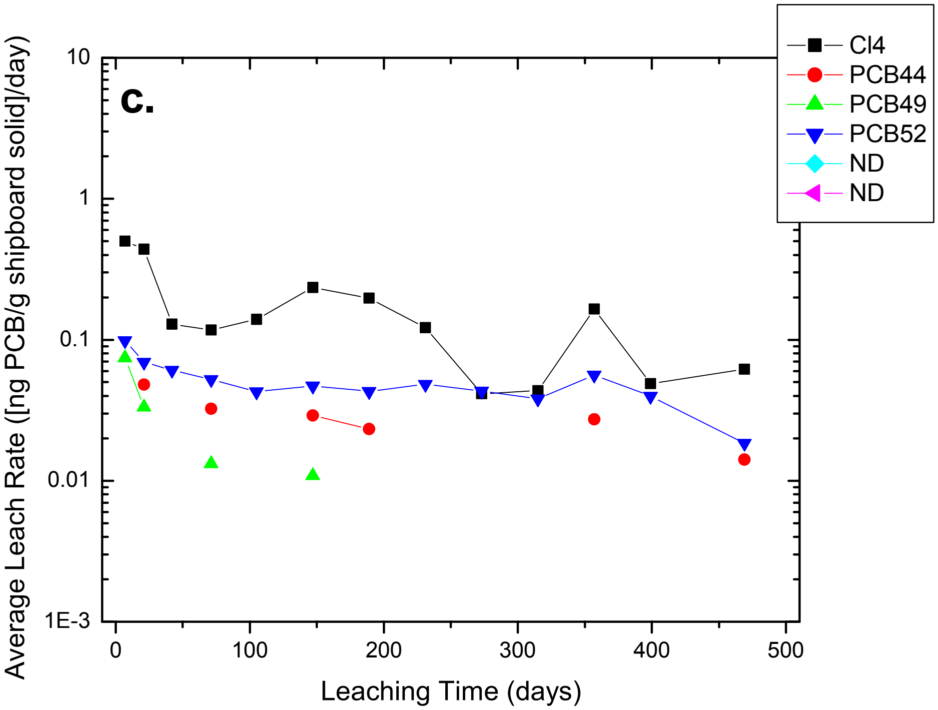
Figure 63. FGO tPCBs average leach rate extrapolation results (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over a 1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

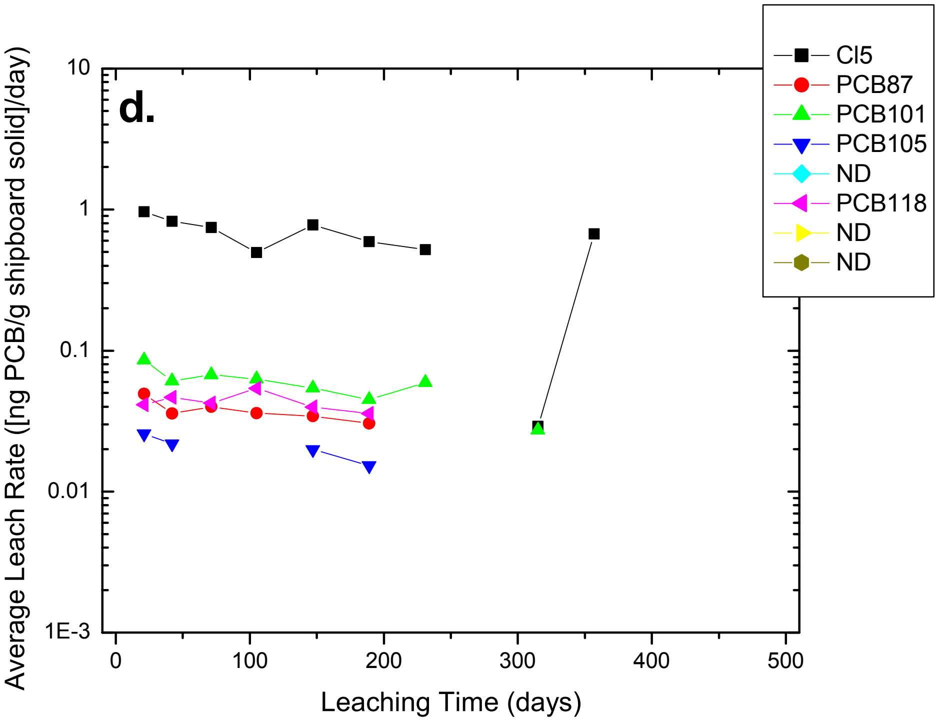
Aluminized Paint (AP) Leach Rate Behavior

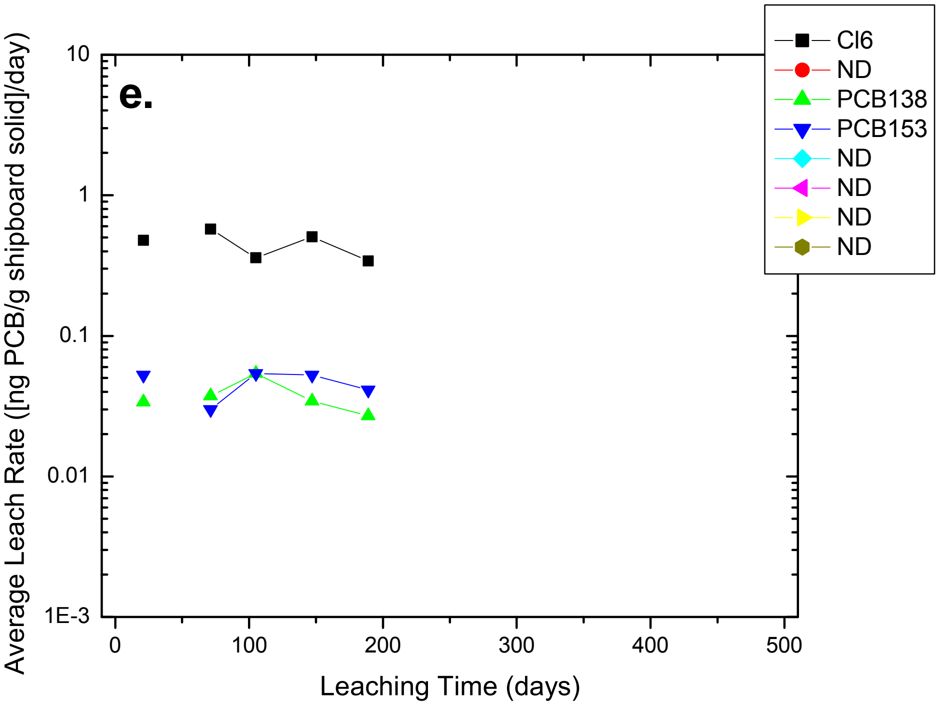
The AP sample contained 0.043 wt%, nominally comprised of 10.6% A1268, 47.8% A1260, and 41.6% A1254 as indicated in Table 10. The average leach rates shown in Figure 64(a-f) for this material were generally much lower than expected for this type of sample, considering the large surface area that resulted when the shipboard solid sample was collected as paint chips. The mechanism for how PCBs might be more strongly bound in this solid matrix is not understood, primarily because of the complexities of paint formulations and application methods/techniques, e.g. repainting frequency/paint thickness. Further investigation of the leaching mechanisms for shipboard solids was outside the scope of this investigation, which has focused only on determining the baseline leaching level itself. Average leach rates for AP were approximately 5 orders of magnitude below those observed for A1268 or A1254 controls. Homologue groups Cl3-Cl7 contributed to the PCB leaching, however, Cl3 and Cl7 were detected only early in the leaching series, and were undetectable after ~25 days. The leaching for Cl6 was consistent until ~200 days, after which it was no longer detected. The remaining (Cl4 & Cl5) target analytes leached in a relatively consistent manner through the entire leaching experiment timeframe.




b.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)
Cl3
ND
PCB28


c.
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)
Cl4
PCB44
PCB49
PCB52
ND
ND


d.
Cl5
PCB87
PCB101
PCB105
ND
PCB118
ND
ND
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)


e.
Cl6
ND
PCB138
PCB153
ND
ND
ND
ND
Average Leach Rate ([ng PCB/g shipboard solid]/day)
10
1
0.1
0.01
1E-3
0
100
200
300
400
500
Leaching Time (days)

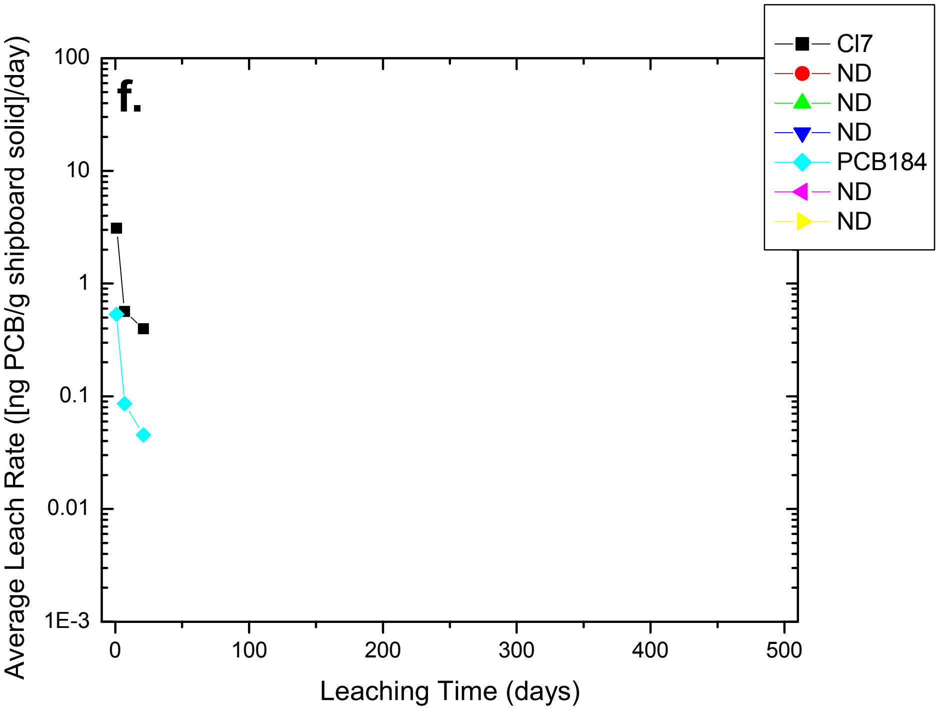
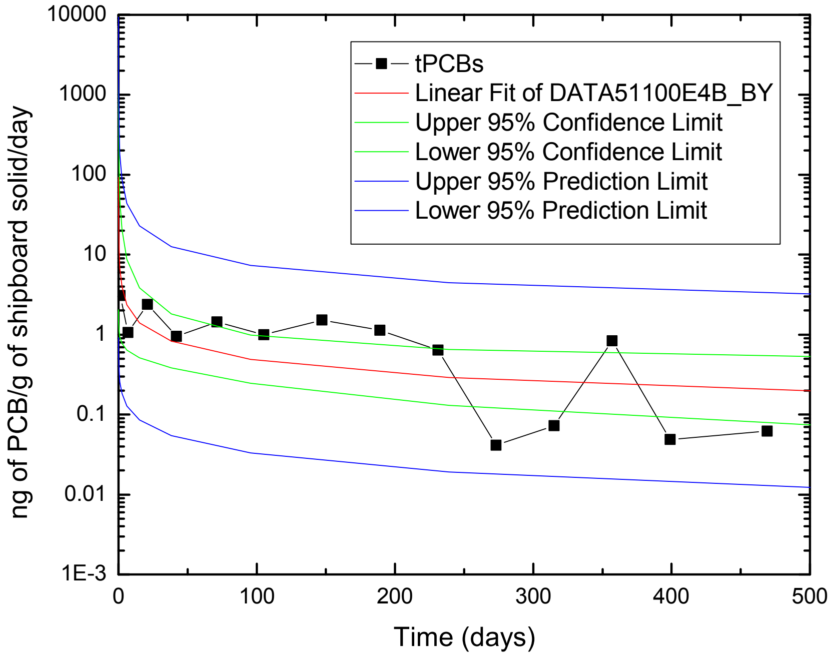


Figure 64 (a-f). Plot a) shows experimental tPCBs average leach rate and contributing homologue group average leach rates vs. leaching time for AP. The sum of the homologue average leach rate curves is represented by the upper tPCBs average leach rate curve (solid black squares). Plots (b-f) show homologue group average leach rates and corresponding target congener average leach rates within homologue groups Cl3-Cl7 vs. leaching time for AP. Lines connecting adjacent data points indicate detection in consecutive leachate samples (continued leaching of that PCB congener or homologue group), whereas no line indicates a discontinuity in leaching (analyte not detected in an adjacent leachate sample). Non-detected target congeners within these detected homologue groups included PCB 18 (Cl3); PCBs 66 & 77 (Cl4); PCBs 114, 123 & 126 (Cl5); PCBs 128,157, 158, 167, & 169 (Cl6); and PCBs 170, 180, 183, 187 & 189 (Cl7).

The average leach rate curves for AP above were curve fit through the decreasing portion of the curves and extrapolated to very long leaching times using the standard data-treatment and curve-fitting described in the Leach Rate Analysis section of this report. These results are included in APPENDIX A, but Figure 65 is included below to summarize the extrapolation results for tPCBs only. These values, extrapolated to 1000 years, are tabulated below the figure. The final empirical tPCBs average value is included as a reference (0.062 ng/g shipboard solid-day at 469 days).



Time (days)	Curve Fit	95% UCI	95% LCI	95% UPI	95% LPI
469	*0.062*				
597.28962	0.78741	1.24357	0.49858	2.017	0.3074
1493.48334	0.66151	1.1786	0.37128	1.8067	0.2422
3734.35667	0.55573	1.12508	0.2745	1.64175	0.18812
9337.51277	0.46687	1.07817	0.20216	1.5091	0.14444
23347.83539	0.39222	1.03562	0.14854	1.39978	0.1099
58379.72389	0.3295	0.99621	0.10898	1.30764	0.08303
145974.65266	0.27681	0.95925	0.07988	1.22841	0.06238
365000	0.23255	0.92431	0.05851	1.15909	0.04666

Figure 65. AP tPCBs average leach rate extrapolation results (red line/tabulated values) beyond the final experimental average leach rate value (included in italics for reference purposes). The 95% upper and lower confidence (UCI & LCI) and prediction intervals (UPI & LPI) are also shown (green and blue lines/tabulated values) over a 1000-year extrapolation period. See APPENDIX A for details and for homologue & congener-specific average leach rate curve-fit results. Average leach rate units are ng PCB/g shipboard solid-day.

CONCLUSIONS AND RECOMMENDATIONS

Leach Rate Results

Leaching data have been collected for a group of representative solid materials commonly found to contain PCBs in shipboard components onboard older, out of service surface vessels and submarines. These PCBs in solid materials (PCBs-ISM) have been shown to leach very slowly over time under laboratory-simulated shallow water conditions expected in typical harbors or estuarine environments. The test conditions used organic-free artificial seawater at a representative pH of 8.1, a salinity of 35^{o}%, ambient hydrostatic pressure (~1 bar) to approximate the shallowest depths (< 50 meters), 25^{o}C temperature, and gentle mixing to simulate dynamic flow. Leaching experiments were designed to avoid any effects due to unintentional PCB saturation in seawater, organic particulate sorptive processes, or biological uptake/metabolism/bioaccumulation of PCBs. Shipboard solids were tested intact, with the exception of paint chips, to simulate what would actually occur in a compartment onboard a sunken vessel. Field samples were deliberately chosen with extremely high tPCB shipboard solid concentrations to represent the most extreme case and to ensure that detection of leaching concentrations would be likely. Such high solid concentrations represent an upper limit, rather than an average or mean concentration typically found in solids onboard the majority of older vessels. These PCB levels are typically only found in a very small fraction of PCBs-ISM onboard decommissioned vessels in existence today. The solids tested included Aroclor 1254 (A1254) and solids containing A1254: Black Rubber Pipe Hanger Liner (BRPHL), Electrical Cable (EC), Foam Rubber/EnsoliteTM (FRE), in addition to Aroclor 1268 (A1268) and solids that contained A1268 or A1268 and A1254: Bulkhead Insulation (BHI), Felt Gasket/Inner (FGI), Felt Gasket/Outer (FGO), and Aluminized Paint (AP). The reasons for testing neat Aroclors were threefold; (1) these Aroclors are the most common types found on vessels as PCBs-ISM, (2) they were the two primary Aroclors identified in the specific shipboard solids tested, and (3) the neat Aroclors represent the worst-case for a release scenario, PCB dissolution uninhibited by a shipboard solid matrix, allowing them to be used as positive analytical controls (maximum PCB concentration observable in seawater from A1254 or A1268 sources) for the shipboard solid leaching experiments. For all experiments, PCBs were measured in the seawater leachate as a function of exposure time as part of a leaching time series. The analytes chosen for study represent environmentally significant PCBs, in terms of their toxicological impact and persistence, both from an ecological and human health perspective. In addition, a true measure of tPCBs was preferred over the conventional estimated (calculated) tPCBs. To accomplish this, each level of PCB chlorination (homologue group) was measured, and these were then summed to provide an empirical tPCB value.

All of the PCB analytes measured during leaching (31 congeners, 10 homologues, and sum of homologues for tPCBs) were the same as those evaluated in the US Navy ecological risk assessment (ERA) and human health risk assessment (HHRA) concerned with utilizing decommissioned Navy vessels for artificial reefs[3, 4]. The leach rate PCB list also contains the PCBs evaluated in the ERA and HHRA for SINKEX (26 congeners, 10 homologues for tPCBs)[6]. The leaching data reported in this study are focused on the former, shallow/reef scenario. In addition, a concurrent leach rate study focused on evaluating these shipboard solids in a deep-ocean scenario (low temperature and high pressure) has been undertaken, and will be the subject of a future report.[7] Some leach rate data from that effort has been summarized and is compared below with data from this study, to provide a sense of how dependent the leaching behavior is upon temperature.

Average leach rates calculated from seawater concentrations during leaching experiments correspond directly to the change in analyte concentration over individual leaching- or exposure-time increments. These leach rates are not instantaneous leach rates; rather, the calculated leach rates correspond to a rate averaged over the time between adjacent sample collections (sampling interval). In all leaching experiments, for all solids tested, leach rate curves were generated across the entire leaching experiment timeframe or leaching series to show the *change in leach rate with time*, a behavior driven both by depletion of PCBs at the seawater-solid interface as leaching occurs, and by changes expected in the amount of surface area defined by that seawater-solid interface as a function of exposure time. As a result, some of the leaching curves exhibited a period of "conditioning", characterized by sometimes initially erratic release behaviors. Despite this, all of the leach rate curves did, exhibit an increase up to some maximum rate, followed by a slow, monotonically decreasing rate with time. This latter decreasing portion of the curve was suitable for curve-fitting, and for extrapolation out to very long leaching times, over an arbitrarily chosen 1000-year timeframe, to determine if indeed the leaching behavior would continue to decrease until depleted of PCBs. Arguably, some portion of PCBs in shipboard solids should be strongly and irreversibly bound, particularly if the solids are organic or polymeric in nature[33, 52]. However, as a conservative approximation, one can assume that all PCBs in the solid are available for leaching.

As indicated previously, a concurrent effort was undertaken to evaluate the leaching behavior of the shipboard solids at high hydrostatic pressures (>300 bar) and low temperatures (4^oC) to simulate a deep-ocean sinking scenario. As part of that effort and to maximize comparability with this study, the shipboard solids evaluated and reported here were also tested at low temperature (4^oC) and ambient pressure (1 bar). Those leach rate results are included in Appendix E for all analytes in Table 4 and Table 5 (congeners, homologues, homologue-derived tPCBs) as a function of time. These low temperature leach rate data are applicable to this study and effectively demonstrate the behavior of leach rates as a function of temperature in a shallow-water leaching scenario. Low temperature leach rates are summarized in Figure 66 (below), for comparing homologue-derived tPCB leaching behavior as a function of temperature and leaching time at ambient pressure (1 bar). In general, leach rates were lower at reduced temperature, as one would expect from thermodynamic (solubility) considerations. Initial kinetics also appear to be somewhat suppressed for many of the solids, as indicated by a more gradual or sluggish leach rate increase up to the maximum low temperature leach rate. The post-maximum leach rate decrease for all solids tested at low temperature are generally slower relative to what is observed at 25^oC, exhibiting flatter, more gradual monotonically decreasing leach rates as a function of time. This is likely related to less PCB depletion with time at the seawater-solid interface as leaching into the seawater progressed. Leach rates for shipboard solids appear to be affected by temperature to a greater extent than the pure solid Aroclors.

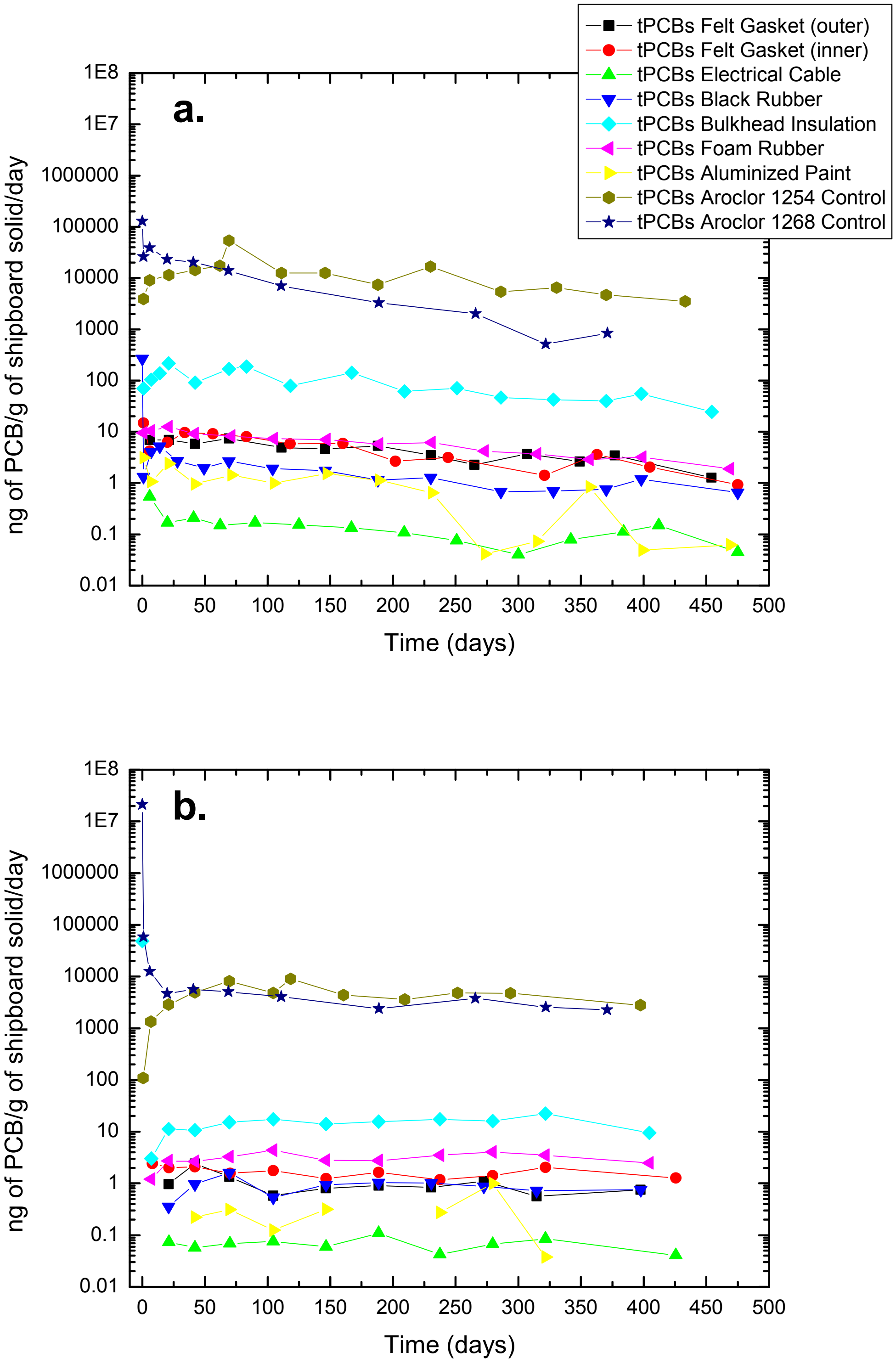


Figure 66. Comparison of tPCB average leach rates at ambient pressure (~1 bar) and a) 25^{o}C, to tPCB average leach rates at b) 4^{o}C for the suite of shipboard solid tested.

Summarized Leach Rate Study Results.

Leach rate study results have been summarized in Table 11 (a-i) below to provide at-a-glance synopses of each of the shipboard solid leaching experiments and Aroclor dissolution experiments. These synopses include calculated minimum, maximum, mean, standard deviation, and medians for leach rates in Appendix C; the recommended empirical leach rate for each analyte to be used as long term conservative leach rate; and also includes the results of regression analyses performed on the decreasing portion tabulated for each of the analyte curves that are detailed in Appendix A. The final leach rate curve endpoints listed in these tables have been evaluated against regression analyses for thos analytes with sufficient data and predictive power (small p-value). None of these final values were shown to lie well outside of the regression analysis confidence limits at the 95th percentile.

Table 11 (a-i). Summary of Empirical Dissolution Rate Behaviors/Curves/Regression Analyses for A1254 and A1268 (a & e), and Empirical Leach Rates for BRPHL, EC, FRE, BHI, FGI, FGO, and AP, (b, c, d, f, g, h, i) respectively. Regression analyses correspond only to the post-maximum portion of those leach rate curves with a significant number of leach rate data points beyond the observed maximum (regressions for $N \geq 4$ including the maximum), as described in Apppendix D and in the **Leach Rate Analysis** section.

a.	**Leach Rate Results**						**Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)**								
Aroclor 1254 (A1254)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
tPCBs	0.0E+00	5.4E+04	9.0E+03	1.2E+04	1.3E+04	3.5E+03	9	-1.2228	-0.67592	-1.76969	6.81093	8.08618	5.53567	0.79974	1.14E-03
Cl1	6.5E+00	5.5E+02	7.5E+01	1.5E+02	1.7E+02	2.7E+01	14	-0.51719	-0.3849	-0.64948	3.02155	3.28889	2.75421	0.85808	<0.0001
Cl2	2.5E+01	1.6E+03	3.1E+02	5.2E+02	4.6E+02	1.4E+02	14	-0.40164	-0.3849	-0.64948	3.38651	3.28889	2.75421	0.86145	<0.0001
PCB8	1.4E+01	4.9E+02	1.3E+02	1.8E+02	1.6E+02	5.6E+01	13	-0.50621	-0.36773	-0.64469	3.24345	3.53386	2.95304	0.85475	<0.0001
Cl3	3.1E+01	8.5E+02	2.6E+02	3.2E+02	2.4E+02	1.3E+02	9	-0.91788	-0.5608	-1.27495	4.58089	5.41354	3.74824	0.84071	5.02E-04
PCB18	2.2E+00	3.6E+02	1.1E+02	1.4E+02	1.1E+02	5.9E+01	9	-0.72088	-0.35063	-1.09113	3.72331	4.58669	2.85994	0.75174	2.47E-03
PCB28	1.6E+01	4.4E+02	1.1E+02	1.4E+02	1.2E+02	3.0E+01	9	-1.26974	-0.91062	-1.62886	4.84606	5.68347	4.00866	0.90897	<0.0001
Cl4	6.5E+02	2.3E+04	3.3E+03	5.1E+03	5.6E+03	1.9E+03	9	-1.11961	-0.65368	-1.58553	6.23989	7.32636	5.15342	0.82182	0.00074907
PCB44	6.5E+01	3.2E+03	7.0E+02	8.9E+02	8.1E+02	2.4E+02	9	-0.92408	-0.37459	-1.47358	4.98846	6.26979	3.70712	0.69316	0.00535
PCB49	8.9E+00	1.5E+03	2.4E+02	3.5E+02	3.9E+02	1.1E+02	9	-1.07215	-0.53342	-1.61089	4.94546	6.20171	3.68921	0.75983	2.19E-03
PCB52	1.9E+02	6.7E+03	1.6E+03	2.0E+03	1.7E+03	6.3E+02	9	-0.91101	-0.39679	-1.42522	5.28843	6.4875	4.08936	0.71487	4.09E-03
PCB66	1.2E+01	8.6E+02	5.9E+01	1.4E+02	2.3E+02	2.7E+01	9	-1.65782	-0.78289	-2.53276	5.78921	7.82942	3.74899	0.74146	0.00286
PCB77	3.1E+00	3.1E+00	3.1E+00	3.1E+00	N/A	3.1E+00									
Cl5	3.4E+02	2.6E+04	1.6E+03	3.9E+03	6.9E+03	1.2E+03	9	-1.4022	-0.73876	-2.06564	6.83448	8.38153	5.28743	0.74982	0.00157
PCB87	5.3E+00	1.8E+03	2.5E+02	3.7E+02	4.6E+02	7.7E+01	9	-1.35828	-0.57518	-2.14139	5.55465	7.38073	3.72857	0.70615	0.00456
PCB101	4.3E+01	2.1E+03	2.6E+02	3.9E+02	5.6E+02	1.3E+02	9	-1.12569	-0.27448	-1.97689	5.1866	7.17149	3.20172	0.58281	0.01668
PCB105	6.7E+00	5.3E+02	2.8E+01	7.8E+01	1.4E+02	8.4E+00	9	-1.93764	-0.92409	-2.9512	6.25348	8.61693	3.89002	0.74485	0.00273
PCB114	3.5E+00	8.7E+00	5.1E+00	6.0E+00	2.2E+00	8.7E+00									
PCB118	1.2E+01	1.2E+03	7.9E+01	2.2E+02	3.3E+02	1.5E+01	9	-2.10255	-1.08461	-3.1205	6.96128	9.33497	4.58759	0.77313	0.00179
PCB123	1.1E+01	1.1E+01	1.1E+01	1.1E+01	N/A	1.1E+01									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	8.8E+01	2.6E+03	3.8E+02	6.2E+02	7.1E+02	1.4E+02	9	-1.29967	-0.56294	-2.0364	5.69548	7.41342	3.97754	0.71313	0.00418
PCB128	4.3E+00	7.4E+01	1.5E+01	2.2E+01	2.2E+01	4.3E+00	8	-1.08297	-0.07485	-2.09109	3.71625	6.03552	1.39698	0.53522	0.03913
PCB138	5.6E+00	2.9E+02	4.2E+01	7.4E+01	9.1E+01	1.2E+01	9	-1.45902	-0.4469	-2.47113	5.13034	7.49043	2.77024	0.62405	0.01131
PCB153	4.2E+00	3.7E+02	4.2E+01	8.8E+01	1.2E+02	1.4E+01	9	-1.37978	0.19641	-2.95596	4.86989	8.54532	1.19446	0.37969	0.07722
PCB156	2.8E+00	1.1E+01	4.8E+00	5.3E+00	2.9E+00	2.8E+00									
PCB157	1.1E+00	1.5E+00	1.3E+00	1.3E+00	2.3E-01	1.5E+00									
PCB167	1.6E+00	4.2E+00	2.9E+00	2.9E+00	1.8E+00	4.2E+00									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

Aroclor 1254 (A1254)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
Cl7	7.2E+01	7.2E+01	7.2E+01	7.2E+01	N/A	7.2E+01									
PCB170	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB180	4.2E+00	4.2E+00	4.2E+00	4.2E+00	N/A	4.2E+00									
PCB183	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB184	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB187	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB206	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl10	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB209	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

b.	**Leach Rate Results**						**Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)**								
Black Rubber Pipe Hanger Liner (BRPHL)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
tPCBs	6.6E-01	2.7E+02	1.5E+00	1.8E+01	6.7E+01	6.6E-01	14	-0.52599	-0.47736	-0.57463	1.27577	1.3821	1.16944	0.97885	<0.0001
Cl1	1.2E-01	9.1E-01	5.2E-01	5.2E-01	3.6E-01	7.5E-01	12	-0.31693	-0.2708	-0.36306	-0.27111	-0.16962	-0.3726	0.95907	<0.0001
Cl2	1.2E-01	2.3E+00	4.0E-01	5.9E-01	5.8E-01	5.4E-01	13	-0.6553	0.0877	-1.3983	0.28399	1.90746	-1.33948	0.25516	0.07828
PCB8	1.2E-01	9.9E-01	2.3E-01	3.8E-01	3.2E-01	8.8E-01	13	-0.40599	-0.30001	-0.51198	-0.94355	-0.71198	-1.17513	0.866	<0.0001
Cl3	1.2E-01	1.0E+00	3.0E-01	3.9E-01	2.9E-01	9.1E-01	13	-0.29684	-0.00037082	-0.5933	-0.19319	0.45459	-0.84098	0.30628	0.04976
PCB18	1.1E-01	5.5E-01	2.2E-01	2.4E-01	1.4E-01	1.2E-01	13	-0.36636	-0.22795	-0.50477	-0.92319	-0.62077	-1.22561	0.75524	0.00011485
PCB28	1.4E-01	8.3E-01	4.1E-01	4.3E-01	2.4E-01	1.5E-01	10	-0.42758	-0.13061	-0.72455	-0.60601	0.00647	-1.21849	0.57947	0.01054
Cl4	2.2E-01	1.5E+00	5.7E-01	7.5E-01	4.8E-01	2.6E-01	13	-0.55437	-0.39107	-0.71767	0.94073	1.29756	0.58391	0.8354	<0.0001
PCB44	1.3E-01	8.4E-01	3.4E-01	4.0E-01	2.5E-01	4.1E-01	13	-0.50696	-0.37214	-0.64178	0.05879	0.35338	-0.23579	0.86163	<0.0001
PCB49	1.2E-01	9.6E-01	3.0E-01	4.1E-01	2.8E-01	1.2E-01	13	-0.61917	-0.45903	-0.77932	-0.14438	0.20555	-0.49431	0.86813	<0.0001
PCB52	1.1E-01	9.2E-01	3.1E-01	3.6E-01	2.6E-01	8.3E-01	13	-0.49425	-0.37285	-0.61565	0.33621	0.60147	0.07095	0.87951	<0.0001
PCB66	1.1E-01	7.6E-01	2.6E-01	3.1E-01	1.7E-01	5.0E-01	13	-0.59485	-0.24066	-0.94904	-0.5919	0.182	-1.36581	0.55401	0.00352
PCB77	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl5	1.7E-01	1.3E+00	6.7E-01	6.1E-01	3.3E-01	1.8E-01	10	-0.99549	-0.40872	-1.58226	1.85473	3.24059	0.46887	0.61383	0.00447
PCB87	1.4E-01	6.4E-01	3.5E-01	3.4E-01	1.6E-01	1.4E-01	7	-0.99977	-0.75437	-1.24518	0.63206	1.18722	0.07691	0.9564	0.00013694
PCB101	1.2E-01	8.9E-01	3.4E-01	4.1E-01	2.8E-01	1.4E-01	10	-1.22506	-0.92318	-1.52694	1.33537	2.04835	0.62238	0.9163	<0.0001
PCB105	1.2E-01	4.1E-01	2.0E-01	2.3E-01	1.3E-01	4.1E-01									
PCB114	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB118	1.4E-01	7.8E-01	3.9E-01	4.3E-01	2.2E-01	7.3E-01	5	-1.44605	-0.95492	-1.93717	1.56213	2.63935	0.48492	0.96696	0.00257
PCB123	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB128	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB138	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB153	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB156	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB157	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB167	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl7	3.5E-01	5.0E-01	5.0E-01	7.3E-01	5.3E-01	3.5E-01	4	-0.87772	-0.54861	-1.20683	0.41963	0.852	-0.01275	0.98504	0.00751
PCB170	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB180	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB183	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB184	2.2E-01	5.7E-01	4.8E-01	4.2E-01	1.8E-01	5.7E-01	4	-0.90943	-0.37214	-1.22762	-0.44569	0.35338	-0.86372	0.98695	0.00655

Black Rubber Pipe Hanger Liner (BRPHL)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
PCB187	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB206	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl10	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB209	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

c.	**Leach Rate Results**						**Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)**								
Electrical Cable (EC)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
tPCBs	0.0E+00	5.4E-01	1.2E-01	1.3E-01	1.3E-01	4.4E-02	14	-0.41634	-0.23313	-0.59955	-0.03602	0.36073	-0.43277	0.67138	3.36E-04
Cl1	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl2	2.2E-01	9.9E-01	3.4E-01	5.2E-01	4.2E-01	2.2E-01									
PCB8	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl3	1.3E-01	2.0E-01	1.6E-01	1.6E-01	5.1E-02	2.0E-01									
PCB18	6.8E-01	6.8E-01	6.8E-01	6.8E-01	N/A	6.8E-01									
PCB28	1.6E-01	1.6E-01	1.6E-01	1.6E-01	N/A	1.6E-01									
Cl4	2.1E-01	6.5E-01	4.2E-01	4.3E-01	1.5E-01	2.1E-01	12	-0.26155	-0.02583	-0.49728	-0.83355	-0.29192	-1.37518	0.37936	0.03297
PCB44	1.2E-01	9.9E-01	5.7E-01	5.3E-01	2.5E-01	2.7E-01	14	-0.28017	-0.15484	-0.4055	-1.62759	-1.35618	-1.899	0.66409	0.00038452
PCB49	1.1E-01	6.8E-01	2.2E-01	2.6E-01	1.5E-01	1.1E-01	13	-0.34807	-0.22605	-0.47009	-1.93671	-1.67562	-2.1978	0.78184	<0.0001
PCB52	1.1E-01	9.9E-01	1.8E-01	3.6E-01	3.3E-01	6.1E-01	14	-0.21297	-0.09694	-0.32899	-1.44774	-1.19647	-1.699	0.57133	0.00176
PCB66	1.3E-01	9.9E-01	2.3E-01	4.1E-01	3.5E-01	2.5E-01	10	-0.11283	0.378	-0.60366	-2.66793	-1.53168	-3.80419	0.03393	0.61045
PCB77	1.6E-01	1.6E-01	1.6E-01	1.6E-01	N/A	1.6E-01									
Cl5	1.2E-01	9.9E-01	6.0E-01	5.5E-01	2.9E-01	2.3E-01	14	-0.2883	-0.06726	-0.50934	-0.61403	-0.13535	-1.09271	0.40227	0.01485
PCB87	1.3E-01	6.4E-01	4.5E-01	4.1E-01	1.5E-01	1.3E-01	10	-0.31829	0.18122	-0.81781	-1.70219	-0.5348	-2.86959	0.21253	0.17992
PCB101	1.8E-01	9.6E-01	6.1E-01	5.9E-01	2.6E-01	2.1E-01	11	-0.51633	-0.06616	-0.9665	-1.05476	0.0032	-2.11271	0.42792	0.02899
PCB105	1.2E-01	9.9E-01	2.2E-01	3.0E-01	2.7E-01	2.2E-01	5	-0.44342	1.27563	-2.16246	-1.76382	2.31839	-5.84604	0.18342	0.47186
PCB114	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB118	2.0E-01	7.2E-01	4.4E-01	4.4E-01	1.9E-01	2.6E-01	9	-0.59373	-0.17608	-1.01138	-1.08308	-0.12405	-2.0421	0.61748	0.01206
PCB123	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	1.7E-01	9.9E-01	2.6E-01	4.3E-01	3.0E-01	1.7E-01	4	-0.9446	0.60789	-2.49709	0.52608	4.20303	-3.15087	0.7741	0.12017
PCB128	2.4E-01	2.4E-01	2.4E-01	2.4E-01	N/A	2.4E-01									
PCB138	1.3E-01	9.9E-01	2.5E-01	3.4E-01	3.3E-01	2.4E-01									
PCB153	2.2E-01	9.9E-01	2.3E-01	3.9E-01	3.4E-01	2.2E-01	4	-0.62444	1.53516	-2.78403	-1.24549	3.86934	-6.36032	0.43626	0.3395
PCB156	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB157	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB167	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl7	2.2E-01	4.9E-01	2.4E-01	3.2E-01	1.5E-01	4.9E-01									
PCB170	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB180	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB183	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB184	1.6E-01	8.3E-01	5.2E-01	5.0E-01	3.3E-01	8.3E-01									

Electrical Cable (EC)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
PCB187	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	2.6E-01	2.6E-01	2.6E-01	2.6E-01	N/A	2.6E-01									
PCB206	1.7E-01	1.7E-01	1.7E-01	1.7E-01	N/A	1.7E-01									
Cl10	1.5E-01	1.5E-01	1.5E-01	1.5E-01	N/A	1.5E-01									
PCB209	1.5E-01	1.5E-01	1.5E-01	1.5E-01	N/A	1.5E-01									

d.	**Leach Rate Results**						**Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)**								
Foam Rubber Ensolite (FRE)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
tPCBs	0.0E+00	1.3E+01	6.1E+00	6.1E+00	3.5E+00	1.9E+00	12	-0.52023	-0.36014	-0.68033	1.86578	2.22366	1.50789	0.83981	<0.0001
Cl1	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl2	1.2E-01	5.5E+00	3.2E-01	6.8E-01	1.4E+00	1.8E-01	14	-0.6714	-0.36067	-0.98213	0.45198	1.09893	-0.19497	0.64874	0.00050749
PCB8	1.7E-01	9.6E-01	3.3E-01	4.1E-01	2.3E-01	1.7E-01	13	-0.38722	-0.32909	-0.44535	-0.64917	-0.52359	-0.77476	0.95132	<0.0001
Cl3	1.2E-01	9.3E-01	1.5E-01	3.6E-01	3.2E-01	8.6E-01	14	-0.31499	-0.24134	-0.38863	-0.20111	-0.04778	-0.35444	0.8786	<0.0001
PCB18	1.4E-01	8.4E-01	2.7E-01	3.5E-01	2.1E-01	1.4E-01	13	-0.41836	-0.27946	-0.55726	-0.66618	-0.36607	-0.96629	0.7998	<0.0001
PCB28	1.3E-01	7.2E-01	3.2E-01	3.3E-01	1.7E-01	1.5E-01	14	-0.5066	-0.45836	-0.55484	-0.3465	-0.24607	-0.44694	0.97759	<0.0001
Cl4	8.6E-01	4.9E+00	1.9E+00	2.3E+00	1.2E+00	8.6E-01	13	-0.41978	-0.33101	-0.50855	1.16854	1.36033	0.97674	0.90782	<0.0001
PCB44	1.5E-01	8.5E-01	3.7E-01	4.3E-01	2.1E-01	1.5E-01	12	-0.48425	-0.37872	-0.58978	0.61183	0.84775	0.37592	0.91269	<0.0001
PCB49	1.1E-01	9.2E-01	2.6E-01	4.0E-01	2.9E-01	3.8E-01	13	-0.42354	-0.32001	-0.52707	-0.07762	0.14607	-0.30131	0.88053	<0.0001
PCB52	2.8E-01	1.6E+00	6.5E-01	7.5E-01	3.9E-01	2.8E-01	12	-0.47532	-0.39046	-0.56018	0.85219	1.04189	0.66248	0.93967	<0.0001
PCB66	1.1E-01	8.2E-01	3.7E-01	4.1E-01	2.7E-01	4.1E-01	11	-0.52733	-0.37066	-0.68401	0.00995	0.35332	-0.33342	0.86562	<0.0001
PCB77	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl5	9.7E-01	5.6E+00	3.3E+00	3.1E+00	1.5E+00	9.7E-01	12	-0.53458	-0.35023	-0.71894	1.57794	1.99007	1.16582	0.80675	<0.0001
PCB87	1.4E-01	8.4E-01	2.5E-01	3.3E-01	1.9E-01	5.4E-01	11	-0.50321	-0.33301	-0.67342	0.40893	0.78196	0.03591	0.8325	<0.0001
PCB101	1.3E-01	8.6E-01	4.2E-01	4.3E-01	2.3E-01	8.6E-01	12	-0.64488	1.42559	0.35182	0.88871	-0.88505		0.78164	-0.40472
PCB105	1.2E-01	9.6E-01	1.9E-01	3.7E-01	3.0E-01	1.7E-01	12	-0.71824	-0.39669	-1.03979	0.45782	1.17665	-0.261	0.7124	0.00055593
PCB114	8.4E-01	8.4E-01	8.4E-01	8.4E-01	N/A	0.0E+00									
PCB118	1.3E-01	6.4E-01	2.5E-01	3.0E-01	1.4E-01	2.4E-01	12	-0.79162	-0.41499	-1.16825	0.92792	1.76988	0.08596	0.68684	0.00086331
PCB123	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	3.2E-01	1.9E+00	8.7E-01	9.0E-01	4.2E-01	4.3E-01	7	-1.1711	-0.45662	-1.88558	2.64134	4.36894	0.91374	0.78025	0.00838
PCB128	1.3E-01	5.6E-01	4.1E-01	4.0E-01	1.2E-01	1.3E-01	6	-0.41847	-0.13159	-0.70536	-0.45226	0.20749	-1.11201	0.80394	0.01548
PCB138	1.3E-01	8.5E-01	1.5E-01	2.9E-01	2.7E-01	2.2E-01	8	-1.38238	-0.61475	-2.15002	2.17049	3.99136	0.34963	0.76394	0.00454
PCB153	1.2E-01	7.5E-01	1.5E-01	3.2E-01	2.7E-01	3.3E-01	7	-1.10639	-0.39833	-1.81445	1.52114	3.17625	-0.13397	0.76341	0.01015
PCB156	1.7E-01	2.3E-01	1.9E-01	2.0E-01	2.6E-02	2.2E-01	4	-0.08289	1.18471	-1.3505	-1.51658	1.2861	-4.31927	0.03808	0.80487
PCB157	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB167	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl7	3.1E-01	2.1E+00	7.2E-01	1.1E+00	9.6E-01	7.2E-01									
PCB170	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB180	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB183	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB184	2.3E-01	4.8E-01	2.8E-01	3.3E-01	1.3E-01	2.8E-01									

Foam Rubber Ensolite (FRE)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
PCB187	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB206	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl10	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB209	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

e.	Leach Rate Results						Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)								
Aroclor 1268 (A1268)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
tPCBs	5.1E+02	1.3E+05	1.4E+04	2.4E+04	3.7E+04	8.4E+02	11	-0.40855	-0.19468	-0.62241	4.48281	4.90291	4.06271	0.67479	1.93E-03
Cl1	3.3E+01	6.8E+01	3.9E+01	4.7E+01	1.8E+01	3.3E+01									
Cl2	7.3E-01	3.1E+03	1.5E+02	7.0E+02	1.0E+03	7.3E-01	8	-2.27589	-1.47668	-3.07509	6.35558	7.89792	4.81323	0.89002	0.00043412
PCB8	7.3E-01	4.2E+03	2.8E+02	1.1E+03	1.7E+03	7.3E-01	8	-2.16556	-1.36426	-2.96687	5.94637	7.49277	4.39997	0.87935	0.00057563
Cl3	3.0E+01	1.3E+04	9.6E+02	3.3E+03	5.0E+03	3.0E+01	9	-1.24578	-0.75547	-1.73609	5.72492	6.71092	4.73891	0.83757	0.00053795
PCB18	1.6E+00	4.6E+03	3.9E+02	1.3E+03	1.8E+03	3.8E+01	9	-1.38098	-0.87355	-1.88842	5.34363	6.36407	4.32319	0.85541	0.00035517
PCB28	3.7E+01	3.6E+03	5.9E+02	1.2E+03	1.3E+03	6.7E+01	8	-1.63604	-1.09239	-2.17969	5.99567	7.14561	4.84572	0.90037	0.00032134
Cl4	3.2E+01	6.3E+03	1.5E+03	2.4E+03	2.2E+03	5.3E+02	7	-1.35657	-0.79815	-1.91499	6.20746	7.44007	4.97485	0.88635	0.00154
PCB44	2.1E+01	1.2E+03	3.7E+02	5.0E+02	4.3E+02	1.3E+02	7	-1.19712	-0.80463	-1.58961	5.06967	5.93603	4.20331	0.92478	0.00054169
PCB49	2.9E+01	5.8E+02	1.9E+02	2.5E+02	2.0E+02	6.2E+01	7	-1.23157	-0.76822	-1.69492	4.83863	5.8614	3.81586	0.90326	0.00102
PCB52	2.1E+01	9.3E+02	1.5E+02	2.9E+02	3.3E+02	1.5E+02	7	-1.08002	-0.69788	-1.46217	4.81729	5.66081	3.97378	0.91347	0.00077226
PCB66	1.3E+01	5.6E+02	9.4E+01	1.8E+02	1.9E+02	2.7E+01	7	-1.57457	-0.975	-2.17415	5.4177	6.74115	4.09425	0.90113	0.00108
PCB77	4.7E+00	1.4E+02	6.0E+01	6.2E+01	4.4E+01	4.7E+00	5	-1.65693	-0.454	-2.85986	4.96588	7.44373	2.48803	0.86496	0.02198
Cl5	2.7E+01	5.3E+02	2.6E+02	2.5E+02	1.8E+02	7.8E+01	7	-0.8633	-0.41026	-1.31633	4.18509	5.18508	3.18509	0.82756	0.00448
PCB87	3.7E+00	2.9E+01	1.3E+01	1.4E+01	9.2E+00	6.3E+00	7	-0.49447	-0.14192	-0.84702	2.10982	2.88802	1.33163	0.7222	0.01546
PCB101	4.1E+00	3.1E+01	1.1E+01	1.4E+01	9.8E+00	7.2E+00	7	-0.89374	-0.64612	-1.14137	3.10529	3.65188	2.55871	0.9451	0.0002446
PCB105	3.7E+00	4.7E+01	1.9E+01	2.2E+01	1.5E+01	6.0E+00	7	-1.05095	-0.51015	-1.59175	3.49777	4.69148	2.30405	0.83308	0.00412
PCB114	1.3E+00	1.3E+00	1.3E+00	1.3E+00	N/A	1.3E+00									
PCB118	1.6E+00	4.9E+01	1.6E+01	1.9E+01	1.7E+01	4.3E+00	7	-1.1964	-0.6761	-1.7167	3.75174	4.90021	2.60326	0.87481	0.00197
PCB123	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	7.7E-01	3.9E+01	1.6E+01	1.8E+01	1.6E+01	7.7E-01	7	-1.47596	-0.03182	-2.9201	4.29809	7.48577	1.11041	0.57991	0.04669
PCB128	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB138	1.2E+00	1.2E+00	1.2E+00	1.2E+00	N/A	1.2E+00									
PCB153	1.4E+00	1.1E+01	3.6E+00	4.7E+00	3.6E+00	2.7E+00	7	-0.79246	-0.46094	-1.12397	2.41699	3.14875	1.68522	0.88306	0.00166
PCB156	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB157	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB167	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl7	1.5E+01	1.2E+02	1.9E+01	4.6E+01	4.3E+01	1.9E+01	5	-1.57541	0.70951	-3.86033	5.39484	10.81474	-0.02506	0.61611	0.11579
PCB170	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB180	2.0E+00	1.4E+01	6.4E+00	6.8E+00	4.2E+00	3.1E+00	6	-0.72045	-0.09062	-1.35028	2.362	3.78733	0.93666	0.71604	0.03367
PCB183	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB184	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

Aroclor 1268 (A1268)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
PCB187	1.6E+00	1.8E+01	9.9E+00	1.1E+01	6.2E+00	8.4E+00	7	-0.49447	-0.14192	-0.84702	2.10982	2.88802	1.33163	0.7222	0.01546
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	1.8E+00	5.8E+00	3.8E+00	3.8E+00	2.8E+00	5.8E+00									
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	3.0E+00	1.3E+05	2.3E+02	4.3E+04	7.4E+04	3.0E+00									
PCB206	2.3E+02	1.3E+05	6.4E+04	6.4E+04	9.0E+04	2.3E+02									
Cl10	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB209	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

f.	Leach Rate Results						Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)								
Bulkhead Insulation (BHI)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
tPCBs	0.0E+00	2.2E+02	7.1E+01	9.1E+01	6.1E+01	2.4E+01	13	-0.59053	-0.33261	-0.84846	3.18177	3.75688	2.60665	0.69775	3.78E-04
Cl1	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl2	1.8E-01	3.6E+00	5.5E-01	1.1E+00	1.3E+00	2.2E-01	7	-1.50353	-0.62246	-2.3846	1.68333	3.30537	0.06128	0.79375	0.00711
PCB8	1.7E-01	8.6E-01	2.8E-01	3.8E-01	2.3E-01	2.2E-01	8	-0.80652	-0.71274	-0.9003	0.247	0.41094	0.08306	0.98663	<0.0001
Cl3	5.5E-01	4.0E+00	1.0E+00	1.4E+00	1.1E+00	6.4E-01	15	-0.48509	-0.37243	-0.59774	1.00729	1.24481	0.76978	0.86939	<0.0001
PCB18	1.2E-01	8.0E-01	4.8E-01	4.5E-01	2.3E-01	5.9E-01	12	-0.5489	-0.38657	-0.71122	0.11837	0.439	-0.20227	0.85022	<0.0001
PCB28	1.2E-01	1.3E+00	4.0E-01	5.2E-01	3.7E-01	8.3E-01	14	-0.65391	-0.52579	-0.78203	0.84677	1.12485	0.56869	0.91155	<0.0001
Cl4	2.2E+00	7.0E+01	2.5E+01	2.9E+01	1.9E+01	7.3E+00	13	-0.58887	-0.40067	-0.77707	2.64565	3.06529	2.22601	0.81174	<0.0001
PCB44	1.2E+00	9.5E+00	3.4E+00	4.3E+00	2.4E+00	1.2E+00	13	-0.53613	-0.36287	-0.70938	1.76176	2.14807	1.37544	0.80832	<0.0001
PCB49	3.8E-01	4.0E+00	1.4E+00	1.7E+00	1.0E+00	3.8E-01	13	-0.57104	-0.39939	-0.7427	1.32855	1.7113	0.9458	0.82975	<0.0001
PCB52	2.3E+00	1.8E+01	6.9E+00	8.2E+00	4.2E+00	2.3E+00	13	-0.45673	-0.28248	-0.63098	1.82136	2.20989	1.43282	0.75159	0.00012483
PCB66	2.3E-01	4.1E+00	1.4E+00	1.5E+00	1.1E+00	2.3E-01	13	-0.74423	-0.48763	-1.00083	1.6542	2.22636	1.08204	0.78744	<0.0001
PCB77	1.8E-01	4.2E-01	3.0E-01	3.0E-01	1.7E-01	4.2E-01									
Cl5	1.1E+01	1.3E+02	3.9E+01	4.7E+01	3.5E+01	1.2E+01	13	-0.62147	-0.3302	-0.91274	3.00176	3.65122	2.35231	0.66721	0.00065415
PCB87	1.5E+00	9.3E+00	3.6E+00	4.3E+00	2.4E+00	1.5E+00	13	-0.54518	-0.31221	-0.77816	1.74346	2.26294	1.22398	0.70688	0.000318
PCB101	1.1E+00	1.5E+01	4.7E+00	5.7E+00	4.1E+00	1.5E+00	13	-0.58658	-0.34104	-0.83212	2.02151	2.569	1.47401	0.71537	0.00026925
PCB105	1.3E-01	4.1E+00	1.5E+00	1.6E+00	1.2E+00	1.3E-01	10	-1.74254	-1.18971	-2.29536	4.05202	5.37013	2.73391	0.86849	<0.0001
PCB114	1.1E-01	7.2E-01	2.1E-01	2.7E-01	2.3E-01	7.2E-01	6	-0.35729	0.26329	-0.97787	-0.17405	1.00875	-1.35685	0.3898	0.18518
PCB118	2.4E-01	9.8E+00	3.6E+00	3.8E+00	3.0E+00	2.4E-01	10	-2.0065	-1.38354	-2.62946	4.97811	6.46343	3.49278	0.87335	<0.0001
PCB123	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	2.7E+00	2.3E+01	7.6E+00	9.5E+00	6.6E+00	4.1E+00	11	-0.86853	-0.43737	-1.29969	2.96041	3.96938	1.95144	0.69763	0.00137
PCB128	1.3E-01	9.8E-01	3.8E-01	4.7E-01	2.7E-01	1.3E-01	7	-1.18069	-0.66151	-1.69986	2.22976	3.42328	1.03625	0.87237	0.00207
PCB138	2.5E-01	4.0E+00	1.2E+00	1.6E+00	1.2E+00	2.5E-01	10	-1.31471	-0.7802	-1.84923	3.14165	4.4161	1.86719	0.80085	0.00046936
PCB153	3.3E-01	2.5E+00	1.1E+00	1.1E+00	5.7E-01	3.8E-01	10	-0.79911	-0.22102	-1.37721	1.89173	3.2701	0.51337	0.5595	0.01285
PCB156	1.2E-01	3.2E-01	1.9E-01	2.0E-01	8.9E-02	1.2E-01	5	-0.7612	0.41895	-1.94135	0.88132	3.33959	-1.57695	0.58412	0.13242
PCB157	3.6E-01	3.6E-01	3.6E-01	3.6E-01	N/A	3.6E-01									
PCB167	4.7E-01	7.2E-01	6.0E-01	6.0E-01	1.8E-01	4.7E-01									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl7	8.9E-01	1.5E+01	1.8E+00	4.0E+00	5.5E+00	8.9E-01	6	-0.42373	-0.09024	-0.75721	0.97157	1.51713	0.426	0.75676	0.02428
PCB170	9.3E-01	9.3E-01	9.3E-01	9.3E-01	N/A	9.3E-01									
PCB180	8.9E-01	9.8E-01	9.3E-01	9.3E-01	6.4E-02	8.9E-01									
PCB183	1.2E-01	5.8E-01	3.5E-01	3.5E-01	3.2E-01	5.8E-01									
PCB184	1.6E-01	1.4E+00	2.0E-01	5.0E-01	6.3E-01	1.6E-01	4	-0.59721	0.15088	-1.34529	0.03783	0.93333	-0.85768	0.85506	0.07531

Bulkhead Insulation (BHI)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
PCB187	1.2E-01	7.9E-01	7.7E-01	5.6E-01	3.8E-01	7.7E-01									
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB206	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl10	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB209	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

g.	**Leach Rate Results**						**Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)**								
Felt Gasket Inner (FGI)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
tPCBs	0.0E+00	1.5E+01	4.2E+00	5.1E+00	4.0E+00	9.3E-01	14	-0.31621	-0.12201	-0.51042	1.23709	1.6336	0.84058	0.51191	4.01E-03
Cl1	1.6E-01	4.5E-01	2.4E-01	2.6E-01	1.2E-01	1.6E-01									
Cl2	2.2E-01	1.1E+01	4.3E-01	1.6E+00	2.9E+00	2.2E-01	14	-0.5808	-0.41269	-0.74892	0.92763	1.27087	0.58439	0.82523	<0.0001
PCB8	1.3E-01	7.6E-01	1.9E-01	2.8E-01	2.0E-01	7.6E-01	14	-0.32329	-0.24549	-0.40109	-0.11289	0.04595	-0.27173	0.87231	<0.0001
Cl3	3.3E-01	2.7E+00	6.9E-01	8.7E-01	6.2E-01	3.5E-01	14	-0.30616	-0.23139	-0.38093	0.44707	0.59973	0.29441	0.86898	<0.0001
PCB18	1.3E-01	9.0E-01	2.7E-01	3.2E-01	2.1E-01	9.0E-01	13	-0.35306	-0.25005	-0.45607	0.05359	0.27184	-0.16467	0.83802	<0.0001
PCB28	1.3E-01	7.5E-01	2.9E-01	3.2E-01	2.1E-01	5.8E-01	13	-0.40695	-0.29592	-0.51798	-0.01333	0.22191	-0.24857	0.85542	<0.0001
Cl4	1.7E-01	1.3E+00	5.3E-01	5.5E-01	3.1E-01	1.7E-01	13	-0.34787	-0.20856	-0.48718	0.35742	0.65259	0.06225	0.73305	0.00018736
PCB44	1.2E-01	9.6E-01	4.4E-01	4.8E-01	2.8E-01	2.3E-01	11	-0.52825	-0.31195	-0.74455	-0.06303	0.42526	-0.55132	0.77228	0.00036825
PCB49	1.2E-01	9.7E-01	2.8E-01	3.4E-01	2.4E-01	1.3E-01	14	-0.34735	-0.25221	-0.44249	-0.81993	-0.62568	-1.01418	0.84059	<0.0001
PCB52	1.3E-01	9.2E-01	5.1E-01	4.9E-01	2.8E-01	3.6E-01	11	-0.4576	-0.25182	-0.66337	-0.17093	0.2936	-0.63546	0.73766	0.00070888
PCB66	1.1E-01	5.6E-01	2.6E-01	2.7E-01	1.3E-01	1.1E-01	11	-0.39015	-0.1868	-0.5935	-0.97206	-0.56353	-1.38058	0.6767	0.00188
PCB77	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl5	1.5E-01	4.5E-01	2.7E-01	2.8E-01	1.1E-01	1.8E-01	8	-0.36768	-0.02658	-0.70878	0.15408	0.87577	-0.56761	0.53693	0.03866
PCB87	1.2E-01	9.0E-01	1.4E-01	3.2E-01	3.8E-01	9.0E-01									
PCB101	1.4E-01	3.4E-01	2.4E-01	2.4E-01	6.7E-02	1.5E-01	7	-0.41925	-0.18364	-0.65487	-0.79257	-0.31086	-1.27428	0.80711	0.00598
PCB105	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB114	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB118	1.6E-01	2.2E-01	1.8E-01	1.9E-01	3.2E-02	1.6E-01									
PCB123	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	1.8E-01	5.9E-01	2.8E-01	3.2E-01	1.4E-01	1.8E-01	5	-1.07497	0.94206	-3.09199	1.35056	5.41067	-2.70954	0.48951	0.18844
PCB128	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB138	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB153	1.3E-01	3.7E-01	2.9E-01	2.7E-01	8.6E-02	1.3E-01									
PCB156	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB157	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB167	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl7	2.5E-01	1.9E+00	5.0E-01	6.9E-01	4.9E-01	2.5E-01	8	-1.87679	-0.39319	-3.36039	4.05365	7.64829	0.45902	0.61493	0.02124
PCB170	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB180	1.1E-01	8.1E-01	2.6E-01	3.3E-01	2.3E-01	3.7E-01	8	-1.03299	-0.47613	-1.58986	1.26151	2.55981	-0.03679	0.77446	0.00394
PCB183	1.4E-01	3.4E-01	2.3E-01	2.4E-01	7.5E-02	2.0E-01	5	-0.47963	0.11795	-1.07721	-0.61016	0.67785	-1.89818	0.68502	0.08363
PCB184	3.7E-01	3.7E-01	3.7E-01	3.7E-01	N/A	3.7E-01									

Felt Gasket Inner (FGI)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
PCB187	1.3E-01	7.3E-01	3.4E-01	3.5E-01	1.8E-01	1.9E-01	9	-1.5905	-0.90589	-2.27511	2.87342	4.49753	1.24932	0.81172	0.0009128
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	1.4E-01	3.9E+00	1.4E+00	1.6E+00	1.3E+00	1.4E-01	9	-1.53299	-0.76229	-2.30369	3.56422	5.39254	1.7359	0.75964	0.0022
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	2.2E-01	1.8E+00	3.8E-01	5.9E-01	5.0E-01	2.2E-01	9	-1.28334	-0.4354	-2.13128	2.4405	4.36889	0.5121	0.6466	0.00899
PCB206	2.2E-01	1.2E+00	7.4E-01	6.6E-01	3.1E-01	4.3E-01	9	-1.71577	-1.19923	-2.23231	3.05277	4.2275	1.87805	0.8981	0.00010247
Cl10	2.0E-01	2.9E-01	2.5E-01	2.5E-01	6.7E-02	2.0E-01									
PCB209	2.0E-01	2.9E-01	2.5E-01	2.5E-01	6.7E-02	2.0E-01									

h.	Leach Rate Results						Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)								
Felt Gasket Outer (FGO)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
tPCBs	0.0E+00	7.4E+00	3.7E+00	3.9E+00	2.4E+00	1.3E+00	10	-0.69812	-0.3193	-1.07695	2.18047	3.07079	1.29016	0.69301	2.80E-03
Cl1	5.6E-01	5.6E-01	5.6E-01	5.6E-01	N/A	5.6E-01									
Cl2	1.6E-01	2.9E+00	5.6E-01	9.0E-01	7.6E-01	3.5E-01	13	-0.52423	-0.32988	-0.71857	0.91968	1.33808	0.50127	0.76215	<0.0001
PCB8	1.3E-01	5.3E-01	1.9E-01	2.5E-01	1.3E-01	1.3E-01	12	-0.49439	-0.37624	-0.61254	0.3979	0.6613	0.13449	0.89683	<0.0001
Cl3	5.3E-01	2.9E+00	1.1E+00	1.4E+00	7.7E-01	5.3E-01	13	-0.35314	-0.23263	-0.47365	0.80081	1.06026	0.54137	0.79088	<0.0001
PCB18	1.6E-01	7.9E-01	3.2E-01	4.1E-01	2.0E-01	1.6E-01	12	-0.46041	-0.31633	-0.60448	0.53762	0.85884	0.21641	0.83524	<0.0001
PCB28	1.4E-01	8.6E-01	2.8E-01	3.8E-01	2.2E-01	8.6E-01	12	-0.5632	-0.40366	-0.72274	0.61799	0.97367	0.26231	0.86086	<0.0001
Cl4	3.6E-01	2.9E+00	1.1E+00	1.2E+00	6.9E-01	3.6E-01	10	-0.77159	-0.43537	-1.10782	1.7476	2.53779	0.95741	0.77781	0.00073547
PCB44	1.1E-01	8.5E-01	2.3E-01	3.6E-01	2.9E-01	6.1E-01	10	-0.6337	-0.38364	-0.88376	0.52756	1.11525	-0.06012	0.8102	0.00038546
PCB49	1.2E-01	7.7E-01	4.2E-01	4.1E-01	2.4E-01	4.5E-01	10	-0.5867	-0.43391	-0.73949	0.11905	0.4649	-0.22681	0.90742	<0.0001
PCB52	1.2E-01	5.6E-01	1.6E-01	2.2E-01	1.2E-01	5.6E-01	10	-0.56837	-0.21962	-0.91713	0.45343	1.27306	-0.3662	0.6384	0.00556
PCB66	1.8E-01	9.4E-01	3.5E-01	3.9E-01	2.4E-01	1.8E-01	9	-0.73831	-0.48891	-0.98771	0.17758	0.70383	-0.34868	0.87501	0.00021152
PCB77	7.9E-01	7.9E-01	7.9E-01	7.9E-01	N/A	7.9E-01									
Cl5	2.8E-01	9.3E-01	5.8E-01	5.6E-01	2.4E-01	2.8E-01	8	-0.46223	0.63782	-4.89632	0.64238	11.68654	-2.02574	0.80851	0.00237
PCB87	2.0E-01	2.8E-01	2.4E-01	2.4E-01	5.8E-02	2.8E-01									
PCB101	2.8E-01	8.3E-01	5.0E-01	5.2E-01	1.7E-01	2.8E-01	6	-0.52642	0.12255	-1.17539	-0.18166	1.2499	-1.61322	0.55909	0.08744
PCB105	7.9E-01	7.9E-01	7.9E-01	7.9E-01	N/A	7.9E-01									
PCB114	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB118	2.6E-01	8.4E-01	5.5E-01	5.5E-01	4.1E-01	2.6E-01									
PCB123	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	2.4E-01	5.5E-01	3.3E-01	3.7E-01	1.6E-01	5.5E-01									
PCB128	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB138	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB153	1.8E-01	4.4E-01	3.3E-01	3.2E-01	1.3E-01	1.8E-01									
PCB156	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB157	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB167	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl7	1.3E-01	1.9E+00	6.1E-01	6.4E-01	4.8E-01	6.1E-01	7	-2.12925	0.63782	-4.89632	4.8304	11.68654	-2.02574	0.439	0.10484
PCB170	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB180	4.6E-01	7.6E-01	5.5E-01	5.8E-01	1.3E-01	4.6E-01									
PCB183	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB184	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

Felt Gasket Outer (FGO)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
PCB187	1.5E-01	9.7E-01	2.6E-01	3.2E-01	2.3E-01	3.9E-01	5	-3.63293	-0.52573	-6.74013	8.39912	16.28719	0.51104	0.82191	0.03379
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	2.3E-01	1.4E+00	3.4E-01	5.7E-01	4.0E-01	5.9E-01									
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB206	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl10	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB209	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

i.	Leach Rate Results						Post-Maximum Regression Results (log[AvgLR] = B log[time] + A)								
Aluminized Paint (AP)	Leachrate MIN Value (ng PCB/g shipboard solid-day)	Leachrate MAX Value (ng PCB/g shipboard solid-day)	Median (ng PCB/g shipboard solid-day)	Mean (ng PCB/g shipboard solid-day)	Standard Deviation (ng PCB/g shipboard solid-day)	Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)	N	B	Upper Confidence Interval B	Lower Confidence Interval B	A	Upper Confidence Interval A	Lower Confidence Interval A	R -squared (COD)	p-value (Probability>F)
tPCBs	0.0E+00	3.1E+00	9.5E-01	9.5E-01	9.1E-01	6.2E-02	14	-0.57148	-0.15908	-0.98388	0.8245	1.68313	-0.03414	0.43171	1.07E-02
Cl1	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl2	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB8	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl3	1.1E-01	1.1E-01	1.1E-01	1.1E-01	N/A	1.1E-01									
PCB18	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB28	1.8E-01	1.8E-01	1.8E-01	1.8E-01	N/A	1.8E-01									
Cl4	1.2E-01	6.2E-01	2.4E-01	3.2E-01	1.9E-01	6.2E-01	13	-0.49601	-0.22643	-0.7656	0.14484	0.72731	-0.43762	0.59853	0.00192
PCB44	1.4E-01	4.8E-01	2.8E-01	2.9E-01	1.1E-01	1.4E-01	6	-0.31476	-0.08735	-0.54216	-0.89169	-0.39419	-1.3892	0.78687	0.01841
PCB49	1.3E-01	7.4E-01	2.6E-01	3.5E-01	2.8E-01	1.9E-01	4	-0.65642	-0.38292	-0.92991	-0.59664	-0.15142	-1.04186	0.98159	0.00925
PCB52	1.8E-01	9.9E-01	4.8E-01	5.2E-01	1.9E-01	1.8E-01	13	-0.24361	-0.12207	-0.36514	-0.81293	-0.55034	-1.07552	0.63891	0.00104
PCB66	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB77	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl5	2.9E-01	9.6E-01	6.7E-01	6.5E-01	2.0E-01	6.7E-01	9	-0.57035	0.30373	-1.44442	0.86565	2.71145	-0.98014	0.25379	0.16675
PCB87	3.4E-01	4.9E-01	3.6E-01	3.8E-01	5.7E-02	3.5E-01	6	-0.17407	-0.04416	-0.30398	-1.10244	-0.85487	-1.35001	0.77578	0.02047
PCB101	2.7E-01	8.6E-01	6.1E-01	5.9E-01	1.8E-01	2.7E-01	8	-0.29445	-0.06825	-0.52066	-0.66416	-0.20045	-1.12787	0.62837	0.01895
PCB105	1.5E-01	2.6E-01	2.1E-01	2.1E-01	4.3E-02	1.5E-01	4	-0.19137	0.07519	-0.45793	-1.33832	-0.83485	-1.84179	0.82672	0.09076
PCB114	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB118	3.6E-01	5.4E-01	4.2E-01	4.3E-01	6.3E-02	3.6E-01									
PCB123	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB126	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl6	3.5E-01	5.7E-01	4.8E-01	4.7E-01	1.1E-01	3.5E-01									
PCB128	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB138	2.7E-01	5.4E-01	3.4E-01	3.7E-01	1.0E-01	2.7E-01									
PCB153	3.0E-01	5.4E-01	5.2E-01	4.6E-01	1.0E-01	4.1E-01									
PCB156	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB157	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB167	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB169	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl7	4.0E-01	3.9E+00	5.7E-01	1.6E+00	2.0E+00	4.0E-01									
PCB170	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB180	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB183	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB184	4.5E-01	8.7E-01	5.3E-01	6.2E-01	2.2E-01	4.5E-01									

Aluminized Paint (AP)	**Leachrate MIN Value (ng PCB/g shipboard solid-day)**	**Leachrate MAX Value (ng PCB/g shipboard solid-day)**	**Median (ng PCB/g shipboard solid-day)**	**Mean (ng PCB/g shipboard solid-day)**	**Standard Deviation (ng PCB/g shipboard solid-day)**	**Leachrate Curve Endpoint (ng PCB/g shipboard solid-day)**	**N**	**B**	**Upper Confidence Interval B**	**Lower Confidence Interval B**	**A**	**Upper Confidence Interval A**	**Lower Confidence Interval A**	**R -squared (COD)**	**p-value (Probability>F)**
PCB187	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB189	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl8	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB195	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl9	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB206	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
Cl10	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									
PCB209	0.0E+00	0.0E+00	N/A	N/A	N/A	N/A									

For purposes of evaluating the choice of Aroclor as analytical controls, the maximum concentrations observed in each shipboard solid leaching experiment are compared to the corresponding maximum concentrations observed for Aroclor 1254 and Aroclor 1268 dissolution experiments in Table 12 below. Also shown is the maximum observed tPCBs concentration in a single sample (calculated as sum of homologues). For comparison as a potential upper experimental limit (effective saturation), the sum of the homologue maxima across all leachate samples is shown for each dissolution and shipboard solid experiment. All of the tPCBs concentrations in shipboard solids are lower than A1254 and A1258, per the goal of the study design. (The tPCBs number is the conventional analysis analogue of the laboratory-screening goal (tPCBs as Aroclor 1254 by immunoassay) that was used to ensure shipboard solid leaching remained below effective saturation.) Upon inspection of Table 12, the majority of analyses are indeed lower, providing credibility to the screening analysis approach, but on an analyte basis vice tPCBs basis, a small number of the homologues and congeners that comprise the tPCBs number(generally Cl7 and above), are higher forthe shipboard solid leaching experiments. In samples where a particular analyte in the shipboard solid experiment was higher, the value is shown in Table 12 with parentheses, and double parentheses further indicating which of these were J-flagged/estimated below MRL. The rationale for why this was observed includes one or more of the following: a) the concentration was a very low value near the detection limit with high uncertainty, b) the concentration of that analyte was not measurable above the minimum detection limit in the neat Aroclor and therefore the effective Aroclor saturation limit could not be determined satifactorily, c) the differences in analyte concentrations were within the expected analytical precision of each other, or d) the concentration could not be explained using the Aroclor results reported here, which assumes the leachable PCBs are distributed similar to the bulk Aroclor PCBs distribution. The latter is suggestive of localized regions of readily leachable PCBs at the interface (SASA). All maxima in the Aroclor experiments represent the effective saturation limit for that particular PCB analyte originating from Aroclor in seawater. Those concentration maxima in shipboard solids below the Aroclor maxima have the least uncertainty with respect to leaching below the effective saturation limit for the Aroclor it contains. The most concentrated sample in each shipboard solid experiment that lies above the Aroclor maxima would be considered the samples with the most uncertainty, in that the sample could be approaching apotential saturation limit for that analyte, meaning suppression is a possibility. This cannot be confirmed without having performed an experiment under the same conditions for that specific analyte (homologue or congener, vice using an Aroclor selected to match the bulk PCB distribution as was done in this study). This means that leach rates derived from the highest concentration values, in those samples only, are potentially influenced by saturation of that analyte in the solution. The impact of these individual leach rate values on the overall empirical leach rate behaviors is minimal, and none of the suggested long-term leach rate values were affected (observed maxima were not the endpoints of curves). It should be noted that samples exhibiting maximum concentrations did not necessarily correspond to the maximum leach rates. This is because the leach rates, by definition, are related to change in concentration as a function of time (time over which a concentration change occurs), not simply the magnitude of the concentration.

Table 12. Comparison of Leaching Experiment Concentration Maxima. Those analyte concentration maxima for shipboard leaching samples that were higher than that for A1254 or A1268 are indicated in parentheses, with double parentheses further indicating which of these maxima were J-flagged (estimated/below MRL). Most of the shipboard solid analyte maxima greater than Aroclor maxima occur for the higher order chlorinated PCBs. Maxima that were non-detects are indicated as zero, meaning the analyte was never detected in the leaching or dissolution experiment. The maximum tPCBs concentration in any single sample is included as sum of homologues. A summation of all maximum homologue values across all samples is also included, which represents the reasonable maximum tPCBs concentration one might expect for a material containing A1254 and A1268, if tested under the leaching conditions of the study. See discussion in the text above for further explanation of the significance of these tabulated observations.

ng/L	A1254 MAX Value	A1268 MAX Value	EC MAX Value	FGI MAX Value	FGO MAX Value	BHI MAX Value	AP MAX Value	BRPHL MAX Value	FRE MAX Value
tPCBs	16051	9118	173	729	230	3944	84	226	828
Cl1-10 (Max Sum)	16229	10027	276	1010	308	3959	94	297	879
Cl1	100	33	0	6.1	2.4	0	0	18	0
Cl2	330	1100	47	140	33	14	0	44	24
PCB8	140	630	0	26	11	1	0	2.1	4
Cl3	330	4800	1.9	110	58	20	2.1	46	17
PCB18	120	1400	0.41	32	18	2.1	0	2.8	3.4
PCB28	110	1300	1.5	20	14	7.3	0.34	8.2	4.3
Cl4	5900	3500	53	71	58	870	13	94	250
PCB44	820	530	8.2	9.8	7.1	120	1.6	14	48
PCB49	410	260	3	3.9	3.6	36	0.62	5.8	13
PCB52	1800	500	18	10	8	200	3.1	27	79
PCB66	200	250	2.3	3.1	3	44	0	3	10
PCB77	1.4	61	1.5	0	1.1	0.82	0	0	0
Cl5	8300	350	120	39	27	2400	43	86	420
PCB87	620	21	6.6	1.9	1.2	140	1.9	4.3	30
PCB101	1000	22	10	3.1	2.4	240	3.3	8	51
PCB105	200	36	3	0	1.1	66	1.1	2	16
PCB114	8.4	2.2	0	0	0	3.1	0	0	1
PCB118	440	26	6.5	2	1.3	170	2.4	4.7	33
PCB123	14	0	0	0	0	0	0	0	0
PCB126	0	0	0	0	0	0	0	0	0
Cl6	1200	44	40	32	24	610	28	0	140
PCB128	47	0	2.3	0	0	16	0	0	4.9
PCB138	210	2.1	2.9	0	0	78	2.4	0	17
PCB153	220	7.3	3	4.1	1.9	42	2.9	0	15
PCB156	11	0	0	0	0	6.5	0	0	2.6
PCB157	1.4	0	0	0	0	0.84	0	0	0
PCB167	4	0	0	0	0	2	0	0	0
PCB169	0	0	0	0	0	0	0	0	0
Cl7	69	180	8.9	130	47	45	7.4	9.3	28
PCB170	0	0	0	0	0	((2.5))	0	0	0
PCB180	4	12	0	(18)	3.3	2.7	0	0	0
PCB183	0	0	0	(3.2)	0	((1.6))	0	0	0
PCB184	0	0	(0.72)	(0.58)	0	(0.95)	((0.85))	((1.1))	((0.81))
PCB187	0	17	0	(41)	12	2.2	0	0	0
PCB189	0	0	0	0	0	0	0	0	0
Cl8	0	10	0	(350)	(59)	0	0	0	0
PCB195	0	0	0	0	0	0	0	0	0
Cl9	0	9.7	2.5	(130)	0	0	0	0	0
PCB206	0	9.6	1.6	(87)	0	0	0	0	0
PCB209	0	0	((1.4))	((2.1))	0	0	0	0	0

Confidence in Leach Rate Study Results.

In this section, the leach rate study is described in terms of built-in conservatisms, uncertainties/limitations, and caveats. This is necessary to provide an adequate level of confidence in the leaching results to objectively select and choose which aspects of the leach rate study results are applicable to any potential users' application. The following discussion is focused on different components of the leach rate study in an effort to provide a reasonably comprehensive summary of the critical issues related to Study Design/Approach, Shipboard Solids containing PCBs, Analytical Chemistry, Leach Rate Results, and Leach Rate Uses/Applications. While it is acknowledged that, with the possible exception of analytical chemistry, many of the issues are not readily quantified, they will be presented in a quantitative manner whenever possible, if necessary, by employing reasonable assumptions to estimate any potential impacts.

Leach Rate Study Design/Approach

Prior to this study, information did not exist to describe the leaching behavior of shipboard solid materials. Consequently, the approach was limited in scope to empirically determine baseline-leaching characteristics for unknown leaching behaviors of unknown magnitudes for unknown PCB congeners from complex mixtures of PCBs (Aroclors) in solid material matrices under abiotic conditions. This study was also temporally constrained to evaluate leaching in the shortest amount of time required to provide adequate analytical results, for all PCB analytes of interest, over an unknown period of release (months to years), in an effort to characterize as many leaching processes, for as many types of shipboard solids and analytes possible, and with maximum overlap with known PCB source compositions. Performing leaching tests under abiotic conditions not only reduces the numbers, types, and increases the defensibility of selected variables in the simulated environment, but also allows for significant control and QA-QC of fundamental parameters. Given these already very ambitious experimental goals, the leach rate study was not designed to address any site-specific effects, such as partitioning equilibria, localized static conditions in reef environments, degradation processes and rates, or influences of biotic processes on leach rates. Although these types of processes can be important processes in natural environments, the leaching study was designed to empirically characterize the conservative process of uninhibited release. This required the simulation of completely advective conditions, meaning no suppression of leaching, a very conservative approach, considering that the majority of PCB-containing shipboard materials reside inside the vessel hulk and would be protected from advective currents. (An evaluation of how well this simulation was accomplished is included in the Analytical Chemistry section below.)

Secondary effects from processes such as biotic or physical degradation in natural environments are effectively considered to be part of the site-specific scenario that would typically be addressed as a component or bounding assumption at the end-use/application, e.g. artificial reef characteristics for risk assessment. More importantly, many such processes are very long-term in nature, and exert minimal influence on PCB leach rates, i.e. effects due to such processes are spread out over very long periods of time (typically decades to centuries). Degradation due to biotic processes in the marine environment is temporally commensurate with other similar man-made materials (e.g. plastics, polymers, described at length in the scientific literature and lifetimes of such materials in the environment is a well-known issue that has led to increased interest in recyclable and biodegradable materials that are engineered to do so in months to years as opposed to decades and centuries, if not longer). These degradation processes should exert only a minimal impact on the leaching behaviors of shipboard solid materials. However, to demonstrate this, a bounding analysis was performed and is presented below for an example shipboard solid (FRE), to estimate the potential effect of degradation on the leaching curve magnitude. In this analysis, a single initial piece of solid was allowed to disintegrate with time, producing many, much smaller particlulates of shipboard solid with an increased surface area defined by that particle size. As will become apparent below, these results are applicable in principle to any shipboard solid with any leaching curve, and for any analyte. The underlying premise is that a shipboard solid, possessing a given leaching behavior that is related to the surface area defined by the seawater leachate exposure, can be adjusted to reflect a %change (increase) in that surface area over various choices for particle production and total degradation time. The assumption is that a small particle will behave like a large particle, with surface area defined by the seawater leachate exposure, and an assemblage of small particles with the same total mass as one large particle will possess a higher surface area and thus release at a higher rate.

To begin this exercise, we can assume a generic piece of shipboard solid such as FRE, to be of size 1cm x 1cm x 1cm, with empirically observed leach rates in units of ng PCB/g-shipboard solid-day, and allow that single piece of FRE to degrade into an increasingly larger number of particles. These particulates represent the formation of new surface area that can be quantified from an analysis of percent increase in surface area of a geometric surface area and volume calculated for the original 1cm^3 particle as compared to the corresponding surface areas and volumes for the degradation particles. This percent increase can subsequently be normalized to how long such a process might occur, and then the incremental surface area increase (per unit time) can be applied to the empirical leach rates (curve) to calculate the incremental increase in leach rate corresponding to the smaller particles with increasingly larger surface areas with time. This analysis maintains conservation of mass, and as a result, the mass of the initial piece of FRE is equivalent to the sum of the masses of all smaller degradation particulates of FRE. This effectively results in the percent increase in surface area translating to a decrease in mass per unit surface area (or increase in surface area/unit mass), and ultimately this translates into an increased leach rate because the mass per unit surface area is in the denominator of the leach rate expression. This can be most easily understood by performing a unit analysis of the following equation and applying varied surface area increases (as a function of particle number increase, resulting particle size decrease) to the shipboard solid leach rate results for the example (FRE) using the analysis presented in Table 13. Equation 9 expresses the shipboard solid-specific *mass*-normalized leach rate to a corresponding shipboard solid-specific *mass-per unit leaching-surface-area*-normalized leach rate by dividing the former by the seawater accessible surface area (SASA) as unity (1 unit of active surface area), independent of geometric units. This equation simply indicates that the reported mass-normalized rate relies on the surface area implicitly, which contributes to the observed/measured value, and the leach rate can be expressed in active-surface area units (units of SASA), despite not having quantified the SASA in geometric units (e.g. cm^2, etc.). As the number of particles/time increases and particle size/time decreases, the SASA/time increases. It is relatively straightforward to adjust the SASA unit factor in the equation while keeping the total mass of the shipboard solid constant to accommodate such an increase in SASA/time to see the effect on a range of leach rates. Table 13 uses this analysis to perform such bounding calculations at different degradation rates (over variable degradation times, with decreased particle sizes/increased particle numbers/increased SASA).

Equation 9.

$$\begin{array}{ccc} \text{Reported AvgLR} & = & \text{Implicit AvgLR} \\ \text{(Mass Normalized)} & & \text{(Mass/SASA Normalized)} \\ \text{[ng PCB/g-shipboard solid-day]} & & \text{[ng PCB/(g shipboard solid/1 SASA unit)-day]} \end{array}$$

Table 13 (A & B). Bounding Analysis for Potential Incremental Increases in Leaching Surface Area as a function of Particle Formation. As described in the text, this analysis starts with a sample of shipboard solid material (e.g. FRE with the empirical tPCB leach rate curve values included below), and in A) Cases 1 and 2, beginning with a known size, assumes degradation into varied small particle numbers and sizes over realistic time periods to derive %-increases in surface areas from such a process. These calculated % increases in surface area are then applied to the FRE leach rates in B) for Cases 1 and 2 in A) over timeframes which the degradation process is expected to take place 1) & 2a) 200 years, 2b) 100 years, 2c) 50 years, to calculate the increase in release from the new surface area associated with the new, smaller particles. This data treatment is non-dimensional (x-units), that is, the increase in leach rate is based on a %-increase in surface area, which is based on a %-decrease in particle size, and increase in the nuber of particles. The treatment is mass-independent and can be applied to any shipboard solid leach rate for any PCB analyte reported in this study, as the increase in leaching calculation is simply a scalar multiplier.

A)

Original Solid Material			
a	b	c	
1	1	1	x-units
SA	6	x-units^2	
Volume	1	x-units^3	
Corners	Edges	Faces	
8	12	6	

Case 1: New, 100X Smaller Materials (Particles)			
a'	b'	c'	
0.01	0.01	0.01	x-units
SA'	0.0006	x-units^2	
Volume'	0.000001	x-units^3	
Corner particles	Edge particles	Face particles	All Partially External Particles
8	96	57576	57680
Volume of Fully Internal Particles (x-units^3)	# of Fully Internal Particles	Equiv # of Fully External Particles	Volume of Fully External Particles (x-units^3)
0.990368	990368	9632	0.009632
SA of New Particles (Added SA) (x-units^2)	Fractional Increase in SA from Original	Increase in New Particles from Original	
594.2208	99.0368 -fold	1.00E+06 -fold	

Case 2: New, 1000X Smaller Materials (Particles)			
a'	b'	c'	
0.001	0.001	0.001	x-units
SA'	0.000006	x-units^2	
Volume'	0.000000001	x-units^3	
Corner particles	Edge particles	Face particles	All Partially External Particles
8	96	5975976	5976080

Volume of Fully Internal Particles (x-units^3)	# of Fully Internal Particles	Equiv # of Fully External Particles	Volume of Fully External Particles (x-units^3)
0.999003968	999003968	996032	0.000996032
SA of New Particles (Added SA) (x-units^2)	Fractional Increase in SA from Original	Increase in New Particles from Original	
5994.023808	999.003968 -fold	1.00E+09 -fold	

B)

FRE	Leaching Time t (days)	0.007	1.099	7.022	21.077	42.045	71.237	105.078	147.083	189.026	231	273.122	315.039	357.003	399.019	469.032
	delta-t	0.007	1.092	5.923	14.055	20.968	29.192	33.841	42.005	41.943	41.974	42.122	41.917	41.964	42.016	70.013
LR [ng PCBs/g SS-day]	tPCBs	0	9.5E+00	1.0E+01	1.3E+01	9.1E+00	8.2E+00	7.3E+00	7.0E+00	5.7E+00	6.1E+00	4.2E+00	3.7E+00	2.9E+00	3.2E+00	1.9E+00
Case 1)	73000 days (200 years)	SA Increase Timeframe														
Additional Release LR incl SA increase timeframe		0	1.3E-02	1.4E-02	1.8E-02	1.2E-02	1.1E-02	9.9E-03	9.5E-03	7.7E-03	8.3E-03	5.7E-03	5.0E-03	3.9E-03	4.3E-03	2.6E-03
Case 2a)	73000 days (200 years)	SA Increase Timeframe														
Additional Release LR incl SA increase timeframe			1.3E-01	1.4E-01	1. 8E-01	1.3E-01	1.1E-01	1.0E-01	9.6E-02	7.8E-02	8.4E-02	5.8E-02	5.1E-02	4.0E-02	4.4E-02	2.6E-02
Case 2b)	36500 days (100 years)	SA Increase Timeframe														
Additional Release LR incl SA increase timeframe		0	2.6E-01	2.7E-01	3. 6E-01	2.5E-01	2.2E-01	2.0E-01	1.9E-01	1.6E-01	1. 7E-01	1.2E-01	1.0E-01	7.9E-02	8.8E-02	5.2E-02
Case 2c)	18250 days (50 years)	SA Increase Timeframe														
Additional Release LR incl SA increase timeframe		0	5.2E-01	5.5E-01	7.1E-01	5.0E-01	4.5E-01	4.0E-01	3.8E-01	3.1E-01	3.3E-01	2.3E-01	2.0E-01	1.6E-01	1.8E-01	1.0E-01

This study was made feasible by using a simple conceptual model that limited the scope to controllable abiotic conditions over a relatively short period of time (< 2 years). The potential effect(s) of biotic processes on the materials in this study was considered to be much less important during this short-term empirically determined release, prior to when the greatest amount of biotic processes could occur. Additionally, the influence of biotic processes is expected be of much lower magnitude relative to the empirically-determined initial release, and potentially in a positive or negative direction, i.e. opposite modes of action by biotic organisms, such as PCB degradation or SASA blocking by organisms, vice shipboard solid degradation such as is demonstrated above, resulting in both decreases and increases in effective PCB leach rate, but with a smaller magnitude relative to the early release. Since biotic processes are not instantaneous/short-term processes, the empirical leach rates in the study timeframe should accurately reflect the initial 1-2 years of release. What becomes important, and is a primary concern, is what one chooses to use as a long-term leach rate. The long-term LR could be affected by biotic or physical degradation conditions, although the magnitude of such an effect would be comparatively small as shown in Table 13. These factors were taken into consideration during the LR experimental design phase and are also reflected in the suggested applicability/use of the empirical results. Specifically, it is not considered valid to adopt and use an extrapolated leach rate value beyond ~2-years as a long-term (>> 2 years) leach rate value. (Neither is it valid to use the regression analysis results to calculate and adopt a leach rate extrapolated back to a time point prior to the maximum rate on the empirical curve.) Extrapolated data beyond ~2-years are only used in this study to demonstrate that the statistical upper limits of regressions performed on the empirical LR curves beyond their maxima either decrease or remain constant. This approach was used purposely to provide confidence in using a constant leach rate from the decreasing portion of the LR curve or regression (1.5 - 2 years) as a reasonable maximum rate to use beyond the initial release timeframe.

Shipboard Solid Sources

The choice of shipboard solids investigated in this study presented a serious technical and logistics challenge during the field sample collection phase. The majority of technical data and information regarding what types of materials, concentrations of PCBs, identity of commercial PCB mixtures (Aroclors) in the solids, and location of ship components with these materials, existed as either anecdotal or historical data for materials that had been remediated already, or the vessel was no longer available for sampling. This presented the leach rate study with a unique problem: locating and collecting existing materials as source material with a known quantity and type of PCB signature. Ultimately the necessary approach consisted of evaluating the existing database to focus on the major classes of materials presented in Table 3 of this report, and then attempt to collect those materials with the highest concentrations above the regulated limit (50 ppm) available in the inactive vessel inventory at the time (1999), but prior to an imminent shipyard remedial action. As a lower limit requirement, it was also necessary to collect a material with sufficient PCB concentration that, given a substantial amount of time to release, could be detected in seawater leachate (e.g. avoid situations where the tPCB concentration in the solid would be diluted to below detection in the leaching vessel minimum required volume (1 L), even if all of the PCBs came out of the solid instantaneously). This generally meant a minimum of hundreds of ppm in the solid was needed to realistically expect to see a measurable PCB concentration, below 10-20 ppb seawater (expected) saturation limits, in leachate samples over a reasonable amount of time. From the PCB database for the inactive fleet inventory during the study, it was apparent that finding and collecting materials with specific PCB fingerprints was outside the scope of the study, as it would have required a dedicated/robust random sampling and analysis effort similar to the existing NAVSEA sampling program. Instead, the database was evaluated for purposes of identifying the most common Aroclors for the leach rate study classes of materials in the database, and subsequent field collection events were then focused on obtaining materials expected to have a similar fingerprint, if they were thought to be available for collection. This resulted in the samples with fingerprints presented in Table 3, which, upon comparison with the NAVSEA PCB program summary statistics in Table 2 overlap significantly. This effectively increased the confidence in assuming a similar fingerprint would be found in shipboard solids onboard other vessels and applying the leach rate results to those materials.

In addition to the PCB content issues in shipboard solids as described above, each of the shipboard solids were tested in a manner designed to conservatively emulate the worst-case form of the solid onboard a vessl during a typical natural leaching scenario. These are decribed on a shipboard solid basis here to clearly demonstrate that the leach rate study results, on a mass-normalized basis, correspond in most cases to leaching performed under very conservative representative physical conditions for each shipboard solid. More detailed descriptions of each class of shipboard solid can be found in the field sampling descriptions included in the **EXPERIMENTAL DETAILS** section and in the shipboard solids described in the **EMPIRICAL DATA AND OBSERVATIONS** section.

Electrical Cable (EC)._This solid sample was tested intact, except for the ends, which were cross-cut, immediately exposing the internal components to seawater during leaching studies. This is representative of ony a small fraction of the cable typically onboard a vessel, unless a substantial amount of cabling has been removed, in which case the ends of cables that reside within the cable runs between bulkheads would be exposed similarly. In addition, the outer armored shielding (painted steel mesh) on the tested EC was removed, negating the possibility of seawater leachate collecting statically between the surface of the EC and the shielding, which would have affected the simulation of complete dynamic advection and instead would have introduced the possibility for leach rate suppression.

Bulkhead Insulation (BHI). This sample was tested intact, without the outer lagging (painted pressboard backing), behind which is BHI material. The as-tested material itself is likely very similar to that found onboard most vessels with the exception that the as-tested sample had no paint on its outer surfaces, unlike many of the materials onboard, which would act to reduce the leach rate due to both sorptive processes and advective flow reduction in and out of this very open-structured material. In addition, the presence of lagging material, as with paint, or the armored shielding for EC, would have also affected the simulation of complete dynamic advection and would have introduced the possibility for leach rate suppression, as would be expected in a natural leaching environment.

Black Rubber (BRPHL). This sample was tested intact, without the presence of paint on its outer surfaces, a common occurrence on vessels. The presence of outer painted surfaces would reduce the leach rate due to sorptive processes, acting as a barrier to PCB release, and thus the leach rate study is evaluating a more conservative leach rate process.

Paint (AP). This sample was tested in a significantly different form than what is found onboard a typical vessel. It consisted of paint chips and particulates, rather than an intact painted substrate. As a result the surface area was artificially increased beyond that found for most paints onboard in a natural leaching scenario. The result of this is that the leach rate study reports a higher, conservative leach rate than would be expected in a natural setting or if an intact painted substrate was tested in the laboratory. The as-tested sample of paint chips is a close approximation for the minimal amount of loose, flaking paint that might become de-bonded from the substrate, although flaking painted surfaces are also generally removed as part of vessel maintenance and preparations. The type of paint tested in the leach rate study is similar to most types of interior and exterior vessel paints, with the exception of antifouling hull paint, which is not a PCB-containing material found onboard Navy or commercial vessels.

Foam Rubber/Ensolite (FRE). The FRE sample was basically what one would expect to find leaching in a natural environment, with the exception that the outer surfaces of most materials of this type are either painted or covered by materials (adhesives or substrata) that would provide a sorptive barrier and impede seawater leachate flow, suppressing the leach rate. The as-tested FRE sample in the leach rate study was painted only on one of its sides and the remaining surfaces were unpainted and freshly exposed by the subsampling process. The lack of paint on >75% of the available surface allowed a conservative measurement of PCB release.

Felt (FGI). Felt gasket material is similar to other types of felt components onboard vessels and in the case of this study is the same gasket material as was protruding out of a heating, ventilation, air-conditioning (HVAC) duct flange, collected as the FGO sample discussed below. The primary difference between this sample and the FGO sample is a very significant one: this type of felt gasket is an internal component of the flange, and would remain compressed between the flange heads in a natural leaching environment. The as-tested FGI sample is not such a sample; rather it was removed from the flange and tested with most of its surfaces exposed. This resulted in a more open, advective condition during the test than would be found onboard a vessel in a natural leaching scenarion, where the felt gasket would be covered by flange materials that would impede seawater leachate flow, suppressing the leach rate. As the flange dissolves away over many years, decades, or perhaps a century, the felt material would become incrementally exposed, vice exposed instaneously in its entirety as tested. Leaching of exposed surfaces after loss (corrosion/dissolution) of the metal flange would continue unihibited in a manner similar to what was measured in the laboratory but any fresh surface would be small and exposed only incrementally over time.

Felt (FGO). This sample, as mentioned above, is part of the same flange gasket as the tested FGI. This sample was tested essentially intact and its surface approximately 30% painted, with the remainder exposed due to the cutting of the material off of the intact flange during the field sample collection and subsampling event in the laboratory. The 30% painted surface likely contributed a smaller fraction to leach rate and the unpainted a larger fraction. The majority of felt material of this type onboard vessels, particularly that protruding from between flange heads, is sealed by paint and not damaged by cutting it away from the flange. As a result, the leaching results for the as-tested sample are conservative in nature, not only from the paint/barrier coating standpoint, but also from the standpoint of testing a freshly cut, exposed surface, unlike what would be the case onboard a vessel.

General Comments. While there is potential for academic pursuits aimed at broadening the scientific understanding of unique mechanisms associated with PCB release, this study was not focused on evaluating the molecular properties of the interfaces each of these materials makes with seawater, probably a dynamic/changing property of each shipboard solid. This study did capture the resultant effect of such properties on the leaching process in the form of quantifying the release in each case, and with normalization to shipboard solid mass vice surface area. This was, from a practical (data use) standpoint, a much more efficient data reduction approach, as shipboard solid materials for vessels are typically described in terms of mass or tonnage vice surface area. Caution is suggested regarding the use of such a surface area approach, simply because it represents the initial or starting surface area and not necessarily the seawater accessible surface area (SASA), a parameter very likely to be dynamic or changing temporal variable.

Analytical Chemistry

The choice to use homologue measurements to determine tPCB concentrations is probably the most effective manner in which the analytical uncertainty level was reduced in this study. Without such an approach, the homologue and tPCB results reported in this study would have been estimated values based on limited congener data combined with assumptions and estimation algorithms with much higher levels of uncertainty. For the majority of detailed uncertainty and confidence issues concerned with study analytics, the reader is directed to the QA/QC sections of Appendix C, the data quality objectives (DQO) specified in this study, and analytical chemistry-related subsections included in the **EXPERIMENTAL DETAILS** section and in Appendix B. In general, the analytical data quality was very high throughout the leach rate study providing high confidence in results. The low levels of detection were particularly useful in determining whether or not leaching could be observed in a minimal amount of leaching time. Of course, with unlimited time and resources, it is possible that one could have run experiments longer in an attempt to observe leaching for analytes that were never detected in this study. However, this is subject to the consideration that one knows very precisely and to very low or trace levels, what is present in and on the leachable surfaces of the solid source materials whether what is measured represents all possible variations of PCB mixtures (multiple Aroclors). In this respect, this study could not evaluate every possible type of Aroclor content in each shipboard solid, nor was it possible to determine what the molecular level composition was at the interface (SASA), which was likely changing with time. In some cases as can be seen in Table 3, all Aroclors in all shipboard solids do not have a corresponding analytical (Aroclor) control. It was outside the scope of this study to evaluate the dissolution behavior under the leaching conditions for all possible neat Aroclors as analytical controls. As a result there are some cases, as noted in Table 12 for each shipboard solid, where an analyte was detected for a shipboard solid leaching experiment, but a corresponding measure of that analyte in seawater from Aroclor analytical control is not available for comparison. This was not a common occurrence in the leaching data, but it occasionally occured because the study was not able to examine every possible perturbation of Aroclor loading possibilities. For similar reasons, there were occasionally samples that did not have corresponding Aroclor analyte maxima against which to compare to evaluate the Aroclor analyte saturation point. This also was rare, and the impact was minimal because of the many other lower incremental leaching sample concentration data collected over the course of the leaching experiment. Regardless, in these rare instances, the analyte maxima in those samples must be interpreted in terms of a possibility (not certainty) that it may have been influenced to some degree by a potential saturation condition. In general, these cases were observed to occur earlier rather than later in the leaching process for a given experiment, exerting minimal impact on long term leach rates at the curve endpoint. Furthermore, though steps were taken to avoid the release of PCB-rich shipboard solid particulates into the leachate, it is possible, though not particularly likely, that an occasional very small particle made it through the cage in the leaching vessel and then into an analytical sample extraction to produce slightly higher leachate concentrations in that sample. A more probable scenario for the non-Aroclor maxima is related to availability of PCB analytes at the seawater interface (SASA), as briefly described below.

Leach Rate Data/Results

With the exception of a few analytes, all shipboard solid PCB leachate concentration maxima were lower compared with Aroclor analytical controls (See Table 12). For the non-Aroclor analyte maxima, it is likely that the shipboard solid interface (SASA) was simply able to release more of that particular PCB than could the A1254 or A1268 matrix. Unfortunately, without more detailed information about the interfacial PCB compositions of shipboard solids, vice assuming it is comprised of PCB distributions similar to bulk compositions, the dissimilarities between these analyte behaviors and Aroclor analyte behaviors can only be characterized as an uncertainty. Regardless, these shipboard solid analyte maxima can be considered the effective saturation limit in seawater for that analyte. Other concentrations for that analyte across the experimental series are below that maximum, and still comprise a valid leach rate dataset.

Maintaining a non-saturated condition was a primary component of the study approach, along with other engineering controls employed in the study, which ensured that leaching results reflect a truly uninhibited release process. The sampling time was also a critical variable in the leaching studies. This was not a parameter that could be optimized to provide a higher temporal leach rate resolution across any given leach rate experiment. The resolution to which we could determine the leach rates was entirely dependent upon the rate of release from the solid, with the result that the time intervals in the leaching experiments are large and not truly differential. This relatively large time interval was out of necessity, not choice, and is a function of allowing the experiment to follow the leach rate, i.e. sampling interval is governed by the time required for a very slow leaching process to occur until sufficient concentrations are reached for analytical quantitation of a significant number of different analytes in each sample (leaching of a reasonable number of analytes above detectable levels to provide an appropriate level of confidence in the overall quantitation.) For slow leaching processes, such as those observed in this study, in which nearly insoluble PCBs are essentially immobilized in a solid matrix, it is reasonable to increase the sampling time to allow the leaching of PCBs to be observed. The alternative would be to shorten the sampling interval and measure non-detects, a clearly unacceptable option for quantitatively characterizing an empirical release behavior. If the solids had contained only a single analyte, vice a complex mixture of PCBs (one or more Aroclors), a study could have been designed where one might have been able to perform analyses at lower detection limits to observe the (lower magnitude) release in a shorter period of time, and sampling interval might have been minimized further within similar criteria. Regardless, the inherent PCB release properties of the solid matrices would have dictated the inherently slow leaching process. The result of long sampling times is that one cannot characterize the dynamic nonlinearities (both faster and slower) leaching that could be occurring within each sampling/leaching interval. Average LR, as described by Equation 2 and Equation 3, captures the total behavior and is numerically correct, truly reflecting an average change in concentration over a time period interval, delta-t. As mentioned above, the underlying issue is one of time resolution. This calculation is numerically dependent upon t_f and t_i, and defines an average for any value of delta-t. It does not provide any information about instantaneous values of LR within the time-period, however, the sum of all instantaneous rates within the time period must equal the average rate defined by Equation 2. While it is correct to consider the average leach rate a low-resolution value, it is not correct to consider the average leach rate to be an underestimation. The average leach rate is comprised of an equivalent number of both low and high values within the sampling interval.

It is acknowledged that the leaching curves are unique results for each solid and do not represent a statistical result in the sense that replicate experiments and analyses were not performed to provide error bars on each leach rate data point (in addition to the expected variance in analytical precision, as demonstrated in the raw concentration data evaluation). It is unlikely that such a set of experiments could provide results considered interpretable, simply because there is not sufficient commonality in terms of PCB source content even within a given solid sample (subsamples of a field sample have been generally shown to contain different concentrations and distributions of PCBs/Aroclors). It is useful however, to make the observation that subsamples of the same solids, tested at low temperature, as described in the General Leaching Experiment Design and Methodology discussion in the **EXPERIMENTAL DETAILS** section, and presented in Appendix E, were qualitatively similar. Ultimately, the regression analyses performed on leach rate curves in this study are used as reasonable approximations for bounding the individual leaching behaviors. For those analyte leach rate regressions with insufficient statistical predictive power (high p-values) or insufficient numbers of points for a regression analysis, the statistical mean and standard deviation in the observed empirical leach rates can provide a reasonable estimation of the overall variance in the data.

A detailed analysis and description of confidence, limitations, assumptions, and uncertainties associated with the use of these leach rate data to describe the source component in a vessel-sinking scenario is best as decribed using the example vessel below in the discussion of Recommendations for the Use of Leaching Data. However, it is also prudent to provide broad, general guidance with respect to what the data ultimately represent, in the event that situations arise in which another type of use for the data is being evaluated/explored. Examples of this might include, but are not limited to, applying the results for a material in this leaching study to another type of material, sinking a vessel under different conditions common to some other environment, or perhaps hazardous material disposal of PCB-containing shipboard solids. Empirical data specific to a situation under consideration should be used preferentially. In some cases a proxy or surrogate is necessary to estimate what the release could be as a worst-case scenario. For this reason, it is necessary to know or obtain information regarding PCB content (concentration and type of PCBs) for the source material in question. Once this is known, the applicability of leach rate results to other materials can be evaluated using conservative assumptions and known commonalities with the materials tested in this study. A method that one might be inclined to try is to use the results for neat Aroclor as a proxy or surrogate and simply scale the leach rate result for the neat Aroclor to match. This is only valid under certain circumstances, one of which is described for the example vessel below. The primary caveat is that the type of material must be similar in terms of its physio-chemical properties. In particular, it is not valid to use Aroclor results to rationalize the mechanism or model the complete leaching behavior of an inert solid material containing PCBs, because the Aroclor matrix, even if it is a solid or semi-solid material, is not inert to dissolution under seawater conditions. This means that neat Aroclor results should not be considered a suitable proxy for A1254 or A1268 PCBs leaching from an inert solid material. However, empirical results for A1254 or A1268 can be used as a surrogate for mobile materials such as oils/greases that might leach Aroclor/PCBs, as is the case described in the example for the ex-Lawe below.

It is also important to understand and describe the uncertainties associated with the use of a) empirical leach rates, b) statistical means of empirical leach rates, or c) leach rates calculated using regression analysis results. In the former two cases, the leach rate could be significantly or perhaps even overly conservative. If the final empirical leach rate value is used, it could be not conservative enough. If regression analysis is used to calculate a value at some time t, a situation might arise wherein the confidence in the regression value is significantly lower than using the empirical data, even to the point of an unacceptable level of confidence. The point is that these approaches should be evaluated on a case-by-case basis and the user is cautioned to verify that the decision to use any particular approach can be rationalized in some reasonable, defensible manner. In general, it is recommended that, for analytes exhibiting stable leaching curves, the final empirical leach rate be used, unless it is noted to be outside of the regression curve as shown in Appendix A and summarized in Table 11. A given regression analysis can be used when a value just beyond the leach rate study timeframe is required; to provide a value across all of the types of solids in a particular leaching scenario that requires a common point in time, e.g. ≤ 2 years for when a reef community might become established on a sunken vessel; or perhaps a leach rate corresponding to the final empirical leaching value for the solid of shortest overall leaching experiment duration. In the latter case, to do a consistent and comparable leach rate analysis for all materials' released analytes at the same point in an overall leaching process, leach rates for the analytes in other materials would be calculated from their statistically defensible regression analyses, but some other approach would be required for those analytes with insufficient data to supoort a regression analysis. At no time are regression analysis results applicable to calculating a pre-maximum leach rate, as regression analyses correspond only to the decreasing portion of leach rate curves and are not statistically related to points on an empirical leach rate curve prior to the maximum leach rate. In all cases where a regression value is selected as a long-term leach rate, it is advisable to compare that value to the upper limit of the regression analysis to ensure that the selected value is $\geq$ the more conservative upper prediction interval (UPI) value, and that the p-value for the regression is of high predictive power. This defensible approach will serve to ensure the use of a conservative value in which one can place a high degree of confidence.

Recommendations for the Use of Leaching Data

The leaching data and leach rates presented in this work are useful for accurately characterizing the leaching of PCBs from solid materials in the context of a risk assessment release and exposure model, under conditions specific to the environment of concern in the risk assessment, i.e. shallow water leaching in an artificial reef environment. The portion of a given leaching curve to use as a source term in such a model depends upon what assumptions are considered reasonable within the risk assessment framework being used. However, to help illustrate the process of choosing and utilizing the leach rate data presented in this report, an example evaluation is included below for a decommissioned US Navy vessel, the ex-William C. Lawe[53]. This vessel was the subject of a report prepared for NAVSEA[54], in which PCBs-ISM were thoroughly evaluated with the goal of providing source information (PCBs-ISM onboard) for the SINKEX study. In the SINKEX study, a sister-ship to the ex-Lawe, the ex-Agerholm, was located at ~2700 feet in the Pacific Ocean off of the coast of California, and was the focus of an intense oceanographic and environmental sampling effort, for purposes of a subsequent risk assessments[6]. The ex-Lawe, although not the typical type of vessel used for artificial reef-building, is used here as a surrogate reef vessel and is considered a valid approach from the PCB leaching perspective, considering that the same types of PCBs-ISM evaluated in this study were found onboard the ex-Lawe. The total estimated amount of each type of PCBs-ISM onboard[54] will be used here to demonstrate how one would apply the leach rate data to a provide a source term in a hypothetical sinking event, i.e. as if the ex-Lawe were to sink in shallow water as an artificial reef.

Shipboard solid-specific leaching data can be utilized to varying degrees of complexity, depending upon the assumptions one is willing to accept. The extremes range from assuming a single, average leach rate over the entire period of time to using the leaching curves for the release over the empirical timeframe, followed by a long-term leach rate; either an extrapolated (changing) rate based on the leaching curve, or an assumed constant rate as an upper limit (worst case). The latter approach is being used in the Prospective Risk Assessment Model (PRAM), initiated as part of the human health risk assessment in the Navy's REEFEX program.[4] The former approach, using only the final empirical leach rate for each shipboard solid over the entire risk assessment timeframe, was used in the REEFEX screening ecological risk assessment[3], with the ex-Agerholm as a surrogate reef-vessel. The constant average leach rates for such an approach is shown in Table 14A as the "(b) Long-term" column of values for use in the ex-Lawe mass loading example. The extrapolated curves found in APPENDIX A support this choice of long-term upper limit leach rate, by demonstrating that the leach rates do appear to continue decreasing with time. Table 14A also summarizes the data for the case where the empirical leach rate (a) applies over the shipboard solid specific-experimental leaching timeframe (Table 14B), and the long-term upper limit (b) applies over the remaining timeframe of interest.

In Table 14B, the quantities and high estimates for PCB concentrations of each shipboard solid are adopted from the ex-Lawe report[54], and the leach rates for the materials tested in the leach rate study are used to calculate depletion times. Note that the leaching amounts and times to depletion for each solid are much different due to the very different amounts of each material onboard and with varied concentrations, leading to a complex mixture of PCB source terms at any particular point in absolute time over a maximum timeframe dictated by the longest time-to-depletion for that particular scenario, from less than a year for highly mobile fast release materials such as oils/greases, to nearly 27,000 years for the electrical cable, to over a million years for felt gasket, at which point PCB leaching would cease. This scenario assumes all of the PCBs are to be mobile and leach in their entirety. This is very conservative as it highly likely that some of the PCBs in the solid would remain permanently bound within the solid matrix. As previously indicated, the pure Aroclor leach rates were used as surrogates for shipboard solids not included in the leaching study (oils and greases). Under the stated assumptions, the rates of PCB release in this table could be used as source terms in a human health or ecological risk assessment, concerned with a hypothetical sinking of the ex-Lawe as a reef at a shallow-water site.

Alternatively, the regression results in APPENDIX A, and summarized in Table 11, could be used to support using a constant long-term leach rate value at for instance, 2 years when a reef community would become established or viable, for regression analyses of PCBs that indicate leach rates will continue to decrease. In general, the leach rate behavior can be described by the power function in Equation 10 below, where y is the average leach rate and x is time. The leach rate data were fit using the logarithmic form of this power function (in "y = mx + b" form), shown in Equation 11, where A = log[a].

Equation 10

$$y = 10^{A}x^{B}$$

Equation 11

$$\log[y] = B \log[x] + A$$

The tail or decreasing portion of the leach rate curves was plotted on a log-log scale, for which a linear regression was performed (only on points $\geq$ the observed curve maximum). The regression details for all shipboard solid leach rate curves with sufficient numbers of data points have been included in APPENDIX A and summarized in Table 11. If this approach is preferred, it is suggested that the experimental leaching results in Table 14A, "(a) Empirical", still be used as the source release term over the experimental leaching period, beyond which, the functions found in APPENDIX A/Table 11 can be used for estimating the long-term source parameter, or to support using the final empirical value as a conservative upper limit leach rate. It is suggested that the use of regression functions be caveated as having been produced from a relatively small amount of data early in the leaching process, leading to low confidence in predicted values at long term extrapolation endpoints (times). Because of this it is recommended that the most conservative, upper prediction interval curve/data be used at such endpoints if this approach is chosen. It should also be noted that in some cases, the predicted upper limit (prediction interval) is nearly equivalent to the final empirical data value. In such a case, the curve fit is still useful in providing confidence in using the final empirical leach rate value as a long-term upper limit leach rate.

Table 14 (A & B). A) Empirical and Long Term average leach rates during and beyond the experimental leaching timeframe for each shipboard solid. B) Example calculations of time-to-depletion for the ex-Lawe, using the empirical and long-term average leach rates in A).

(A)	Felt Gasket-Outer		Felt Gasket-Inner		Electrical Cable		Foam Rubber-Ensolite		Bulkhead Insulation		Black Rubber-PHL		Aluminized Paint		Oils/Greases with A1254		Oils/Greases with A1268	
PCB Content[f]	11.74 wt% tPCBs		23.03 wt% tPCBs		0.12 wt% tPCBs		0.89 wt% tPCBs		0.044 wt% tPCBs		0.16 wt% tPCBs		0.043 wt% tPCBs		100 wt% tPCBs		100 wt% tPCBs	
Average Leach Rates (ng/g shipboard solid-day)	Empirical[a]	Long-term[b]	Empirical[a]	Long-term[b]	Empirical[a]	Long-term[b]	Empirical[a]	Long-term[b]	Empirical[a]	Long-term[b]	Empirical[a]	Long-term[b]	Empirical[a]	Long-term[b]	Empirical[a]	Long-term[b]	Empirical[a]	Long-term[b]
Cl1	3.7E-03		8.7E-03	1.6E-02							9.2E-02	7.0E-02			1.6E+02	2.7E+01	8.6E+01	
Cl2	7.7E-01	3.5E-01	1.4E+00	2.2E-01	2.3E-02		5.1E-01	1.0E-01	3.9E-01		2.5E-01	5.4E-02			5.2E+02	1.4E+02	2.3E+03	
PCB8	2.1E-01	1.0E-01	2.1E-01	7.6E-02			3.4E-02	1.7E-02	5.5E-02		1.7E-02	8.7E-03			2.0E+02	5.6E+01	1.0E+03	
Cl3	1.1E+00	5.0E-01	8.1E-01	3.5E-01	1.8E-04		1.7E-01	8.1E-02	1.2E+00	6.0E-01	1.6E-01	9.1E-02	7.5E-03		4.2E+02	1.3E+02	6.2E+03	2.1E+02
PCB18	3.4E-01	1.5E-01	2.4E-01	9.0E-02	4.2E-05		2.9E-02	1.4E-02	1.1E-01		2.1E-02	1.2E-02			1.6E+02	5.9E+01	1.8E+03	3.7E+01
PCB28	2.6E-01	8.5E-02	1.6E-01	5.8E-02	9.4E-05		7.2E-02	1.5E-02	4.2E-01	8.3E-02	3.0E-02		1.2E-03		1.4E+02	3.0E+01	1.4E+03	6.7E+01
Cl4	1.0E+00	3.6E-01	4.9E-01	1.7E-01	3.7E-02	2.1E-02	2.0E+00	8.1E-01	2.8E+01	7.3E+00	6.3E-01	2.6E-01	1.5E-01	6.2E-02	5.6E+03	1.9E+03	3.4E+03	5.3E+02
PCB44	1.3E-01	6.1E-02	6.2E-02	2.3E-02	5.8E-03	2.7E-03	3.9E-01	1.5E-01	4.6E+00	1.2E+00	1.0E-01	4.1E-02	1.2E-02	1.4E-02	9.0E+02	2.4E+02	4.7E+02	1.3E+02
PCB49	6.5E-02	4.5E-02	3.8E-02	1.3E-02	2.0E-03	1.1E-03	1.2E-01	3.8E-02	1.5E+00	3.8E-01	4.1E-02	1.2E-02	8.8E-03		3.8E+02	1.1E+02	2.3E+02	6.2E+01
PCB52	1.5E-01	5.6E-02	7.5E-02	3.0E-02	1.2E-02	6.1E-03	7.0E-01	2.8E-01	7.6E+00	2.3E+00	2.0E-01	8.3E-02	4.4E-02	1.8E-02	1.9E+03	6.3E+02	4.5E+02	1.5E+02
PCB66	3.5E-02		1.6E-02		1.0E-03		7.0E-02		1.4E+00	2.3E-01	1.6E-02	5.0E-03			1.4E+02	2.7E+01	1.8E+02	2.7E+01
PCB77	4.7E-03				9.4E-05				8.8E-03						2.1E-01		4.0E+01	
Cl5	3.0E-01		1.5E-01		6.0E-02	2.3E-02	2.6E+00	9.1E-01	5.0E+01	1.2E+01	4.6E-01	1.8E-01	3.7E-01		4.8E+03	1.2E+03	2.0E+02	7.8E+01
PCB87	3.2E-03		3.2E-03		3.1E-03	1.3E-03	1.9E-01	5.0E-02	3.7E+00	1.0E+00	2.0E-02		1.5E-02		3.2E+02	7.7E+01	1.0E+01	6.3E+00
PCB101	2.7E-02		1.3E-02		5.7E-03	2.1E-03	3.2E-01	8.1E-02	5.9E+00	1.5E+00	4.2E-02	1.0E-02	3.1E-02		4.5E+02	1.3E+02	1.4E+01	7.2E+00
PCB105	4.7E-03				1.1E-03		8.4E-02	1.7E-02	1.4E+00	1.3E-01	3.5E-03		5.5E-03		9.0E+01	8.4E+00	1.6E+01	6.0E+00
PCB114							5.6E-04		5.6E-02						2.0E+00		1.2E-01	
PCB118	7.3E-03		3.4E-03		2.9E-03		1.8E-01	2.4E-02	3.2E+00	2.0E-01	1.7E-02		1.7E-02		2.0E+02	1.5E+01	1.5E+01	4.3E+00
PCB123															7.3E-01			
PCB126																		
Cl6	7.2E-02		8.1E-02		9.3E-03		5.7E-01		9.3E+00	4.1E+00			1.5E-01		5.0E+02	1.4E+02	1.5E+01	7.7E-01
PCB128					1.4E-04		2.6E-02		3.0E-01						1.5E+01	4.3E+00		
PCB138					7.0E-04		7.9E-02		1.3E+00	2.5E-01			1.2E-02		6.3E+01	1.2E+01	1.1E-01	
PCB153	6.1E-03		8.9E-03		6.6E-04		6.9E-02		9.8E-01	3.1E-01			1.5E-02		5.8E+01	1.4E+01	3.8E+00	2.7E+00
PCB156							9.2E-03		7.1E-02						2.4E+00			
PCB157									2.1E-03						1.7E-01			
PCB167									7.0E-03						3.8E-01			
PCB169																		
Cl7	3.8E-01	6.1E-02	5.2E-01	2.5E-02	3.2E-03		2.1E-01		1.4E+00		1.7E+01		2.7E-01		4.8E+00		4.9E+01	1.8E+01
PCB170									5.3E-03									
PCB180	1.5E-02		6.7E-02						1.0E-02						2.8E-01		3.7E+00	3.1E+00

(A)	Felt Gasket-Outer		Felt Gasket-Inner		Electrical Cable		Foam Rubber-Ensolite		Bulkhead Insulation		Black Rubber-PHL		Aluminized Paint		Oils/Greases with A1254		Oils/Greases with A1268	
PCB183			8.0E-03						1.1E-02									
PCB184			2.5E-03		4.7E-04		2.0E-02		1.1E-01		2.6E+00		4.4E-02					
PCB187	1.5E-01	3.9E-02	1.6E-01	1.9E-02					1.6E-02								7.5E+00	8.4E+00
PCB189																		
Cl8	2.7E-01		1.2E+00	1.4E-01													1.5E+00	
PCB195																		
Cl9			4.0E-01		1.6E-04												1.2E+04	
PCB206			2.5E-01		1.0E-04												1.2E+04	
Cl10			3.3E-03		8.8E-05													
PCB209			3.3E-03		8.8E-05													
tPCBs (sum of homologues)	3.9E+00	1.3E+00	5.1E+00	9.3E-01	1.3E-01	4.4E-02	6.1E+00	1.9E+00	9.1E+01	2.4E+01	1.8E+01	6.6E-01	9.5E-01	6.2E-02	1.2E+04	3.5E+03	2.4E+04	8.4E+02

(B)	**Example: ex-William C. Lawe**								
	Felt Gasket (outer)	Felt Gasket (inner)	Electrical Cable	Foam Rubber/Ensolite	Bulkhead Insulation	BRPHL	Aluminized Paint	Oils/Greases with A1254	Oils/Greases with A1268
g shipboard solid (ex-Lawe JJMA estimates)	45359.2	45359.2	15169489.8	9071.8	9071.8	1496854.8	55882580.5	3215969.9	3215969.9
Weight fraction (ex-Lawe JJMA high estimates)	4.0E-01	4.0E-01	4.4E-04	5.0E-04	5.0E-04	2.0E-02	4.9E-05	1.2E-03	1.2E-03
Weight% in shipboard solid (PCB-LRS)	11.74	23.03	0.12	0.89	0.044	0.16	0.043	100	100
Empirical Leaching Range[(c)] (days)	454.1	475.0	475.0	469.0	454.3	475.1	469.0	433.3	371.0
Years to Depletion[(d)], for tPCBs, assuming all materials release all PCBs in their entirety.	860311	1173719	26900	723	56	83758	2173	0.9	3.8
Years to Depletion[(e)], for tPCBs, assuming all materials release all PCBs in their entirety.	860307	1173712	26896	719	51	83721	2153	0.3	0.1

(a) Mean of all experimentally-determined rates determined over the empirical timeframe (c).
(b) The final empirical leach rate value is used as a long-term constant upper limit, to represent a constant upper limit rate beyond the experimental timeframe (c).
(c) This is equivalent to the total experimental leaching or exposure time for the materials in this study.
(d) Calculated assuming the constant rate in (b) only.
(e) Calculated using the empirical rate (a) over experimental time period (c), and the constant upper limit rate (b) thereafter.
(f) Concentration of PCBs in the solid.

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