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TECHNICAL REPORT 2088
May 2014

Investigation of PCB Release Rates from Selected Shipboard Solid Materials Under Laboratory-Simulated Deep Ocean Conditions

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Approved for public release.

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ADMINISTRATIVE INFORMATION

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Sciences Division

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EXECUTIVE SUMMARY

BACKGROUND

A potential contaminant of concern (PCoC) on board deactivated Navy vessels for use in sinking scenarios are 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. Investigations of PCBs associated with decommissioned vessels have included monitoring and evaluating the release of PCBs from former U.S. Navy ships that have been sunk to create artificial reefs in shallow water or have been sunk in deep ocean waters during weapons testing exercises (SINKEX).[1, 2, 3, 4, 5] Additionally, sampling and analysis conducted at Navy shipyards of materials found on board decommissioned vessels in the reserve fleet, vessels being scrapped, and vessels slated for title-transfer and resale has resulted in a detailed database of PCBs in Solid Materials (PCBs-ISM) that are commonly found on Navy ships that were in service between 1950 and 1990.[6] Previously, we performed a study focused on evaluating leaching behaviors of a representative set of PCBs-ISM under laboratory-simulated, shallow ocean water (25 °C, nominally 1 bar) conditions.[7] The results of a complementary technical effort is presented in this report for the same set of PCBs-ISM tested under laboratory-simulated, deep-water (>2700 m depth, 4 °C, nominally 300 bar) conditions to measure leach rates applicable to a SINKEX vessel. This study report also directly addresses data requirements that are cited as enclosure 1 under the 1999 USN-USEPA SINKEX Agreement(US EPA. 1999), included in Appendix A of this report.

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[1] R. M. Matore, T. D. Mathews, and M. Bell. 1998. “Levels of PCBs and Heavy Metals in Biota Found on ex-Military Ships Used as Artificial Reefs,” Draft Report. Marine Resources Division, South Carolina Marine Resources Center, South Carolina Department of Natural Resources, Charleston, SC.

[2] Space and Naval Warfare Systems Center San Diego. 2005 (May). “A Screening Level Ecorisk Assessment for Using Former Navy Vessels to Construct Artificial Reefs.” Final Report prepared for U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxic Substances and Office of Water, and U.S. Department of Navy, Chief of Naval Operations and Naval Sea Systems Command, San Diego, CA.

[3] Naval Environmental Health Center Environmental Programs Directorate. 2003. “SINKEX Program: Human Health Risk Assessment for Potential Exposure To Polychlorinated Biphenyls From Deep-Water Sunken U.S. Navy Vessels.” May 2003 Final Edition. Prepared For Chief of Navy Operations, Naval Sea Systems Command, U.S. Department of Navy and Office of Water, Office of Pollutions Prevention and Toxic Substances, U.S. Environmental Protection Agency.

[4] Naval Environmental Health Center Environmental Programs Directorate. 2004. “A Human Health Risk Assessment for Potential Exposure to Polychlorinated Biphenyls (PCBs) from Sunken Vessels Used as Artificial Reefs (Food Chain Scenario).” Volumes 1 and 2. Final Report prepared for U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxic Substances, and U.S. Department of Navy, Chief of Naval Operations, and Space and Naval Warfare Systems Center San Diego.

[5] Space and Naval Warfare Systems Center San Diego. 2006. “Risk Assessment of the Potential Release of PCBs and Other Contaminants from Sunken Navy Ships in the Deep Ocean: ex-USS AGERHOLM Case Study,” Final Report to Program Executive Office Ships and Naval Sea Systems Command (PMS 333).

[6] John J. McMullen Associates. 1999. Database of PCBs in Solid Materials (PCBs-ISM) Inventory Onboard Navy Vessels.

[7] R. D. George, C. In, R. K. Johnston, C. A. Kurtz, P. F. Seligman, R. D. Gauthier, and W. J. Wild. 2006. “Investigation of Polychlorinated Biphenyl (PCB) Release-Rates from Selected Shipboard Solid Materials Under Laboratory-Simulated Shallow Ocean (Artificial Reef) Environments.” Technical Report (TR) 1936. Space and Naval Warfare Systems Center San Diego, San Diego, CA,

METHODOLOGY

Leaching data were collected for a representative set of solid materials commonly found to contain PCBs on board older, out-of-service surface vessels and submarines. Solids known to contain high levels of PCBs were purposely chosen for this study because they represented the highest concentrations of PCBs expected on current and future vessels that may be sunk during SINKEX activities in deep water. Deep-water leaching tests were performed under constant representative abiotic conditions of pH 8.1, salinity of 34 psu, high hydrostatic pressure (up to ~300 bar), 4 °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. The experiments were conducted to isolate the leaching process by eliminating processes that would inhibit leaching such as organic particulate sorptive processes, biofouling, biodegradation, uptake/metabolism, or bioaccumulation of PCBs. The shipboard solids were tested intact whenever possible to simulate what would actually occur onboard a sunken vessel inside a vessel compartment containing PCBs-ISM. The solids evaluated included Black Rubber Pipe Hanger Liner (BRPHL), Electrical Cable (EC), Foam Rubber/Ensolite® (FRE), Bulkhead Insulation (BHI), Felt Gasket/Inner (FGI), Felt Gasket/Outer (FGO), and Aluminized Paint (AP).

The PCB distributions in the shipboard solids tested were consistent with distributions expected for Aroclor® 1254 (A1254), Aroclor® 1268 (A1268), or a mixture of both A1268 and A1254. Thus, neat Aroclor® 1254 and 1268 reference materials were used as analytical concentration controls for the shipboard solid leaching experiments. In addition, neat Aroclor® 1254 and 1268 dissolution rates were used as surrogates for Aroclor®-containing mobile/soluble oils and greases, to represent materials with no shipboard solid influence. A total of 31 PCB congeners and all 10 PCB homolog groups were measured in seawater leachate as a function of exposure time to represent release of environmentally relevant (toxicologically persistent) PCBs to assess potential ecological and human health risk. Total PCBs (tPCBs) were empirically determined by summing each level of PCB chlorination (summing the measured homolog groups). All of the PCB analytes measured in this study were identical to the PCBs used to evaluate human health and ecological risks of sinking decommissioned Navy vessels. In general, the leaching data collected in this study are applicable to the deep ocean scenario. Furthermore, data from the deep ocean scenario were contrasted with leaching data from the previous shallow water study to evaluate the effects of temperature and pressure on the leaching behavior of the solids tested.

RESULTS

Leach rate curves were generated from all the leach rate experiments across the entire leaching experiment timeframe to determine the change in leach rate as function of time. Most leach rate curves exhibited an initial period of instability, lasting days to several weeks. However, in all cases, leach rate curves eventually stabilized and 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 can 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 were available for leaching, even though it is possible that some PCBs are most likely irreversibly bound to the source material matrix.

The relative leach rates for the materials tested in this study are summarized in Figure 1. The leach rate values in Figure 1 are plotted from lowest to highest and correspond to the stabilized final empirical leach rates determined in each leaching experiment for each material. Leach rates for warmer temperature (25 °C) at ambient pressure (~1 bar) and low temperature (4°C) at higher pressure (~300 bar) are also shown for comparison. This figure demonstrates that each shipboard solid attenuates the leaching of PCBs to differing degrees and ultimately stabilizes at significantly different rates.

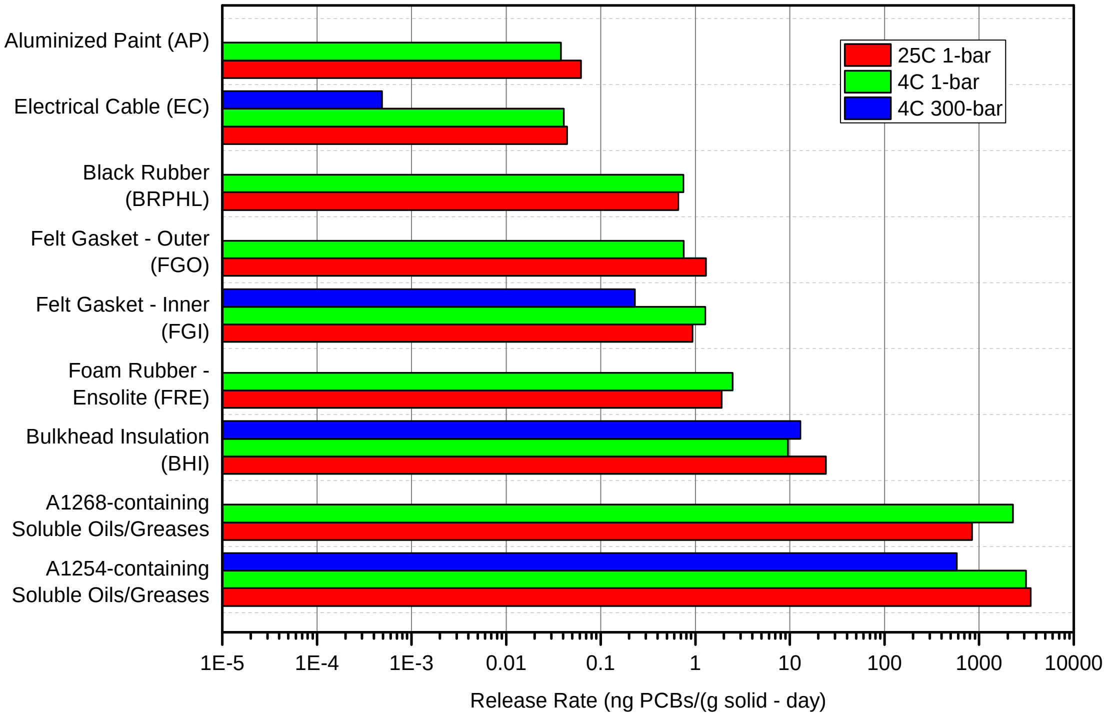


Figure 1. Experimental tPCB leach rate differences determined for shipboard solids compared with dissolution rates for Aroclor®1254 and 1268, which are surrogates for soluble Aroclor®-containing oils and greases, tested under the following three scenarios: 4 °C at ambient pressure (1 bar), 4 °C at 300 bar, and 25 °C at 1 bar. The leach rate data are the long-term stabilized values observed at the end of each experiment (final empirical value), generally after 14 to 16 months of leaching for each material in seawater, and are from curve endpoints described in this report (Table 10) for 4 °C at 1 bar and 4 °C at 300 bar results, and from George et al. (2006) for 25 °C at 1 bar results.

For the materials tested, the Aroclor® 1254 (A1254) and Aroclor® 1268 (A1268) surrogates for non-inert host matrices such as soluble oils and greases had the highest release rates. A1254 showed reduced release rates for lower temperature and higher pressure, but A1268 resulted in higher release rates for lower temperature. For the shipboard solids tested, BHI had the highest release rates and showed reduced releases in response to low temperature and high pressure. Tests with FRE, FGI, and BRPHL showed slightly higher release rates with lower temperature while all materials tested at high pressure had lower release rates than the release rates measured at ambient pressure. Note that while there were observed differences in release rates for the same materials tested at different temperatures and pressures, the release rates were similar and within the same magnitude as the release rates reported for 25 °C and ambient pressure. These results also indicate that variability between individual solid samples, primarily the composition of the solid matrix and secondarily the make up and distribution of PCBs contained within, are as important or perhaps even more important than environmental factors such as temperature and pressure in governing the resulting release rate. Sufficient descriptions of experimental limitations, repeatability of results, and analytical data quality assurance are detailed throughout this report to provide the level of confidence required for using and interpreting these data for assessments of human and ecological health risks related to sinking vessels under shallow and deep ocean environmental conditions.

CONCLUSIONS AND RECOMMENDATIONS

The deep ocean simulated leaching provided empirical data that are useful for characterizing the time- and temperature-dependent leaching behaviors of PCBs from different shipboard solid materials under physical and chemical conditions similar to a deep-ocean (SINKEX) environment. In addition, the deep ocean experiments provided additional information on the effect of pressure and temperature on PCBs leaching from PCB-ISM in the marine environment. The acceptable leach rate source term in the context of a release and exposure model for risk assessment depends on what assumptions are considered reasonable within the appropriate risk assessment framework. Shipboard solid-specific leach rate data provides a means of estimating the releases from shipboard sources that can range from (1) assuming a single, mean leach rate over the entire period of time to (2) using the leaching curves for the empirical release, followed by a long-term leach rate, as an extrapolated (changing) rate based on the leaching curve, or an assumed constant rate as an upper limit (conservative case). The regression analysis and extrapolated curves reported in George et al. (2006) are examples of using a long-term leach rate described in (2) by demonstrating that leach rates continued to decrease with time. Alternatively, the regression analysis itself can be used as a source term function to predict a continued decreasing release. In general, the empirical leaching results can be used to characterize the early release beyond which, empirical curve endpoints or regression functions from curve analyses can be used for estimating a long-term source parameter or to support using a conservative constant leach rate. Furthermore, the use of regression functions should 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). Thus, it is recommend that the statistically-derived upper prediction interval curve data be used at such endpoints if this approach is chosen.

CONTENTS

Appendices A through E are on the supplied CD.

Figures

Tables

Equations

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 Homolog Minimum
FGI	Felt Gasket (Inner)
FGO	Felt Gasket (Outer)
FRE	Foam Rubber (Ensolite®)
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 (general context)
MDL	(Sample-specific) Minimum or Method Detection Limit
MESO	Marine Environmental Support Office, SSC San Diego
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	picograms (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 Homolog 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 (SSC Pacific)	Space and Naval Warfare Systems Center San Diego (Pacific)
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
WT%	percent by weight

1. INTRODUCTION

1.1. PURPOSE

This effort was undertaken to evaluate the leaching of polychlorinated biphenyls (PCBs) from shipboard solid materials present on out-of-service U.S. Navy (USN) vessels used as targets in training exercises. The Navy uses the Sink Exercise (SINKEX) program for training and weapons testing by sinking decommissioned ships previously cleaned and prepared for disposal. Under an agreement with the US Environmental Protection Agency (U.S. EPA, 1999), the vessels are sunk in waters deeper than 1,000 fathoms (6,000 ft, 304.8 m) and more than 50 nautical miles (92.6 km) from shore (MARAD, 2010; U.S. Navy, 2014). The agreement requires all hazardous substances to be removed from the ship prior to sinking, including the removal of PCBs contained in liquid form and easily removable solid materials that contained PCBs (U.S. EPA, 1999). However, on some vessels there are PCBs in solid materials (PCBs-ISM), such as electrical cable insulation (EC), bulkhead insulation (BHI), rubber products, felt gaskets, and some types of aluminized paints (AP) that are impossible or impractical to remove. The specific goal of the leach rate study described in this report was to measure the release of PCBs from representative PCBs-ISM found on board U.S. Navy ships under laboratory conditions that simulated the temperature, pressure, and seawater conditions likely to occur at SINKEX sites. The study measured PCB releases from the solid materials under abiotic conditions and evaluated leaching dynamics over time periods of hours to days, weeks, and many months. The data produced from this study was used to partially satisfy the conditions of the SINKEX agreement with EPA(U.S. EPA. 1999) and provide data (SSC San Diego, 2006) to support the human health (NEHC, 2003) ecological (Johnston et al., 2006) risk assessments and modeling studies conducted according to the agreement.

This report describes the leach rate study (LRS) carried out to assess leaching of PCBs-ISM under laboratory conditions that simulated the deep sea environment. Results from the shallow water leach rate study (SW-LRS) using similar methods and PCBs-ISMs are reported in George et al., (2006). The PCBs-ISM were representative solids collected from Navy ships that were known or suspected to contain high levels of PCBs. The background on PCBs-ISM, terminology and chemistry, environmental fate of PCBs, factors influencing PCB leaching and partitioning, and the conceptual model for shipboard PCB leaching is presented in Section 1. Section 2 presents the experimental details including the experimental design, collection of PCBs-ISMs from Navy ships, laboratory procedures for sampling and collecting leaching data and data management and analysis. Section 3 presents emprical data obtained for the materials tested and the shipboard solid-specific leaching data. The average leach rate calculations for each of the materials tested are reported and discussed in Section 4. The references are found in Section 5 and supporting information is provided in the appendices. Appendix A contains a copy of the deep ocean leach rate study data requirements that are cited as enclosure 1 under the 1999 USN-USEPA SINKEX Agreeement (U.S. Environmental Protection Agency, 1999). Appendix B contains descriptions of the laboratory operations, methods, and the analytical and laboratory standard operating procedures (SOPs) used in the study. Appendix C contains raw data tables from the samples collected during 4 °C high pressure (300 bar), and 4 °C low-pressure (1 bar) leaching studies, including quality assurance and quality control (QA/QC) measures used. Appendix D contains transformed analytical data, including cumulative leaching curves and leach rate calculations for PCBs-ISM measured at 4 °C and high pressure (300 bar), and 4 °C at low pressure (1 bar).

1.2. PCBs IN SOLID MATERIALS (PCBs-ISM)

The shipboard solids tested in this study contained the highest PCB concentrations available on inactive vessels when the study was conducted. Vessels that might be used in SINKEX oeprations after this study could have higher or lower PCB concentrations. The shipboard solid materials investigated included felt gaskets (both inside the flange – FGI, and outside the flange – FGO), electrical cable (EC), aluminized paint (AP), foam rubber (Ensolite®, FRE), black rubber (shock mounts used as pipe hanger liners, BRPHL), and bulkhead insulation (inorganic manmade vitreous fiber, BHI). These classes of PCBs-ISM represent shipboard solid materials commonly found on board surface vessels and submarines. Oils and greases are a class of shipboard solids that contain PCBs, but these materials were not a focus of this study because PCB-containing oils and greases are routinely removed with other liquid materials during remedial actions performed as part of the process of decommissioning vessels to the inactive fleet (U.S. Environmental Protection Agency, 1999).

1.3. PCB TERMINOLOGY AND CHEMISTRY

Polychlorinated biphenyls are classified as persistent pollutants, environmental health hazards, and known and suspected carcinogens (ATSDR, 2000, 2011). PCBs 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 freshwater 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 that, 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 seldom 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 (Miller et al., 1984; Shiu and Mackay, 1986) and materials similar to shipboard solids (Mackay, Shiu, and Ma, 1992) rather than in the aqueous phase. This tendency slows or suppresses leaching processes, and a large portion of PCBs that do leach at a low level into the aqueous phase tend to be degraded forthright (Tabak, Quave, Masahni, and Barth, 1981; Rochlind, Blackburn, and Saylor, 1986) or are sequestered into natural organic materials (MacFarland and Clarke, 1989) by absorptive/adsorptive partitioning processes.

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

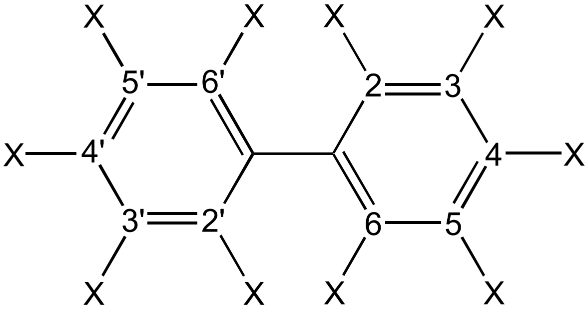


Figure 2. Polychlorinated Biphenyl molecular structure, where X at each numbered carbon can be a hydrogen (H) or chloro- (Cl) substituent. Each phenyl ring can rotate independent of the other around the covalent bond linking them together (i.e., the phenyl rings can be, but are not forced to be, coplanar). The total number of possible isomers, typically referred to as congeners, 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 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 [Ballschmiter and Zell] numbers [Ballschmiter et al., 1992]) (BZ1 toBZ209), 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). One should note slight differences in numbers and molecular naming conventions between IUPAC and BZ (U.S. EPA, 2006) when looking at historical PCB congener data. Additionally, all 209 PCB congeners can be grouped according to chlorination level. These groups are referred to as homolog groups (Cl1, Cl2, Cl3…Cl10). Within each homolog group there can be different substitutions, resulting in positional isomers that possess the same number of chloro-substituents and thus have the same molecular weight. The summation of all 10 homolog groups corresponds to total PCBs (tPCBs), comprised of all 209 congeners.

Commercial PCBs were originally marketed under the trade name Aroclor®. These PCBs 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® products were manufactured by bulk chlorination in the United States through the middle to late 1970s, forming mixtures with differing distributions of individual congeners, which results 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 (Kennish, 1992). A notable exception is Aroclor® 1016, which is 41.5 percent chlorine. In practice, all 209 congeners are very difficult to separate, which has led to analyses of PCBs reported as select individual congeners; tPCBs estimated from select congeners; Aroclor® (or Aroclor® equivalents) and, in some instances, homologs; and tPCBs as the sum of homologs.

1.4. PCBs IN THE ENVIRONMENT

Although PCBs in natural environments can exist as one or more of the 209 distinct molecular isomers described above, only some of these congeners are found at significant levels in the environment. The least persistent of the PCBs are those that have less than five chlorines per molecule, caused, in part, by (1) availability and use of only certain industrial PCB mixtures (Aroclors® with different, but distinct chlorination levels and congener distributions), and (2) selectivity by aqueous-organic phase partitioning and by PCB degradation processes (Tabak et al., 1981). More heavily chlorinated PCBs persist to a much greater extent in the environment because of 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 tend to accumulate more in lipid tissues (Rochlind, Blackburn, and Saylor, 1986). 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 considered more toxic than their non-planar counterparts because of their specificity toward important biochemical receptors that are responsible for toxic and other biological effects (Miller et al., 1984; Stalling et al., 1985; ATSDR, 2011). The more toxic coplanar congeners are also generally less soluble in seawater than other PCB congeners (Miller et al., 1984; Opperhutzen, Gobas, van der Steen, and Hutzinger, 1988; Shiu and Mackay, 1986). 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.

1.5. FACTORS AFFECTING PCB LEACHING AND PARTITIONING IN NATURAL ENVIRONMENTS

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 congeners (isomers) initially residing in the source material, and the physico-chemical nature of that source material (Figure 3). In a closed system, the absence of advective processes will supress transport out of the solid matrix and the release dependent on partitioning between the solid surface and the surrounding seawater. Release under closed conditions would eventually stop and become static until solvated PCBs are removed from the system by external processes or external partitioning equilibria.

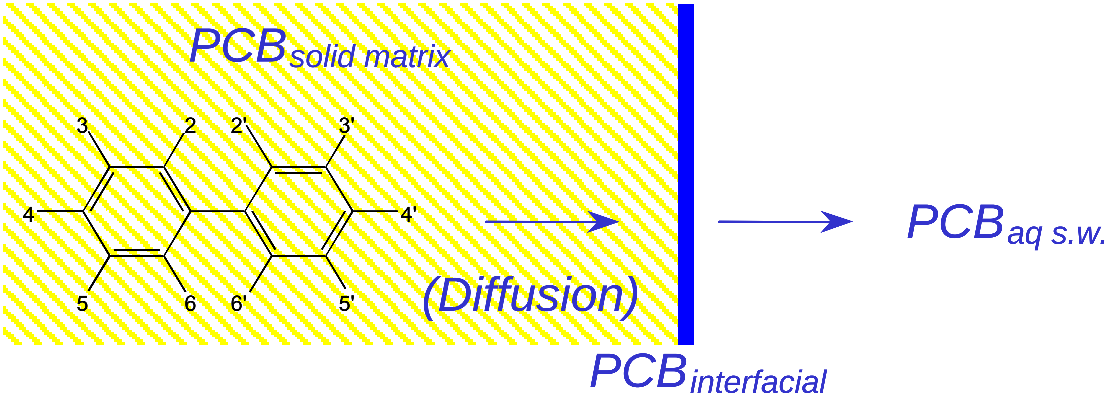


Figure 3. Primary PCB leaching process illustrated for an open system such as is simulated in this study. PCB transport occurs within a PCB containing material primarily by diffusive processes ($PCB_{solid\ matrix}$) and through the material-seawater interface ($PCB_{interfacial}$), before becoming available to the surrounding seawater environment ($PCB_{aq\ s.w.)}$ for subsequent advective transport and sorption onto sediments, particulate matter, and biological materials in the natural ocean environment.

The leaching pathway is further influenced by diffusion of PCBs within the solid, the depletion layer at the interface of the solid, and dissolution and dispersion in the external phase (Figure 4). In the context of fundamental diffusion, dissolution, and dispersive processes C_{bulk} is generally constant while L, $C_{gradient}$, and $C_{external}$ are variables that depend on the chemical and physical properties of the bulk and external phases. Dispersion in the external phase is composed of advective and diffusive components; relative magnitudes of each depend on physical constraints imposed on the external phase (Figure 4,). Diffusion in the solid is fundamentally considered Fickian, and can be explicitly described in mathematical terms (Crank, 1979) for well-defined systems if phase-coupled microscopic/molecular properties are known. Such properties were not known or determined for the shipboard solid-PCB congener–seawater systems for the leach rate studies described here. However, empirical release behaviors of homologs and tPCBs were quantified macroscopically, and correspond to complex release of groups of PCB congeners that can be considered equivalent to the summed release behaviors occurring simultaneously for all PCB congeners present in the homolog group.

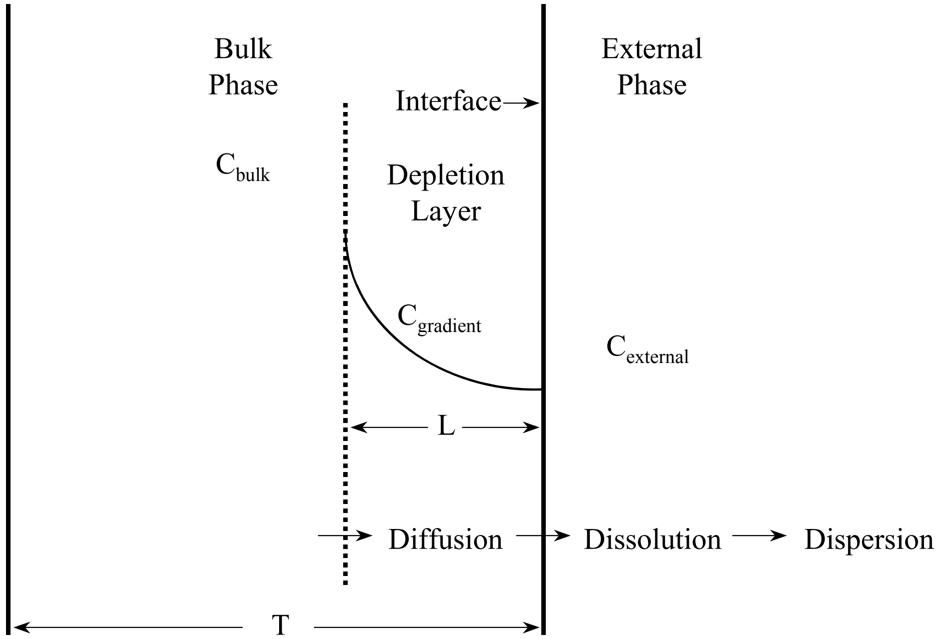


Figure 4. Schematic of release/leaching processes expected for PCBs in shipboard solids. C_{bulk} is the concentration of a PCB congener in the bulk material, $C_{external}$ is the concentration of that PCB congener in the external phase (seawater, organic material, biological material, etc.), T is thickness of the material, L is the PCB congener-specific diffusion path length corresponding to the thickness of the depletion layer at the interface between bulk and external phases, and $C_{gradient}$ is the PCB congener-specific concentration that varies across the diffusion path length.

The processes and parameters associated with leaching from a PCB-containing bulk material into the external phase (Figure 4) consists of three types of migration/release scenarios, (1) simple dissolution of a pure compound, (2) complex dissolution of a mixture of pure comounds, and (3) leaching of a mixture of pure compounds from a solid matrix. The potential dependencies/effects on the release and/or the variables involved are described below for each scenario.

1. **Simple Dissolution of a Pure Compound or Substance (e.g., a single PCB congener).** Although the dissolution of a single PCB congener is not a system that corresponds to anything that was measured in the leach rate study, and probably not even found in the natural environment, it is instructive to consider this case for understanding the dissolution process associated with an Aroclor® (scenario 2). For the dissolution of a single PCB congener PCB_x, the matrix is 100% PCB_x congener and the dissolution process is erosive, i.e., the physical dimensions decrease (represented by thickness, T. There is no diffusion out of the bulk, only dissolution at the interface. L is infinitely small, and $C_{gradient}$ is vertical, representing a sharp concentration decrease at the interface between C_{bulk} and $C_{external}$. Under conditions of high dispersion, $C_{external}$ does not increase, and dissolution is greater than zero, occurring at a rate that depends on its molecular interaction with the external phase (solubility in the external phase). In a system with little or no transport of PCB_x in the external phase away from the interface, $C_{external}$ approaches saturation and dissolution ceases.
2. **Complex Dissolution of a Mixture of Neat Compounds or Substances (e.g., Aroclor® 1254).** For the dissolution of a pure PCB congener (hereafter referred to as PCB_x) in a

neat Aroclor® matrix, only a fraction of that matrix is pure PCB_x. Dissolution of available PCB_x occurs at the interface as for a pure PCB congener described in scenario 1. Similarly, under conditions of high dispersion, $C_{external}$ does not increase, and dissolution is greater than zero, occurring at a rate that depends on its molecular interaction with the external phase (solubility in the external phase). In a system with little or no transport of PCBs in the external phase away from the interface, $C_{external}$ approaches saturation and dissolution ceases, leaving a concentration gradient in the material that may equilibrate again with the bulk over time if dissolution remains at zero. However, for the case of an Aroclor®, a significant difference exists for the PCBs in the dissolution process; availability of PCBs at the interface is now also controlled by diffusion of PCB_x out of the bulk Aroclor®, leading to a gradient in concentration at the interface, $C_{gradient}$. The bulk Aroclor® matrix (composed of the "other" PCB congeners) is also dissolving, thus release of PCB_x is complicated by the depletion layer thickness, L, which is dynamically varying as a function of a diffusive process and a dissolution process. The net result is that as the physical dimension of the bulk decreases because of both of these processes, the thickness, T, at any given moment is dictated by the relative magnitudes of these processes. Finally, to illustrate the complexity further, one should consider the influence of this situation on PCB_x; *i.e.* the process just described is simultaneously occurring for each of as many as 116 of the "other" PCB congeners present in the bulk Aroclor® 1254 matrix.

3. **Leaching of a Mixture of Pure Compounds or Substances from a Solid Matrix (e.g., Aroclor® 1254 release from a Shipboard Solid Matrix).** In the case of pure PCB congener (PCB_x), now leaching from an inert or non-dissolving bulk matrix like a shipboard solid, only a fraction of the bulk matrix is pure PCB_x, similar to the situation for neat Aroclor®. As for scenarios 1 and 2 above, dissolution of available PCB_x occurs at the interface. Similarly, under conditions of high dispersion, $C_{external}$ does not increase, and dissolution is greater than zero, occurring at a rate that depends on its molecular interaction with the external phase (solubility in the external phase). In a system with little or no transport of the external phase away from the interface, $C_{external}$ approaches saturation and dissolution ceases. As in the case for neat Aroclor® above, the availability of PCBs at the interface for dissolution are now also controlled by diffusion of PCB_x out of the bulk matrix, in this case, shipboard solid, resulting in a gradient in concentration at the interface, $C_{gradient}$. The bulk shipboard solid matrix is composed of shipboard solid and the "other" PCB congeners; the latter are also diffusing to the interface and dissolving. However, unlike the Aroclor® in scenario 2 above, the depletion layer thickness, L, is now only increasing as a function of the diffusive process, because the matrix is stable (not dissolving), and T is a constant. Again, the process for leaching PCB_x is also simultaneously occurring for each of as many as 116 of the "other" PCB congeners present in a bulk shipboard solid containing Aroclor® 1254. The release behavior should, of course, be distinct from the neat Aroclor® case above because of the bulk matrix stability, and the fact that a shipboard solid is largely composed of high molecular weight polymers, which, in many cases, contains multiple types of polymers and/or other materials in a composite structure. This structure is very different chemically from a bulk neat Aroclor® matrix, leading to a broad distribution of attenuations (slight to extreme) for different PCB congeners as they migrate through the various bulk matrices. Again, in a system with little or no transport of PCBs in the external phase away from the

interface, C_{external} approaches saturation and dissolution ceases, leaving a concentration gradient in the material that may equilibrate again with the bulk over time if dissolution remains at zero.

The above analysis of PCB diffusion and depletion at the leaching surface of a solid matrix provides a reasonable hypothetical mechanism or conceptual model of PCBs leaching from shipboard solids. The behavior of PCB congeners escaping from a shipboard solid should be similar to the case of PCB congeners escaping from an Aroclor® matrix if diffusion of PCB congeners out of the shipboard solid matrix is significant. Furthermore, the PCB dissolution component also makes an important contribution to the leaching mechanism. Most reported Aroclor® solubility experiments can take weeks to months to allow sufficient time for concentrations for all of the solvated PCB congeners to stabilize or reach steady state conditions. A solubility experiment for a pure molecular substance like a congener might take only hours to stabilize because it is a simple dissolution without a slower diffusion component. In this respect only, Aroclor® dissolution is similar to a pure molecular substance because all of the PCB congeners present in the Aroclor® matrix are also dissolving, though on different timescales (at different rates). Dissolution of Aroclor® can be effectively described as two simultaneous processes: (1) diffusion of pure molecular substances, where there is significant interaction with the Aroclor® as a solid matrix; and (2) dissolution of a mixture of pure molecular substances in an eroding (dissolving) matrix. For such a system, the rate of release will be a function of the expected depletion at the interface, formation of a depleted layer, and subsequent diffusion through that depleted layer. In addition, the thickness of the depletion layer is increasing as a function of diffusion and decreasing as a function of the surface erosion as the matrix itself dissolves at a variable rate. In a depletion-regulated system, the rate of diffusion through the depletion layer at the interface will eventually slow down with time because of the increasing path length/depletion layer thickness and perhaps even a dependence of diffusion coefficient on concentration of PCBs. As a result, the measured rate for such a system should decrease as function of time, regardless of sampling interval. This type of behavior should be further attenuated by the presence/influence of the shipboard solid matrix.

In a closed system, the leaching pathway indicated in Figure 3 and Figure 4 becomes an equilibrium partitioning process between the solid and the seawater leachate. However, equilibrium may not be reached in a natural environment because various 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 natural processes that reduce the PCB concentration in the seawater leachate (Figure 5).

In the presence of these additional processes, PCB saturation is unlikely to occur (except under static, isolated conditions such as in a closed system), and PCB solvation occurs freely or is unsuppressed near the solid surface interface with seawater. As a result, leaching continues unimpeded until PCB depletion of the source material is (theoretically) attained, although, in organic-based solid material matrices, many PCBs would likely be irreversibly bound. Without specific leaching information, fate and transport models generally conservatively 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 generally hold for PCBs in all source matrices because of (1) attenuation processes related to solvent/fluid properties, (2) properties inherent to the source material, and (3) spatial and temporal dependencies of leaching processes. Such processes/properties do not allow the PCBs to leach in their entirety or at a rate commensurate with the timescale required for an observable effect 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. As a consequence, these properties will result in a unique leaching behavior for any PCBs-ISM as a function of time. Accordingly, the leaching experiments were designed to evaluate specific baseline leaching behaviors as a function of time for different representative solid matrices of interest and under laboratory conditions designed to simulate the leaching of PCBs into natural seawater environments. This approach included controlling or removing the additional processes (Figure 5) from the laboratory simulation so that the experimental focus was on determining the rate of leaching corresponding to an unsuppressed leaching pathway (Figure 3). Thus, transport away from the solid surface and other processes that would reduce the PCB concentration in the seawater near the solid surface could be *simulated* by a dynamic leaching and sampling design that will be described later.

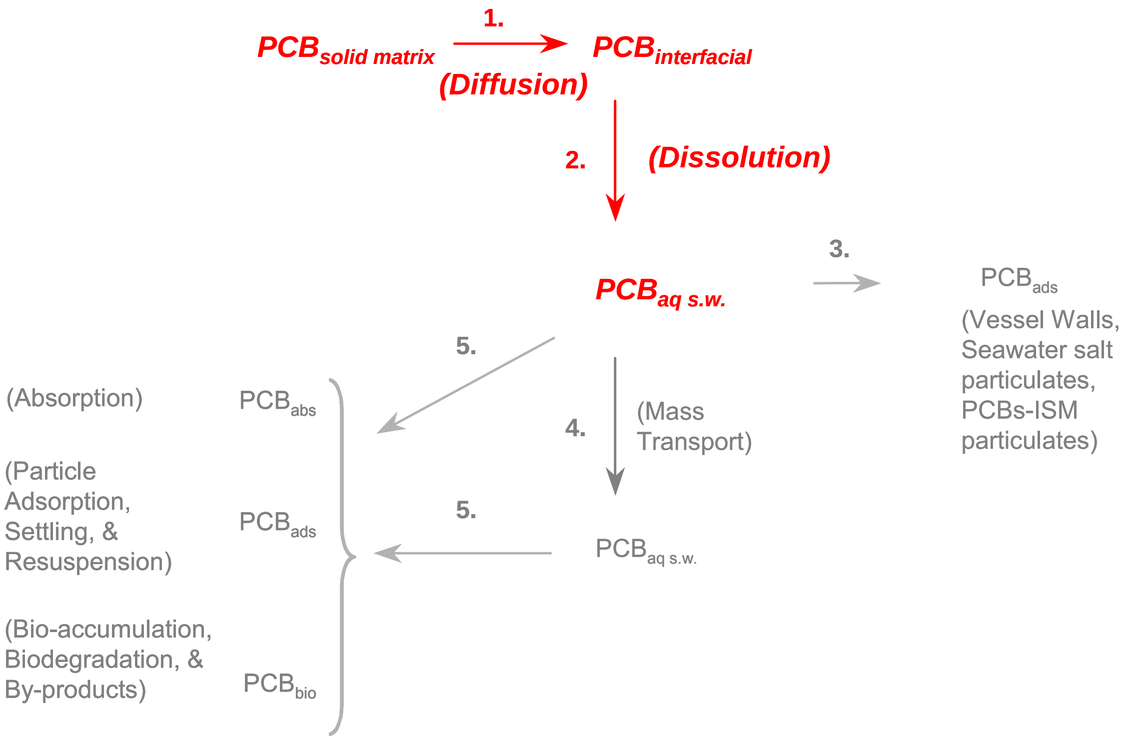


Figure 5. Primary PCB leaching process in red bold italics, (1) and (2), as described in Figure 4, with subsequent transport/depletion mechanisms for PCBs in seawater, PCB(aq s.w.). The experimental design removes or minimizes the potential processes represented by (3), while processes represented by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

A realistic leaching experimental design must consider parameters that 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); the molecular structure of each PCB congener; and differential PCB congener solubilities (in the PCBs-ISM matrix versus in seawater). For example, an industrial-grade PCB mixture, Aroclor® 1254, occasionally found in shipboard solid materials, is principally composed of molecules with 4-6 chloro-substituents, containing up to 116 different congeners (Alford-Stevens, 1986; Alford-Stevens et al., 1986). Some of these different congeners will behave in essentially the same manner, while others will exhibit leaching behavior differences related to, but not limited to, variation in properties such as solubility, differential interactions with the solid matrix, dynamic leaching surface area of the solid, PCB solid–liquid phase transition temperature, etc. Any one or more of these properties can potentially impact PCB transport, both within the material (diffusion) and subsequently through the PCBs-ISM/seawater interface (solubility-driven behavior), and must be evaluated/quantified for appropriate inclusion before the collection and interpretation of empirical leaching data. By identifying and incorporating these key parameters into the experimental design, well-defined empirical leaching data can be collected to develop leach-rates for different PCBs-ISM tested under controlled or systematically varied chemical/physical leaching conditions.

1.6. CONCEPTUAL MODEL FOR SHIPBOARD PCB LEACHING

By simulating the leaching conditions in the laboratory as they are likely to exist on board a sunken vessel, the leaching of PCBs from solid matrices, inclusive of inherent material properties that control the release process, was evaluated in this study. The experiments were designed (Figure 6) to measure the empirical leaching behavior of PCBs-ISM that would occur within a shipboard compartment on board a sunken ship (Figure 7), as the PCBs-ISM is exposed to seawater as a function of time. For this study, PCB release was evaluated for seawater flowing through open compartment(s) such as shown in Figure 7 (a) and (c) under 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.

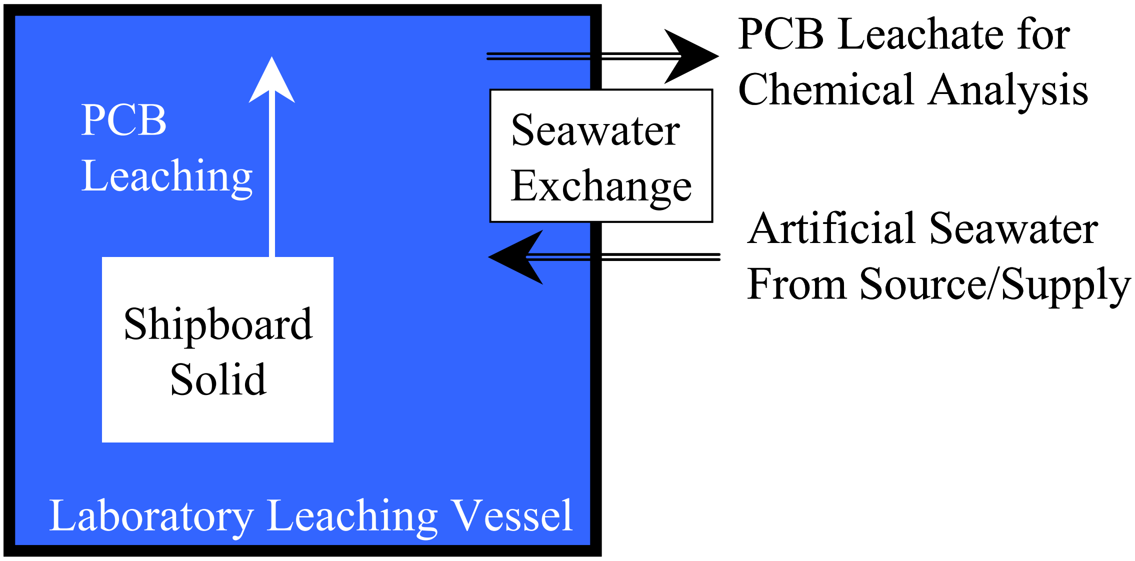
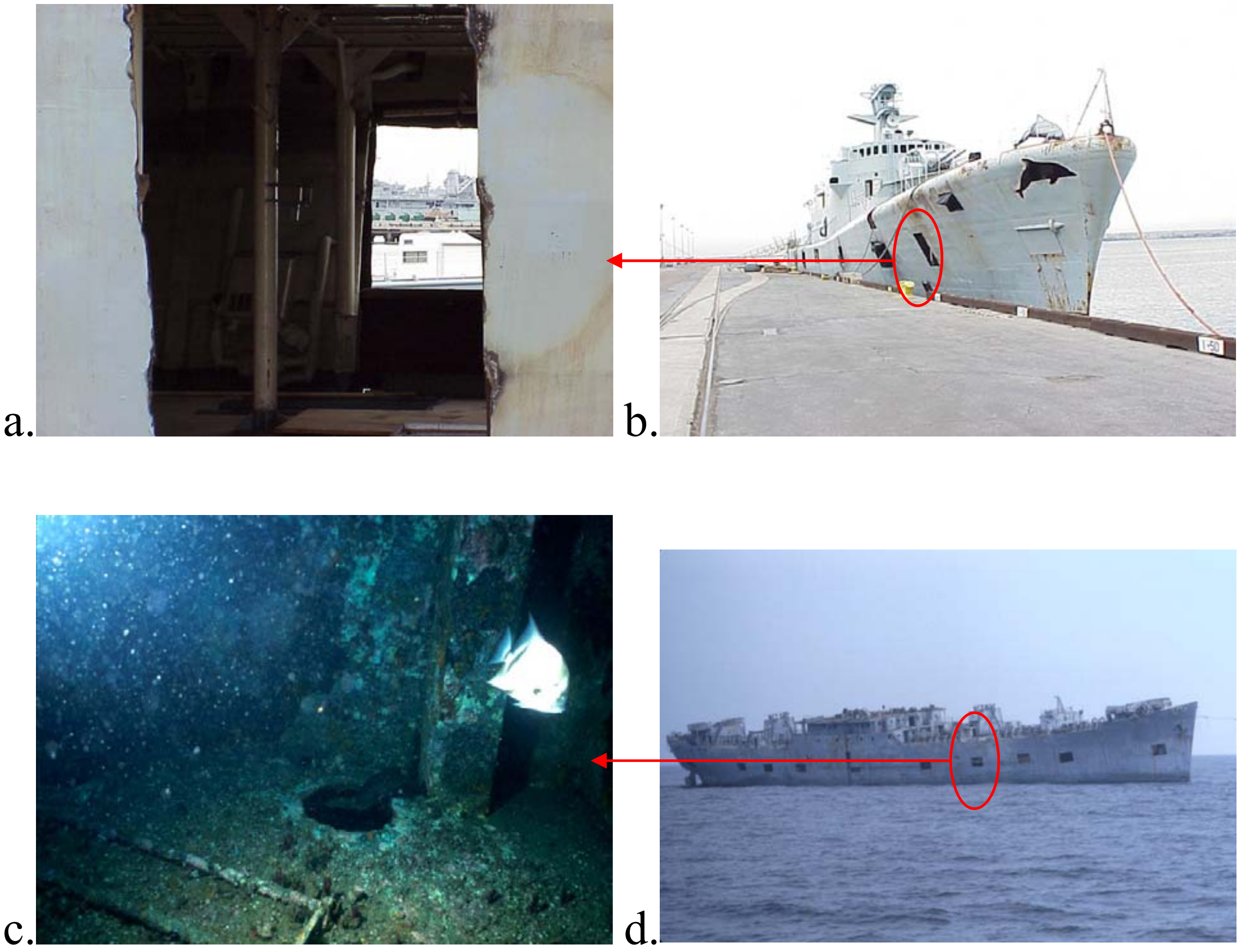


Figure 6. Conceptual schematic for simulating the PCB leaching process expected to occur for PCBs-ISM inside of a compartment onboard a sunken vessel similar to that shown in Figure 7.



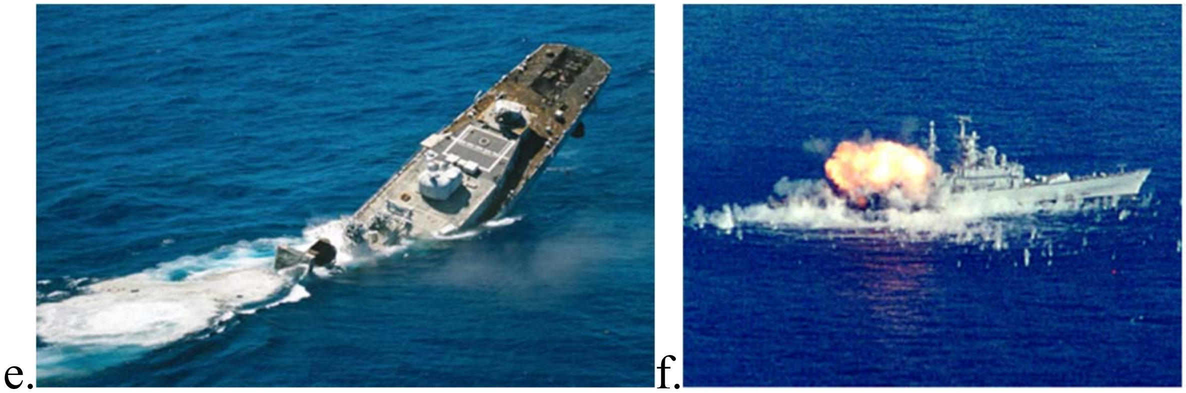


Figure 7. Photos of vessel compartments on board vessels prepared as shown in (b) and (d) and sunk in shallow water as artificial reefs or targets in exercises. Photos (a) and (b) are of ex-Yukon, a Canadian vessel, prepared for use as an Artificial Reef in San Diego coastal waters. Photo (c) is an underwater compartment on ex-Vermillion, a U.S. Navy vessel sunk off the coast of South Carolina in 1988 as an Artificial Reef, and (d) is ex-Vermillion after being prepared and towed to the site. Photos (a) and (b) are Marine Environment Support Office photos and photos (c) and (d) are courtesy of South Carolina Department of Natural Resources, and (e) Ex-Buchanan (DDG 14) sunk in June 2000, and (f) Ex-Richmond K. Turner (CG 20) sunk in August 1998, are U.S. Navy SINKEX photos downloaded in 2001 from http://www.chinfo.navy.mil/navpalib/ships/destroyers/decoms/.

In a natural leaching scenario, some materials will possibly degrade and/or eventually lose their structural integrity on exposure to seawater over a very long period of time. It is likely that degraded PCBs-ISM or smaller individual particles will continue to leach PCBs similarly to the intact solid; however, such effects would tend to spread out over very long periods of time and result in only a slight influence, if any, on long-term rates because the total surface area increase would not be instantaneous. The physical deterioration of solid material results in natural surface area increases that cannot keep up with the PCB release rate, as these two processes are on significantly different timescales, and the degraded surface would be depleted by the time particulates would be produced from that surface. This process would be confounded if the surfaces become encrusted or covered by marine debris, affecting particulate production and/or reducing the surface area exposed to leaching.

In the laboratory, the solid matrix must still be allowed to undergo any physical or chemical degradation caused by 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 (1) simulate a shipboard solid remaining in the relatively protected environment inside a vessel compartment, (2) avoid artificially degrading or compromising the shipboard solid structural/physical integrity by agitation needed to simulate seawater current flow, and (3) minimize the loss of and interferences from very small, PCB-containing shipboard solid particulates formed as artifacts of the shipboard solid sampling, leachate sampling during leaching experimentss, and during 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 that freely allows seawater (and solvated PCBs) transport through the pores, but does not allow the transport of shipboard solid particulate matter. Caging was a key component of the experimental design that leads to a true evaluation of the release for only solvated PCBs from the shipboard solid matrix. Caging the shipboard solid simulated a realistic leaching scenario because (1) the material remains localized except for natural structural degradation caused by seawater exposure, (2) the naturally occurring surface area available for leaching is incorporated, and (3) leaching artifacts (e.g., through damage introduced by solid sampling) that might occur by disturbing this natural structural degradation and particle production and release are minimized. Subsection 2.4 provides a more detailed description of this conceptual model as it is applied in the laboratory.

2. EXPERIMENTAL DETAILS

The experimental approach was conducted in several phases with the following goals, as discussed in detail below:

- Evaluation of experimental leaching parameters and protocols
- Field collection of PCBs-ISM from Navy ships
- Laboratory subsampling of field collected PCBs-ISM
- Laboratory leaching of PCBs-ISM under deep ocean conditions
- Leachate collection and analysis of PCBs

2.1. EVALUATION OF EXPERIMENTAL LEACHING PARAMETERS AND PROTOCOLS

The following summary describes the possible experimental parameters and variables, and assesses their potential impact on the leaching experiments (Table 1). This evaluation generally follows an approach similar to the evaluation reported for development of Toxicity Characteristic Leaching Procedure (TCLP) protocols (U.S. Environmental Protection Agency, 1997) and methodologies (U.S. Environmental Protection Agency, 1991a).

Table 1. Experimental parameters of possible concern for leaching studies. Variables indicated as "N/A" are not applicable to this study because they were 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	Surface physics/ Electrostatics	Solvent access and flow control	Experimental variable	Not controlled
Solid matrix	Matrix heterogeneity	Localized morphological/chem 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

Table 1. Experimental parameters of possible concern for leaching studies. (cont)

Phase or Process	Property or Parameter	Effect(s)	Classification	How Treated or Controlled
Solid matrix	Photo/Biodegradability	Solid matrix changes	CONSTANT-Controlled	Degradative biological organisms unlikely, 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 and 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

Table 1. Experimental parameters of possible concern for leaching studies. (cont)

Phase or Process	Property or Parameter	Effect(s)	Classification	How Treated or Controlled
Solvent	Chemical composition	PCB transport and leachability; matrix wetting	CONSTANT-Controlled	ASTM artificial seawater
Solvent	Ionic concentration (salinity)	PCB transport and leachability; matrix wetting	CONSTANT-Controlled	ASTM artificial seawater
Solvent	Lipophilicity/Contaminants, Dissolved organic matter	Leachability enhancement, PCB partitioning and transport	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

Table 1. Experimental parameters of possible concern for leaching studies. (cont)

Phase or Process	Property or Parameter	Effect(s)	Classification	How Treated or Controlled
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 (deep ocean conditions)	Matrix integrity; PCB solubility	Experimental variable	Controlled for, nominal pressure variance of 10-40 bar during filing and sampling operations.
Temporal/Spatial	Pressure dependence (shallow water conditions)	Matrix integrity; PCB solubility	Experimental variable	Not controlled, minor 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

Table 1. Experimental parameters of possible concern for leaching studies. (cont)

Phase or Process	Property or Parameter	Effect(s)	Classification	How Treated or Controlled
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

The primary parameters relevant to ocean depth in leaching studies are temperature and hydrostatic pressure. The effect of temperature were reported as part of a previous study (George et al., 2006). The main objective of the studies described in this report is experiments performed at low temperature and varied hydrostatic pressure. Other experimental parameters in Table 1 were measured or controlled. In some cases, a parameter was considered part of the solid specific leaching mechanism, was not present, or its contribution was minimized by the experimental design altogether.

2.2. FIELD COLLECTION OF PCBs IN SOLID MATERIALS (PCBs-ISM)

Three field saple collection events occurred on board USN vessels and submarines between June and December 1999 to collect PCBs-ISM from components on existent decommissioned vessels and submarines available in the inactive fleet. The goal of the PCBs-ISM -sampling effort was to locate and collect sufficient quantities of PCBs-ISM for each class of shipboard solid to allow subsampling in the laboratory and subsequent leaching of those subsamples under the experimental leaching conditions. The field sampling proceeded by performing the following tasks:

- Analyzing PCB levels found in target materials from the Inactive Fleet PCB Survey Program historical database and selecting the target materials to collect
- Selecting ships to sample with target materials thought to be onboard
- Following a specific collection method
- Describing the collected materials

2.2.1. PCBs-ISM Selection

The sampling effort used the most current data for PCB concentrations in PCBs-ISM from Naval Sea System Command's (NAVSEA) PCBs-ISM survey program (Naval Sea Systems Command, 1995) to identify and locate materials for the leach rate study. The types of materials and levels of PCBs measured in shipboard solids sampled onboard U.S. Navy vessels and included in the Inactive Fleet PCB Survey Program database are summarized in Table 2. These PCBs-ISM were selected as representative solids for the leach rate study based on analysis of concentration data collected as part of the NAVSEA ship survey program, and the probability that PCBs were present as a functional component of the solid (imparting some specific beneficial property to the solid matrix). This study did not focus on materials likely to have acquired PCBs as contamination. Note that these historical concentration data in Table 2, like many other historical PCB data, were typically reported as total Aroclor® rather than by individual Aroclor®, congeners, or homologs. This type of data made it difficult to quantify Aroclor® distributions, even though the type of Aroclor® was at times qualitatively identified as present in the material.

Table 2. Summary statistics compiled from the NAVSEA Inactive Fleet PCB Survey Program, February 2001.[8] Some Aroclors® had been individually quantified in more recent analyses, and are included, but most historical data available at the time of the Leach Rate Study (1999–2002) were reported as total Aroclor®. The identity of Aroclors® was usually reported only qualitatively. The construction date of vessels, which these data represent, range from the late 1940s through the early 1990s, with PCB sampling performed from the late 1980s through the late 1990s.

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	
Foam Rubber/ Ensolite® (FRE)	Detections										642	(only 1254 noted)
	Mean										1523.9	
	St Dev										3336.3	

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[8] Data provided by John J. McMullen Associates, Navy Inactive Fleet Database, February 2001.

Table 2. Summary statistics compiled from the NAVSEA Inactive Fleet PCB Survey Program, February 2001. (cont)

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										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	

2.2.2. Vessel Selection

Before a field-sampling event, the most recent shipyard PCBs-ISM survey was obtained for each inactive vessel at a shipyard. In most cases, the more recent the report, the more likely (but not certain) the remedial action[9] had not yet begun or was not yet completed. PCBs-ISM samples at or above 500-ppm PCBs were required to realistically expect a detectable level of leached PCBs as a function of time on the scale dictated by the leaching experimental design. Locating and sampling PCB-ISM with such high concentrations were a unique challenge for the PCBs-ISM-sampling effort, resulting in a “race” to collect the shipboard samples before 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 the prior sampling location might be marked (by shipyard personnel) on a vessel. For example, on-board ships slated for use as a SINKEX vessel, a potential PCBs-ISM sampling area (shipboard compartment) had frequently already been surveyed for PCBs, remediated, and and all debris or floatable materials removed, including, most notably, any previous sampling tags.

2.2.3. PCBs-ISM Sample Collection

Sample collection methods depended on the type of shipboard solid sample and amount available. If an intact PCBs-ISM vessel component could be collected, it was removed and placed in clean plastic sample collection bags for later subsampling 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 by using NAVSEA’s PCBs-ISM survey program methodologies (Naval Sea Systems Command, 1995). This method included using pre-cleaned glass sample vials/containers for the sample, and sample-dedicated utility blades, pre-cleaned with hexane prior to sample collection. Sample naming conventions typically followed shipyard sample-naming conventions, which reflected the type of sample and where the sample was located onboard a vessel, using such information as ship identifier, deck level, frame number, compartment name, and/or a physical three-dimensional location/description within a given compartment.

2.2.4. PCBs-ISM Sample Description

Table 3 provides a summary and description of the shipboard solid samples colected and used in the leach rate study. A specific brief description of each PCBs-ISM sample collected is included in the subsections that follow. One field sample of each shipboard solid was selected and then subsampled for leaching studies.

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[9] This remediation policy is based on the power industry standard and regulatory limit of 50 ppm used to classify bulk PCB solid waste, as adopted by various regulatory programs such as the USEPA Toxic Substances Control Act program. PCBs-ISM found on board a decommissioned vessel at or above this concentration were routinely removed and disposed of as hazardous material.

Table 3. Descriptive summary of shipboard solid (PCBs-ISM) samples used in the leach rate studies.

PCSs-ISM Description	PCB-LRS Abbreviation	Representative PCB-LRS Sample ID	Reported Shipyard Analysis	Representative Solid Analysis (PCB-LRS)	Representative Leached Solid Pre-leaching Concentration	Comments
				By best-fit of PCB Congener Fingerprint	By sum of homologs	
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)	117,400 ppm	Intact—protruding from between flange heads, painted
Foam Rubber (Ensolite®)	FRE	PSNS-647-165-9A	5,100-ppm (A1254)	7,100-ppm (A1254), 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 (A1254), 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) (NavSource Online Destroyer Photo Archive. 2006a). 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. (Throughout this report, this type of sampled gasket is called 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 150,000 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. Throughout this report, the felt gasket found between the flange heads is called the "inner" felt gasket. We expected it 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 Subsection 2.3. Both 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) (NavSource Online Destroyer Photo Archive. 2006a) and an ex-Barracks Ship (APL 34) (NavSource Online Destroyer Photo Archive. 2006b). 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/reuse). 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 1,800 ppm, as indicated by the shipyard analysis. This intact cable sample was subsampled in the laboratory later, 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) (NavSource Online Destroyer Photo Archive. 2006a). 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, which shipyard surveys indicated as 570-ppm Aroclor® 1260. The paint sample was collected by scraping the paint with a new, dedicated, pre-cleaned utility knife and capturing the paint chips into a clean glass container as the paint flaked off of the underlying substrate. Unlike intact paint on a substrate surface, the sampling procdure resulted in paint particles as field samples, and subsequent homogenized laboratory subsamples for leaching experiments.

Bulkhead Insulation. Sampling Location: Norfolk Naval Shipyard, 15 June 1999, ex-Dixon (AS 37) (NavSource Online Destroyer Photo Archive. 2006a). A sample was collected into solvent pre-cleaned sample containers by using a dedicated solvent pre-cleaned utility knife similar to shipyard survey methods (Naval Sea Systems Command, 1995). This yellow man-made vitreous fiber (MMVF) 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 found the insulation sample to contain 2,000-ppm Aroclor® 1254. The insulation sample (not the pressboard backing/lagging) was subsampled for leaching per protocols described in Subsection 2.3.

Black Rubber. Sampling Location: Puget Sound Naval Shipyard, 29 July 1999, ex-Nathaniel Greene (SSBN 636) (NavSource Online Destroyer Photo Archive. 2006c). This PCBs-ISM was collected as a nearly intact shock mount on an equipment bracket. The sample was an unpainted, soft, rubbery polymer material with no apparent oil or grease present. Shipyard survey analysis indicated that it contained 500 ppm. It was subsampled for leaching studies in the laboratory per protocols described in Subsection 2.3.

Foam Rubber. Sampling Location: Puget Sound Naval Shipyard, 29 July 1999, ex-Pogy (SSN 647), a Sturgeon Class Attack Submarine (NavSource Online Destroyer Photo Archive. 2006d) and ex-Nathaniel Greene (SSBN 636) (NavSource Online Destroyer Photo Archive. 2006c). Several samples of a foam rubber, also called Ensolite®, were collected. These samples are probably polyvinyl chloride (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 probably present for head protection and to provide anti-sweat properties. The shipyard survey analysis indicated 5,100 ppm for this material, which was later subsampled for leaching studies in the laboratory per the protocols described in Subsection 2.3.

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 complex PCB mixtures, neat Aroclor® 1254, and neat 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 neat materials. These Aroclors® represent a PCB-ISM sample not influenced by a shipboard solid matrix. The neat 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, although a maximum cohesive-type (PCB–PCB) interaction was present rather than the minimal cohesive interaction expected in the shipboard solids because of low PCB concentrations. The most distinctive differences between neat Aroclors® and shipboard solids are related to matrix characteristics, i.e., Aroclor® 1254 and 1268 are mobile, dynamic matrices that can themselves dissolve away, very much unlike a shipboard solid matrix. This difference is significant and, as a result, using Aroclor® results are only valid in understanding dissolution properties that may contribute toward observed leaching behaviors. A possible exception is that results from Aroclor® 1254 and 1268 experiments can perhaps be used as reasonable proxies for Aroclor® 1254 or 1268 containing matrices that are highly mobile, such as oil film and semi-solid greases.

2.3. LABORATORY SUBSAMPLING OF SHIPBOARD SOLID MATERIALS

Field-collected shipboard solid 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 (1) leaching under different laboratory-simulated shallow/estuarine or deep-ocean conditions, and (2) chemical analysis of the solid to confirm that the PCB concentration was similar to that reported in the shipyard survey analysis. These latter representative solid concentrations are discussed in Subsection 3.1. 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.

In three cases, the collected shipboard solid sample was an assembly or composite that first required disassembly before subsampling the PCBs-ISM portion:

- 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, in areas where the paint had bled through the armored shielding onto the cable itself, small amounts of residual paint were present.
- Bulkhead insulation was subsampled for leaching without the previously described pressboard backing.

Except for paint particles and analytical Aroclor® controls, each subsample was prepared on a tray that had been twice-cleaned with high-performance liquid chromatography (HPLC)-grade methanol and lined with a large sample-specific laboratory wiper (low-lint or cleanroom Kimwipe®). The PCBs-ISM subsample was collected each time with a new, stainless-steel dissection blade, twice-cleaned with HPLC-grade methanol before use. For subsamples of EC, the final operation required using wire cutters to sever the inner copper core once the dissection blade cut through the outer layers of material. The wire cutters were pre-cleaned with HPLC-grade methanol before 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 identification (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 identical manner as the shipboard solid subsamples.

2.4. LABORATORY LEACHING OF PCBs-ISM

2.4.1. Saturation Avoidance

A primary goal of the experimental design was to avoid a saturation condition in the leaching vessel that could result in suppression of the dissolution component of the leaching process. This was achieved by performing the following:

- Gentle mixing of leachate in the leaching vessel to simulate constant flow and avoid saturation at the shipboard solid–seawater interface.

- Seawater exchange/replacement of total or known partial volume of seawater leachate with a known amount of fresh, clean seawater leachate prior to saturation. Removal of an aliquot of leachate and replacing with fresh seawater during sampling effectively provided a dilution of the leachate prior to reaching saturation.

In the presence of 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. The seawater exchange effectively simulated advective transport of PCBs in the leachate away from the solid surface. When a leachate exchange was performed, the leaching was effectively restarted at near zero or a diluted PCB concentration in the seawater leachate after each sampling event. In the case of leaching experiments under high hydrostatic pressure, the seawater leachate was diluted ~2-fold during the leachate exchange (~1-L leachate removal), to allow the sample to remain submerged underwater at the leaching pressure conditions during sampling.

2.4.2. Artificial Degradation/Disintegration Avoidance

A second issue of concern centered on the possibility that natural disintegration of the shipboard solid might be artificially enhanced because of stirring in the leaching vessel. Disintegration during the leaching experiment would produce particulates of PCBs-ISM material that could then contribute towards false positives as noted in solubility studies previously performed on similar (acoustic felt) samples (NOSC, 1989). In that study, results were confounded by felt material disintegration; the study reported that PCB-rich particulates significantly skewed the analytical chemical results and noted that the mixing process significantly altered the physical integrity of the tested samples. 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 during the experiments, resulting in PCB extraction and chemical analysis difficulties.

In the present study, steps were taken to ensure that matrix integrity would be maximized. The experimental design incorporated a stainless steel (SS) cage to minimize physical damage to the sample during the experiment and to localize any particulates that might be produced within that cage. The cage consisted of a SS mesh covering, nominally 1/8-inch mesh size, pre-cleaned with hexane and dried before use (Figure 8). Within the SS cage, a small pore size (nominally 1-micron), binder-free, pre-cleaned, glass-fiber filter was wrapped around the shipboard solid and minimized the transport of any PCBs-ISM particulate matter into the leachate, while simultaneously 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 Subsection 2.6.

The increased leaching vessel surface area introduced by these materials was considered a portion of the total leaching experimental surface area. The additional surface area introduced by the SS cage and fiber filter would probably adsorb a small amount of PCBs until its surfaces were passivated (saturated or inert to further adsorption). This expectation is an experimental uncertainty, but 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 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 were still allowed to occur, but particulates remained localized within the cage, and the observed PCB concentration in the leachate reflects increases or decreases in surface area and/or PCB dissolution caused by such processes. These effects, if they exist, are considered part of the shipboard-solid-specific leaching behavior.

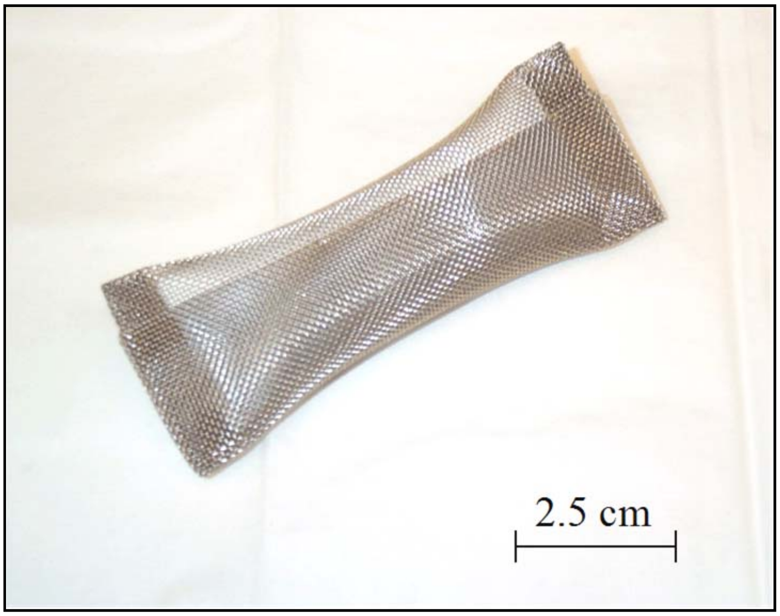


Figure 8. Shipboard solid sample cage used to localize shipboard solid particulates in the leaching vessel, as described above. An identical cage was used for negative analytical controls (procedural blanks without shipboard solid) and positive analytical controls (neat Aroclor® compounds) as described below.

2.4.3. Positive and Negative Leaching Controls

Samples consisting solely of the stainless-steel cage and glass-fiber filter barrier described above were prepared and treated under each of the different leaching experimental conditions to control for system contamination. These samples, called 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 positive analytical controls for A1254 and A1268 solvation capacity, leaching procedural blanks are considered 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. The negative control also provided a QA/QC performance measure for experimental contamination.

2.5. ARTIFICIAL SEAWATER LEACHATE PREPARATION

Leaching of PCBs-ISM was performed in artificial seawater (ASW), rather than fresh or reconstituted natural seawater, to maintain consistent exposure conditions. This ASW leachate was prepared using an American Society for Testing and Materials (ASTM) standard (ASTM, 1992) per the standard operating procedure (SOP) included in Appendix B. This ASW is prepared from pure ACS reagent-grade inorganic salts to provide a constitutional equivalent to typical seawater, with a salinity value of 34.0 ±0.5 psu (34,000 ±500 ppm), and a pH of 8.0 ±0.2. Natural and reconstituted seawater can contain dissolved organics and particulate organic matter, with the latter present at levels significant enough to remove trace amounts of PCBs through sorptive processes. Using ASTM ASW avoided possible processes that would interfere in the leaching process and provided assurance that all materials were leached under the same exposure conditions. Additionally, unlike reconstituted ASW, higher levels of heavy metals in ASTM ASW source salts were sufficient to inhibit biological growth (not observed at any time in ASW leachate throughout), thus minimizing significant biological pathways to PCB/leachate loss in the experiment.

ASW was prepared in 20-L 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 through laboratory operations during ASW preparation. When a new ASW preparation (batch) was completed, it was 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, when another seawater batch was prepared. New seawater batches were prepared approximately every 4 to 6 weeks throughout the leaching study. In this manner, the ASW remained relatively fresh over time, with less possibility of degradation effects such as salt precipitation or losses in buffering capacity (pH instability).

2.6. GENERAL LEACHING EXPERIMENT DESIGN AND METHODOLOGY

The approach to performing the leaching experiments in this study emphasized achieving and maintaining simulated leaching conditions related to a deep-ocean scenario, while simultaneously performing analytical sampling of PCB leachate as a function of time. The sampling design is also useful for 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 (Subsection 2.7), while simultaneously 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 remove PCBs (by occlusion or sorption) from the ASW leachate, thus artificially decreasing the PCB concentration in the leachate. If allowed to form, salt precipitates could also adhere to or become trapped on the PCBs-ISM filter/cage, effectively blocking the leaching pathway, and contributing toward an artificially decreased leachate PCB concentration.

2.6.1. Sampling Intervals

Hypothetically, leaching might occur as an initial pulse or fast short-term release of PCBs followed by a slower long-term release, with the maximum leach rate observed somewhere between or perhaps even as the initially observed rate itself. Rapid PCB release requires sampling more often (short sampling interval) early in a leaching experiment, and perhaps less often (longer sampling interval) as leaching begins to slow down later in the experiment. Thus, sampling intervals varied for each leaching experiment depending on individual PCB-ISM behaviors.

The generic sampling approach for a leaching series included following an approximate sampling schedule similar to the following:

- Collecting a sample immediately after submerging the shipboard solid (t = 0) to characterize any initial rapid PCB release (t ~ minutes, initial rinse)
- Continued sampling on a progressive escalating sampling interval at t ~ 1 hour, 2 hours, 4 hours, and 8 hours throughout the first day
- Sampling once on day 2 (t ~ 24 hrs)
- Sampling once on day 4 (t ~ 96 hrs)
- Sampling once on day 7 during the first week (t ~ 7 days)
- Sampling once on day 14 (t ~ 14 days)
- Once on day 28 during the first month (t ~ 28 days)
- Continued sampling on a longer sampling interval, approximately once every 6 to 8 weeks over many months (*e.g.* t ~ 75 days, 135 days, 195 days, …N days)
- Final sample collection at experiment termination. (*e.g.*, t = N + 60–90 days)

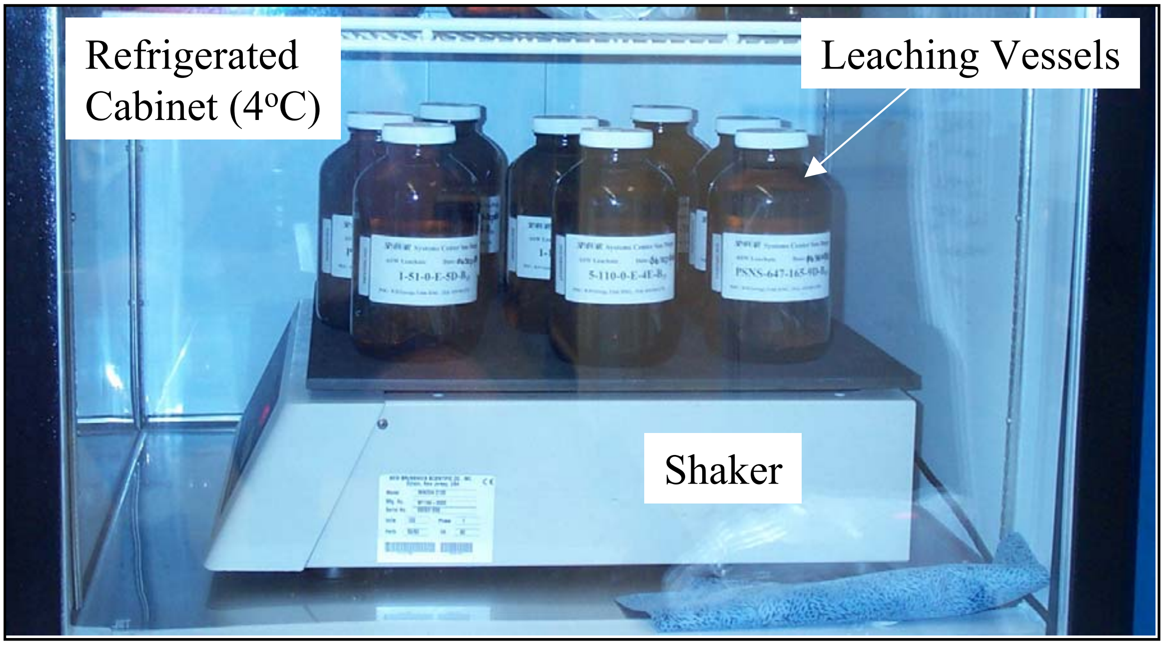
For each sample collected during ambient pressure leaching experiments, the entire leaching volume (~1 L) was collected from the leaching vessel for conventional chemical analysis. The leaching vessel was then replenished with clean ASW, effectively restarting the leaching at minimal or zero PCB concentration in the leaching vessel. Additionally, to avoid time-dependent adsorption issues (Sullivan, Atlas, and Giam, 1981) on the glass surfaces of the ambient pressure leaching vessel, ambient pressure leaching vessels were replaced once weekly with new/fresh, pre-cleaned amber glass leaching vessels. While most of these used amber glass leaching vessels were disposed of over the course of an experiment, a selection of them that were exposed to high-PCB leachate concentrations were analyzed to characterize any possible (but unlikely) PCB adsorption on the leaching vessel walls.

In the case of high pressure leaching experiments, leaching vessels were not composed of glass, but high grade surgical stainless steel (SS), which were precleaned prior to use with supercritical fluid carbon dioxide (SC-CO_2) and analytical solvent to minimize the availability of adsorption nucleation sites. Because these vessels were permanent, unlike disposable glass ambient pressure vessels, analyses of the internal surfaces of SS pressure vessels were performed at the conclusion of the leaching study to evauate any possible long-term PCB adsorption during the course of any given experiment.

2.6.2. Experimental Conditions

Low-pressure (ambient, ~1 bar) leaching conditions were simulated in this study by immersing caged shipboard solids in ASW, inside 950-mL pre-cleaned amber glass leaching vessels with Teflon®-lined caps, and placing the leaching vessels in a 4 °C constant temperature bath (Figure 9a) to maintain a constant deep ocean leaching temperature selected to represent an average temperature of the deep-ocean (Brown et al., 1995). The leaching vessels were labeled and weighed before placing the caged sample in them and before filling with a known mass of ASW leachate. Ambient pressure (~1 bar) was chosen for experimental simplicity as a low-pressure extreme. Results from a concurrent study (George et al., 2006) indicate that a temperature increase at ambient pressure (see leaching results summarized in this report in Sections 4 and 5) has a very significant effect on the leaching process.

A laboratory bench-top shaker operating at 45 rpm supplied adequate gentle mixing to simulate dynamic flow around the shipboard solids under test. The low-temperature/ambient pressure experiments were conducted in a refrigerated forced air cabinet (Figure 9a) to maintain a constant 4 °C temperature. This system maintained a constant temperature throughout the leaching experiments (1 to 2 years). The leaching data at warmer temperatures, reported previously (George et al., 2006), were collected in a similar manner on a benchtop shaker, except leaching vessels were placed in a water bath maintained at 25 °C.



a)

b) 

Figure 9. The apparatus for maintaining constant temperature for ambient pressure leaching at 4 °C (a) and the apparatus used for leaching studies simulating deep-ocean conditions of high pressure (~300 bar) and 4 °C (b).

High pressure (deep) leaching conditions were simulated in this study by immersing caged shipboard solids in ASW, inside the high pressure leaching vessels (Figure 9b). This system uses pressure-sealed magnetic mixers to affect gentle mixing and aluminum coolant filled jacketed surgical stainless steel pressure vessels to maintain constant temperature and pressure over the leaching experimental timeframe. The volume of these vessels was 2 L, and the caps used PTFE Teflon® seals to maintain hgh pressure conditions. Each pressure vessel (P-V) was maintained at 4 °C through use of external chillers that circulated coolant fluid through the aluminum cooling jackets on each P-V. Sampling was performed while maintaining the P-Vs at constant pressure above the minimum pressure threshold (300 bar) by pumping inert gas into the top of the P-V during removal of ASW leachate sample from the bottom of the P-V. Samples were collected into 950 mL pre-cleaned amber glass sample bottles with Teflon®-lined caps. In all cases, the amount of ASW leachate removed was weighed for tracking the reduction in volume inside the P-V. Subsequent to a sampling event, the P-V was then replenished with clean fresh ASW, again tracking the amount of ASW pumped into the system by weight. This replenished ASW mass added to the P-V, along with the analytical PCB concentrations in the leachate sample removed was used to calculate the dilution that occurred during the replenishment process, which was used as the starting concentration for the next leaching interval. This sampling process was repeated throughout the leaching experiment timeframe for each of the solids tested. A representative P-V initial pressurization is shown graphically in Figure 10 below, showing the sampling (processing) window, and other related descriptive parameters.

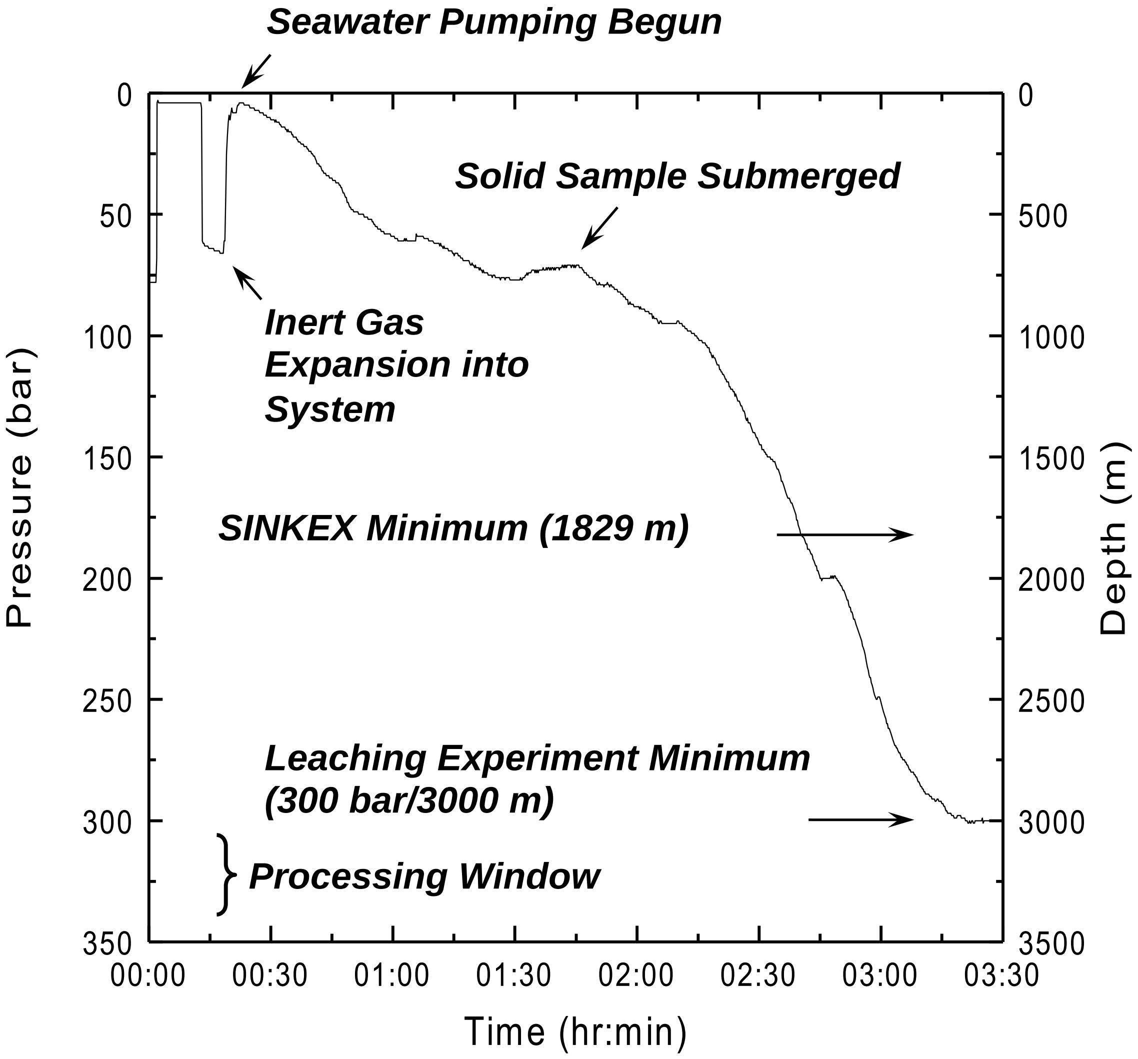


Figure 10. Representative initial pressurization plot of pressure vs time for a P-V leaching experiment. Temperature was held constant at 4 ^{o}C.

Conditions were similar for each of the solids tested in all low temperature/ambient pressure (4 °C/1 bar), low temperature/high pressure (4 °C/300 bar), and in previously reported (George et al., 2006) warm temperature/ambient pressure (25 °C/1 bar) leaching studies. Experimental variables such as pressure, temperature, salinity, and pH were controlled or maintained at constant values. Sample-specific variables were measured (e.g., shipboard solid mass, sample size, leachate volumes, etc.) to use for leaching data reduction and analysis.

Sampling methods and protocols recommended by U.S. Environmental Protection Agency (US EPA) were followed 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 Poly Tetra Fluoro Ethylene (PTFE) (Teflon®) in that order of preference, were allowed to come into contact with ASW leachate containing PCBs. This is based on published literature concerning PCB loss and degree of reversibility for common laboratory polymers/plastics (Cseh, Sanschagrin, Hawari, and Samson, 1989). The PCB leachate was extracted along with the glass sample collection bottles when the analytical chemistry commenced for that sample.

2.7. ANALYTICAL CHEMISTRY OF PCBs

2.7.1. PCB Screening Analyses

When necessary, during each sampling interval, screening-level PCB analyses were performed using commercial immunoassay techniques (measured as Aroclor® 1254, modification of EPA Method 4020 (U.S. Environmental Protection Agency, 1997b). 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 (In, Guerrero, Lane, and George, 2001a). These screening analyses were performed on aliquots of small-volume (2-mL) ASW leachate samples to aid in defining primary sampling intervals in real time (In et al., 2001b).

2.7.2. Conventional PCB Analyses

For each sampling interval, conventional high-throughput analyses were performed under a performance-based contract with Arthur D. Little, Inc. (ADL), Cambridge MA. PCBs were quantified in seawater and in leached solids using gas chromatography (GC)/mass spectrometry (MS) in selected ion monitoring (SIM) mode (EPA Method 680), entitled "Test Methods for Determination of Pesticides and PCBs in Water and Soils/Sediment by Gas Chromatography-Mass Spectroscopy" (U.S. Environmental Protection Agency, 1985). GC-MS/SIM analyses were performed using SOP ADL-2845, a modification of Method 680, entitled "PCB Congeners, Homologs, and Aroclors® by Gas Chromatography/Mass Spectrometry in the Selected Ion Monitoring Mode." This method uses a DB5 Column, under the following conditions, as documented in the 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 electron capture detector (ECD). The GC/MS was first tuned with perfluoro-tributyl-amine (PFTBA = $n\text{-}(C_4F_9)_3N$), 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 that consisted of five calibration standards at different concentration levels spanning the concentration range of interest, typically 0.10 pptr to 10 ppm. Average response factors for each target compound and surrogate were calculated from the initial calibration standards relative to the internal standard compounds added to the sample extracts just before instrumental analysis. Continuing calibration standards at a mid-range concentration level were analyzed at the beginning of each analytical 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 before 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 subpart per trillion levels for congeners (Tabel 4) and homologs (Table 5) using GC-MS/SIM methods. Method 680 was most useful for empirical determinations of tPCBs as the sum of measured homologs. The conventional method for estimating total PCBs uses an empirical algorithm derived from specific congener data (measured using GC-ECD Methods 8081M or 8082 (U.S. Environmental Protection Agency, 1997c), similar to how Aroclors® are quantified. Representative subsamples of shipboard solids were initially analyzed for Aroclor® content (total PCBs as the sum of all Aroclors® in Table 6) 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 ASW 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, used 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 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.

Before sample analysis, an initial calibration was performed that 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 were 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, whichever 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 the primary and confirmation columns and (2) the analyst’s best professional judgment. The recoveries of the surrogate compounds spiked into the sample before 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.

A comparative MDL study was conducted between EPA Method 8081M and EPA Method 680 for the representative electrical cable subsample only. Method 680 (GC-MS/SIM) was used as the conventional analytical method of choice for all ASW 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 11). The MDL study showed that the SIM method was able to obtain similar detection limits as the more expensive ECD methods with the added benefit of quantifying all the homologs present, which provided an unequivocal measurement of total PCBs (tPCBs). A more detailed description of sample-specific method detection limits (or "minimum detection limits") is provided in Appendix B. U.S. EPA (1986) defines the method detection limit (MDL) as "the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero."

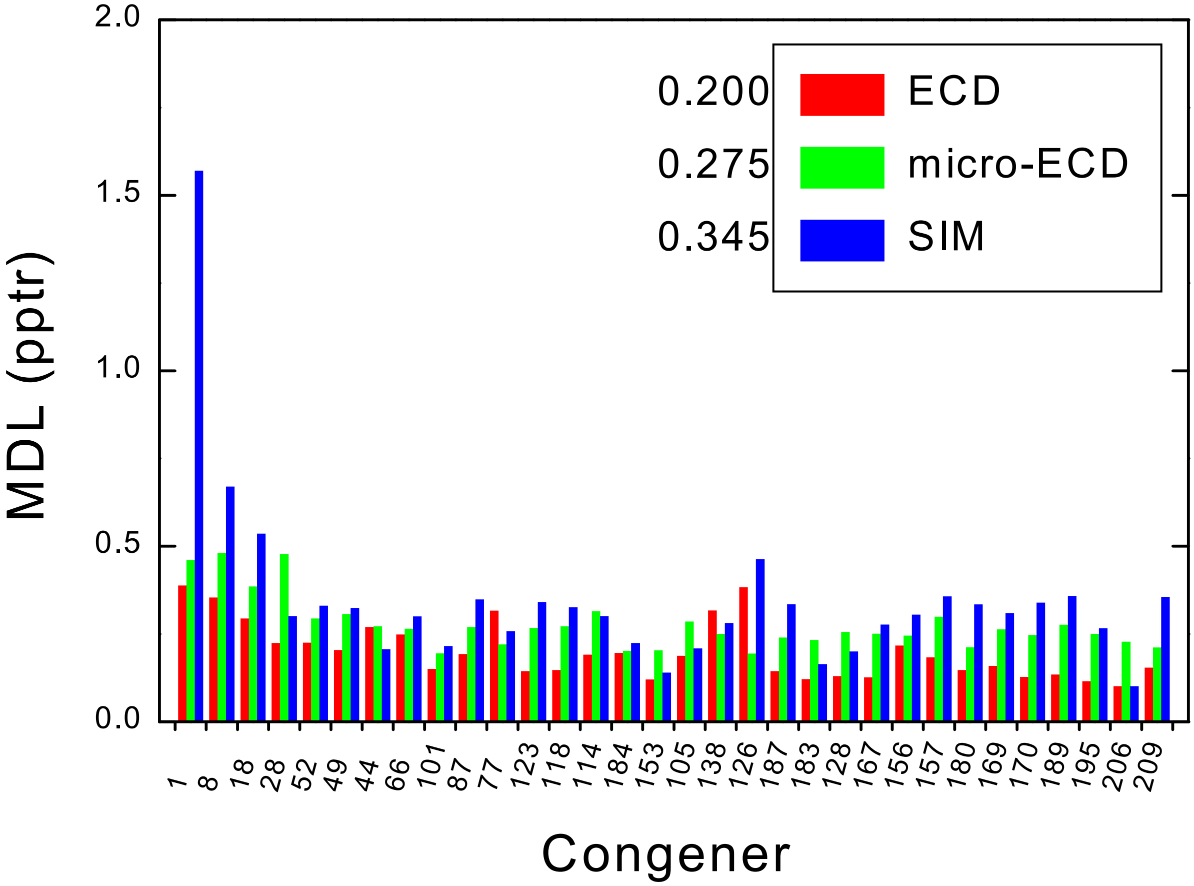


Figure 11. The Method Detection Limit (MDL) study values for PCB target congeners in representative PCB-LRS water samples using three different GC detection methods, ECD (EPA Method 8081M), Micro-ECD (modified EPA Method 8081M), and SIM (EPA Method 680). Micro- ECD is shown for comparison purposes only and was not used in this study. The average congener MDL using each method is shown next to the legend.

The PCBs in Table 4 and Table 5 are the analytes of interest in this work and are the same analytes of concern in previous studies of the fate and effects of PCBs (ASTDR, 2000, 2001). The measurement of homolog 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 homolog groups allows for an unambiguous empirical determination of tPCBs.

The PCB congeners analyzed were those considered important in ecological and human health risk assessments a the time of study inception. These included PCB congeners thought to interact with biological receptors in a manner similar to dioxins, and are thus called dioxin-like PCBs. The dioxin-like PCBs in Table 4 (annotated in red/asterisks), correspond to non-ortho (CP0) and mono-ortho (CP1) PCBs that, when this study began, were considered dioxin-like by the EPA (U.S. EPA, 2000) and the World Health Organization (WHO, 1997). At that time, the WHO also considered di-ortho (CP2) PCBs (170 and 180) dioxin-like. PCB 170 and PCB 180 were PCB analytes included in this study, but PCB81 (3,4,4',5-tetrachlorobiphenyl) was 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 toxicity equivalency factor (TEF) listings, which relate toxicity to mammals as the ratio to the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), have recently been re-evaluated (NAS, 2003; WHO, 2005; U.S. Environmental Protection Agency, 2006). The re-evaluation studies have since added this congener PCB81 and removed PCB170 and PCB180, and now defines TEFs for 12 dioxin-like PCB congeners (Table 4).

Table 4. Congener analytes of interest in the PCB leach rate study. Those shown in red and noted with an asterisk have been considered dioxin-like and the current TEF is listed.

IUPAC Number	IUPAC Name	TEF
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	0.0001
81*[#] (CP0)	3,4,4',5-Tetrachlorobiphenyl	0.0003
87	2,2',3,4,5'-Pentachlorobiphenyl	
101	2,2',4,5,5'-Pentachlorobiphenyl	
105* (CP1)	2,3,3',4,4'-Pentachlorobiphenyl	0.00003
114* (CP1)	2,3,4,4',5-Pentachlorobiphenyl	0.00003
118* (CP1)	2,3',4,4',5-Pentachlorobiphenyl	0.00003
123* (CP1)	2',3,4,4',5'-Pentachlorobiphenyl	0.00003
126* (CP0)	3,3',4,4',5-Pentachlorobiphenyl	0.1
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	0.00003
157* (CP1)	2,3,3',4,4',5'-Hexachlorobiphenyl	0.00003
167* (CP1)	2,3',4,4',5,5'-Hexachlorobiphenyl	0.00003
169* (CP0)	3,3',4,4',5,5'-Hexachlorobiphenyl	0.03
170* (CP2)	2,2',3,3',4,4',5-Heptachlorobiphenyl	
180* (CP2)	2,2',3,4,4',5,5'-Heptachlorobiphenyl	

Table 4. Congener analytes of interest in the PCB leach rate study. Those shown in red and noted with an asterisk have been considered dioxin-like and the current TEF is listed. (cont)

IUPAC Number	IUPAC Name	TEF
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	0.00003
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl	
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	
209	Decachlorobiphenyl	

* Dioxin-like congener
$^{\#}$ Not included in this study
CP0 – coplanar non-ortho
CP1 – coplanar mono-ortho
CP2 – coplanar di-ortho

Table 5. Homolog group analytes of interest in the PCB leach rate study.

Homologue Group (number of Cl)	**Number of Congeners**
Monochlorobiphenyl (Cl1)	3
Dichlorobiphenyl (Cl2)	12
Trichlorobiphenyl (Cl3)	24
Tetrachlorobiphenyl (Cl4)	42
Pentachlorobiphenyl (Cl5)	46
Hexachlorobiphenyl (Cl6)	42
Heptachlorobiphenyl (Cl7)	24
Octachlorobiphenyl (Cl8)	12
Nonachlorobiphenyl (Cl9)	3
Decachlorobiphenyl (Cl10)	1
Σ Homologues = Total PCB (tPCB)	

The Aroclors of interest have different Cl content (%Cl), precentage of homolog groups, and molecular weight (MW g/mole) according to their formulation (Table 6, compiled from tabulation in ATSDR 2000 from data reported in Frame et al., 1995).

Table 6**.** Aroclor® analytes of interest in the PCB leach rate study. The percentage of Cl (%Cl), percentage of individual homologs, and average molecular weight (MW g/mole) is shown for each Aroclor® type.

	Aroclor® Types									
	1016	1221	1232	1242	1248	1254 Lot A4	1254 Lot G4	1260	1262	1268
%Cl	41.50	21.00	32.00	41.50	48.00	54.00	54.00	60.00	62.50	68.00
%Cl1	0.70	60.06	27.55	0.75	0.07	0.02		0.02	0.02	
%Cl2	17.53	33.38	26.83	15.04	1.55	0.09	0.24	0.08	0.27	
%Cl3	54.67	4.22	25.64	44.91	21.27	0.39	1.26	0.21	0.98	
%Cl4	22.07	1.15	10.58	20.16	32.77	4.86	10.25	0.35	0.49	
%Cl5	5.07	1.23	9.39	18.85	42.92	71.44	59.12	8.74	3.35	
%Cl6			0.21	0.31	1.64	21.97	26.76	43.35	26.43	
%Cl7			0.03		0.02	1.36	2.66	38.54	48.48	
%Cl8							0.04	8.27	19.69	
%Cl9						0.04	0.04	0.70	1.65	
MW	262	206	240	272	300	334	334	378	395	453

From data complied in ASTDR, 2000 and reported in Frame et al., 1996.

The list of congeners analyzed in PCB leach rate study samples compares reasonably well to congeners commonly reported in studies of natural environmental samples. Table 7, reproduced from McFarland and Clarke (1989), shows the 36 congeners commonly found in the environment.

Table 7. PCB congeners of concern found in the environment grouped by enzyme induction potential. Congeners listed in McFarland and Clarke (1989), but not analyzed in the PCB leach rate study 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 (1989) described their list of 36 congeners by enzyme-induction type. Induction of some enzyme types may be linked to metabolic carcinogenic processes. Groups 1A and 1B congeners are the most likely to contribute to adverse biological effects. 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. Group 2 congeners are phenobarbitol-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.

2.8. SHIPBOARD SOLID EXTRACTION

Samples of shipboard solids were extracted using ADL's 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. Each environmental and quality control sample was spiked with PCB surrogate solution before the first addition of the extraction solvent. Table 8 lists the sample surrogates. The quality control (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 additon to the surrogate solution, the BS, BSD, and QC samples were spiked with a subset of the target PCB compounds.

Organic compounds were extracted from the solid samples using a 50:50 mixture of the organic solvents dichloromethane and acetone. For each sample, approximately 75 grams of sodium sulfate was mixed into each sample, followed by the addition of 100 mL of 50:50 dichloromethane/ acetone and the container was 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 time. The three 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 Kuderna-Danish (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.

2.9. LEACHATE EXTRACTION

PCB-leachate (ASW), procedural (leaching) bottle blanks, and 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" (U.S. EPA, 1997a). The following description is excerpted from SOP ADL-2824, included in Appendix B, and in the ADL Sample Preparation and Analysis Method Summaries section of Appendix B. With every sample preparation batch the following QC samples were prepared: PB, BS, and BSD. Each environmental and QC sample was transferred to a separatory funnel and spiked with PCB surrogate solutions (Table 8) before the first addition of the extraction solvent. The concentration of the surrogate compounds spiked into the samples was based on the expected contamination level in the samples. For this project, all surrogates were spiked at low levels in the water samples. In additon to the surrogate solution, the BS and BSD QC 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. The nominal spiking level for ASW leachate is listed, but these were increased as needed for analyses of the higher PCB concentrations in shipboard solid samples.

Internal Standard	Concentration (ppb)
Tetrachloro-M-Xylene (TCMX)	5.0
Surrogates	
4,4'-Dibromo-Octafluoro-Biphenyl (DBOFB)	5.0
PCB 103	5.0
PCB 198	5.0

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 to 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 three sovent 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.

2.10. DATA MANAGEMENT

A master electronic database was designed, populated, maintained, and compiled from each individual leaching experiment. It included specific experimental information, screening analysis results, draft results of conventional sample analysis, and final results of conventional sample analysis (including quality control results).

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) before input into the SSC Pacific 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.

2.11. DATA EVALUATION AND DATA REDUCTION

Throughout each leaching experiment, project personnel continuously evaluated experimental data 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 procedure 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.

Each leachate sample was an independent evaluation of the leaching behavior of the solid under test in that leachate volume over a specific time period. That specific time period started from when fresh ASW was introduced to the leaching vessel until the sample was collected for conventional chemical analysis. This time corresponds to the sampling interval.

A complete leaching experiment included a series of such partial or batch 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 previously, repeated over the entire leaching experimental timeframe). Figure 12 illustrates the sampling process for a hypothetical dataset, where each concentration data point plotted versus time corresponds to the concentration in each partial leaching evaluation.

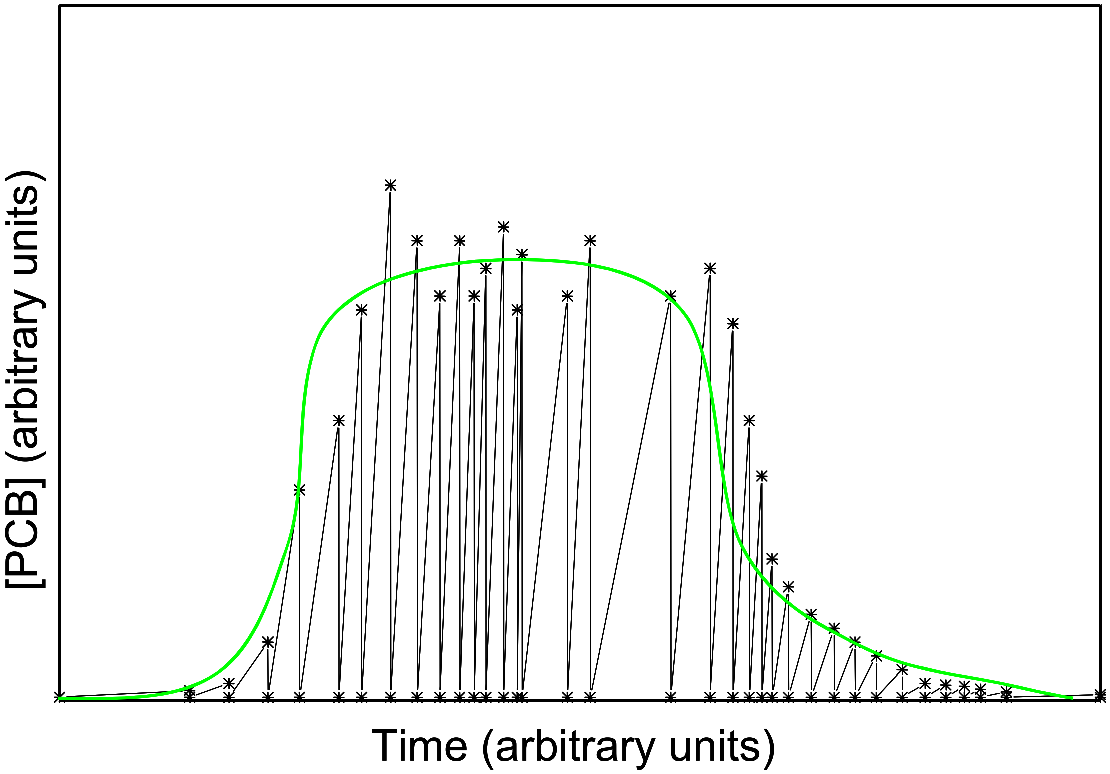


Figure 12. Hypothetical leachate concentration data, in generic arbitrary units. In this study, [PCB] is commonly ng/L and time is days. Each positive slope (straight line) between asterisks is proportional to the average leach rate for that partial or batch incremental leaching experiment as described in the text. Average leach rates for these hypothetical data are plotted versus absolute leaching time in Figure 13.

2.12. CALCULATION OF LEACH RATE

The generic leach rate 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 leach rate can be calculated by using the exposure volume in each given leaching interval to determine the mass released as a function of time as shown in Equation 2 and illustrated in Figure 13.

Equation 1 – Generalized leach rate (mass of PCB/time)

$$LR = V\frac{d[PCB]}{dt}$$

Equation 2 – Differential change in concentration over a given sampling interval

$$V\frac{d[PCB]}{dt} = V\frac{\Delta[PCB]}{\Delta t} = V\frac{([PCB]_f - [PCB]_i)}{t_f - t_i},$$

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, subscripts i and f represent “initial” and “final”, respectively, t_i is the beginning of the leaching interval, and t_f is the endpoint of the leaching interval.

In this study, units for these parameters are measured and reported for concentration in ng/L (pptr), time in units of days (d), and volume in liters (L). The generic leach rate in Equations 1 through 3 are thus in units of ng/day. This leach rate can be further normalized to mass of shipboard solid tested in grams, as described later in Equation 5, providing a mass-normalized average leach rate (AvgLR) in units of ng/g shipboard solid-day, the specific leach rate units used throughout this study. “AvgLR” hereafter represents this mass-normalized average leach rate.

The final concentration in a leachate sample is equivalent to the change in PCB concentration ($[PCB]_f - [PCB]_i$) over the change in time. The change in time (Δt), or time that the solid spends in a particular ASW leachate sample volume for a partial/incremental leaching experiment is conveniently equivalent to the sampling interval ($t_f - t_i$). For high pressure leaching experiments $[PCB]_i$ was calculated as a starting dilution (the concentration of the previous sampling interval divided by the total volume of the current sampling interval) and Equation 2 is used. For ambient pressure leaching vessels, the batch sampling interval starts with a PCB concentration $[PCB]_i$ effectively equal to zero (fresh ASW) and leaches with time until it is collected at the end of that incremental leaching experiment and Equation 2 can be simplied to the following batch reactor equation.

Equation 3 – Leach rate with complete ASW exchange (mass of PCB/time)

$$LR = V\frac{[PCB]_f}{t_f - t_i}$$

A leach rate curve describing the behavior for the shipboard solid under test can be prepared by plotting the leach rates for each of the partial/incremental leaching experiments in the complete leaching series versus 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 as an AvgLR curve in Figure 13 for the hypothetical concentration data plotted in Figure 12 by assuming a hypothetical leaching volume of 1 L for each partial/incremental leaching experiment (over each interval, Δt), and normalizing to an assumed mass of 1 gram of shipboard solid tested.

Figure 13. Example of a hypothetical changes in AvgLR with time for the hypothetical leached PCB concentration data in Figure 12. In this study, AvgLR is commonly ng PCB/g shipboard solid-day and time is days.

2.13. LEACH RATE ANALYSIS

Complete leaching curves for each shipboard solid tested were derived to represent the average leaching behavior as a function of absolute leaching time or ASW exposure time. Comparisons of leaching curves for different shipboard solids also demonstrate the degree to which each shipboard solid matrix attenuates PCB release. Evaluating these leaching curves to determine leach rate dynamics or stability as a function of time is also particularly useful.

If a decreasing AvgLR is observed during a leaching experiment, with at least four decreasing AvgLR data points, they can be best-fit to an appropriate curve and evaluated using analysis of variance (ANOVA) (Ryan, 1990). This curve-fitting approach can provide a crude predictive capability subject to statistical validity and confidence, but is most useful to evaluate whether the 95% confidence or prediction limits for such an extrapolated curve would support using the empirical endpoint of the AvgLR curve beyond the experimental timeframe. This type of analysis was also useful to evaluate if the data could still provide sufficient statistical power if the leaching experiment was terminated.

Confidence and prediction limits for extrapolated future AvgLR values can be calculated using standard statistical equations available in most curve-fitting and analysis programs. The latter (prediction) limits are generally larger than confidence limits because of decreased precision in predicting future specific values as opposed to predicting future average values (confidence limits). If a decision is made to use this approach, the fit should include only the observed curve maximum and points beyond the observed maximum.

3. EMPIRICAL DATA AND OBERVATIONS

3.1. PCBs-ISM CHARACTERIZATION

The shipboard solids used in the leach rate study (Table 3) were subjected to further detailed solid Aroclor® analyses. These include three additional analyses for the physically separable/ dissectible components of electrical cable (middle – ECM and inner – ECI) and foam rubber paint chips (FRPC) (Table 9). Separate determinations of different physical dissections of both electrical cable and foam rubber subsamples were made to identify the primary PCB-containing components for these samples. These included the paint-only portion of the foam rubber shipboard sample (FRPC), the inner component only of the electrical cable shipboard sample (ECI) comprised of resin binder adjacent to outer plastic sheath, and the middle component only of the electrical cable shipboard sample (ECM) comprised of paper/resin insulation adjacent to copper center conductor. In all cases, the concentration of primary Aroclor® (1254, 1260, or 1268) was greater than 100 ppm, and in some cases, the solid contained congeners for which a best-fit analysis indicated the possibility of more than one Aroclor® (Table 9). The representative solid results were considered an estimate of the nominal PCB concentrations in the solid subsamples before leaching.

The initial starting concentrations for each leached solid was determined by measuring the PCB concentration in the solid after leaching and adding that to the mass released during the experiment. This mass balance approach provided a way to indirectly determine the starting concentration in the solid at the beginning of the leaching experiment for each leached subsample and leaching experiment (Equation 4).

Equation 4 – Mass balance for initial PCB concentration in leached solids (mass of PCB/mass of shipboard solid)

$$[PCB]_I = \frac{(M_R + M_L)}{M_S},$$

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

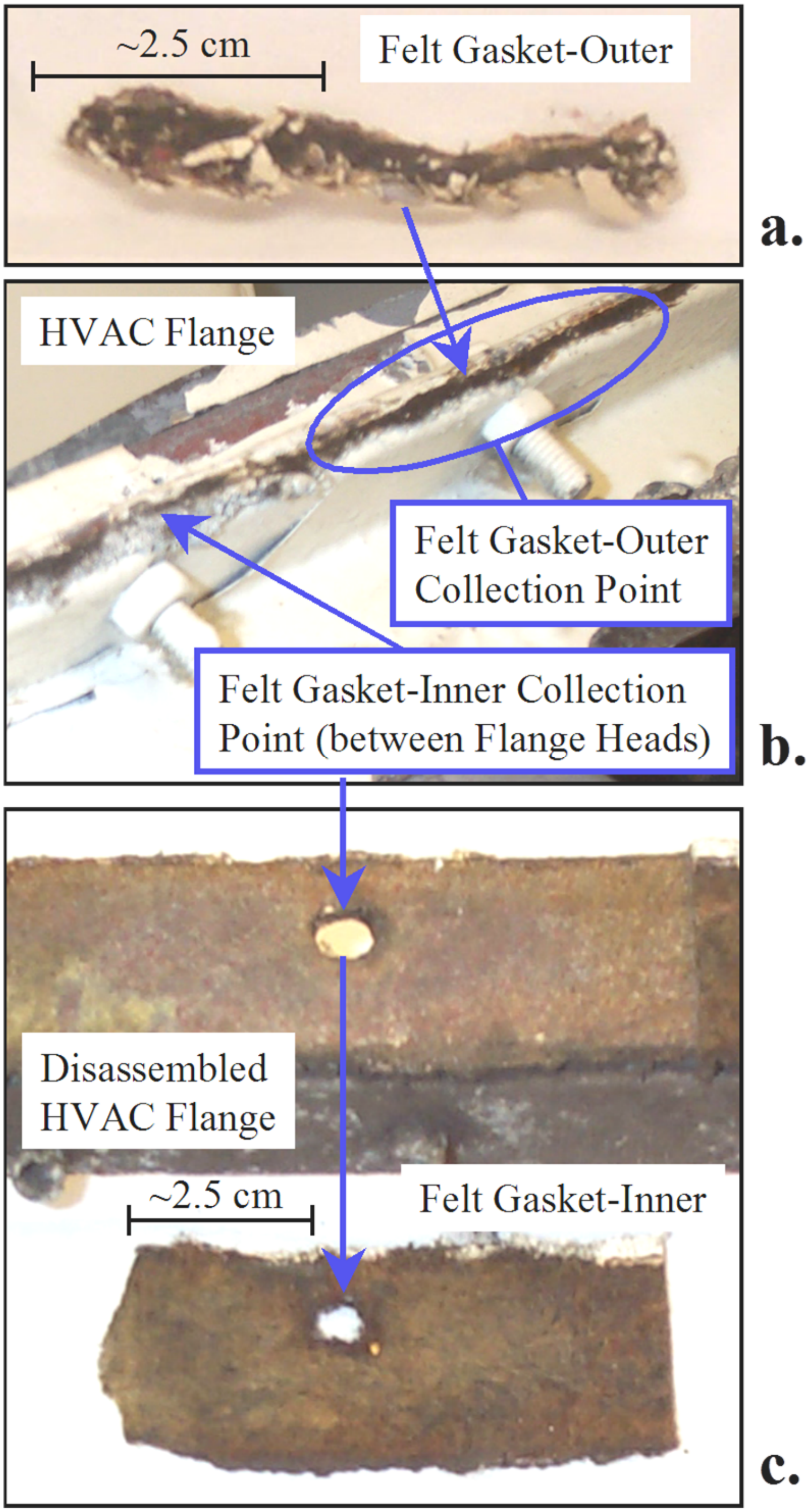
Representative photographs of the shipboard solids tested and schematics of the electrical cable components and foam rubber samples are shown in Figure 14. Electrical cable was separated into inner core (ECI consisting of the resin binder adjacent to outer plastic sheath) and middle (ECM consisting of the paper/resin insulation adjacent to copper center conductor) components and analyzed in addition to the intact cable (EC - all components including center copper wire). Paint chips were removed from the foam rubber (FRPC) and analyzed in addition to the intact foam rubber with paint (FRE) analysis. These Aroclor® results show that PCBs were present at quite significant levels in all three components of electrical cable and in both components of foam rubber (Table 10). Note that for the foam rubber sample, unlike the A1254 distribution, the A1260 concentration in the intact solid is lower, indicating that it was likely more closely associated with the paint component instead of the foam rubber itself.

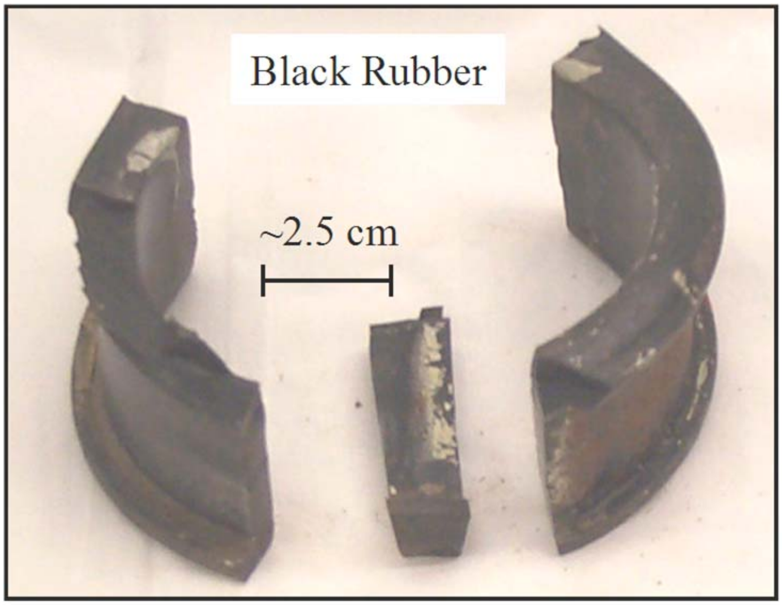
Table 9. Concentrations of Aroclor® types in μg/g (ppm) as determined for best-fit analyses of the congener distribution for *representative* subsamples of each shipboard solid used in leaching experiments.

	Concentration of Aroclor® Types (ppm dry weight)								
	1221	**1232**	**1242**	**1248**	**1254**	**1260**	**1262**	**1268**	**Total**
Electrical cable EC			8.4		1800	160			1968.4
Electrical cable (middle) ECM			3.0		610	78			691.0
Electrical cable (inner) ECI			2.9		1200	100			1302.9
Felt gasket (inner) FGI								140000	140000.0
Felt gasket (outer) FGO								100000	100000.0
Foam rubber FRE					7100	550			7650.0
Foam rubber paint chips FRPC					3300	1100			4400.0
Aluminized paint AP					470	540		120	1130.0
Bulkhead insulation BHI					160	94		46	300.0
Black rubber BRPHL					2100	72			2172.0
blank cells indicate Aroclor® was not detected									

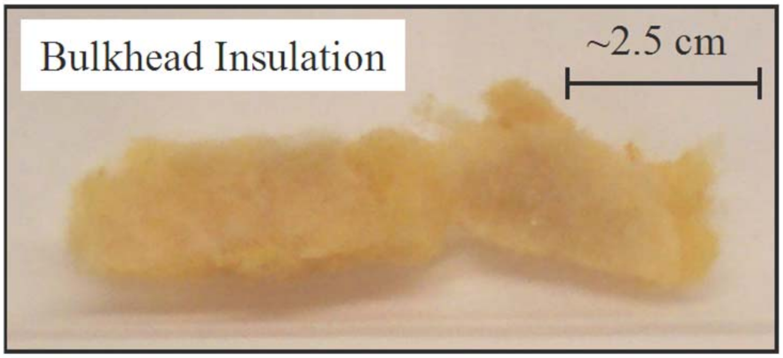
3.2. SHIPBOARD SOLID MATERIALS

Figure 14 shows photos of each representative shipboard solid and subsample before leaching. Generally, the solids did not differ in appearance from these photos after ASW exposure over the experimental (leaching) timeframe. The length of each solid (as leached) corresponded to ~3 inches, except for those solids shown in Figure 13a and d, which were both ~2 inches long. The neat Aroclor® 1254 and Aroclor® 1268 control samples were placed on 1-inch x 3-inch pieces of binder-free, glass-fiber filter, similar to the one in the paint sample photo (Figure 14f). The masses of the shipboard solids were recorded before leaching. Shipboard solids were previously described in Section 2.

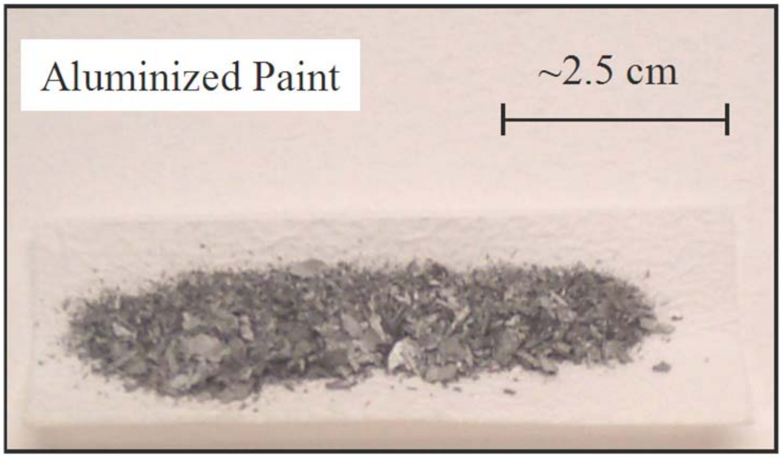

~2.5 cm
Felt Gasket-Outer
a.
HVAC Flange
Felt Gasket-Outer Collection Point
Felt Gasket-Inner Collection Point (between Flange Heads)
b.
Disassembled HVAC Flange
~2.5 cm
Felt Gasket-Inner
c.


Black Rubber
~2.5 cm

d.


Bulkhead Insulation
~2.5 cm

e.


Aluminized Paint
~2.5 cm

f.

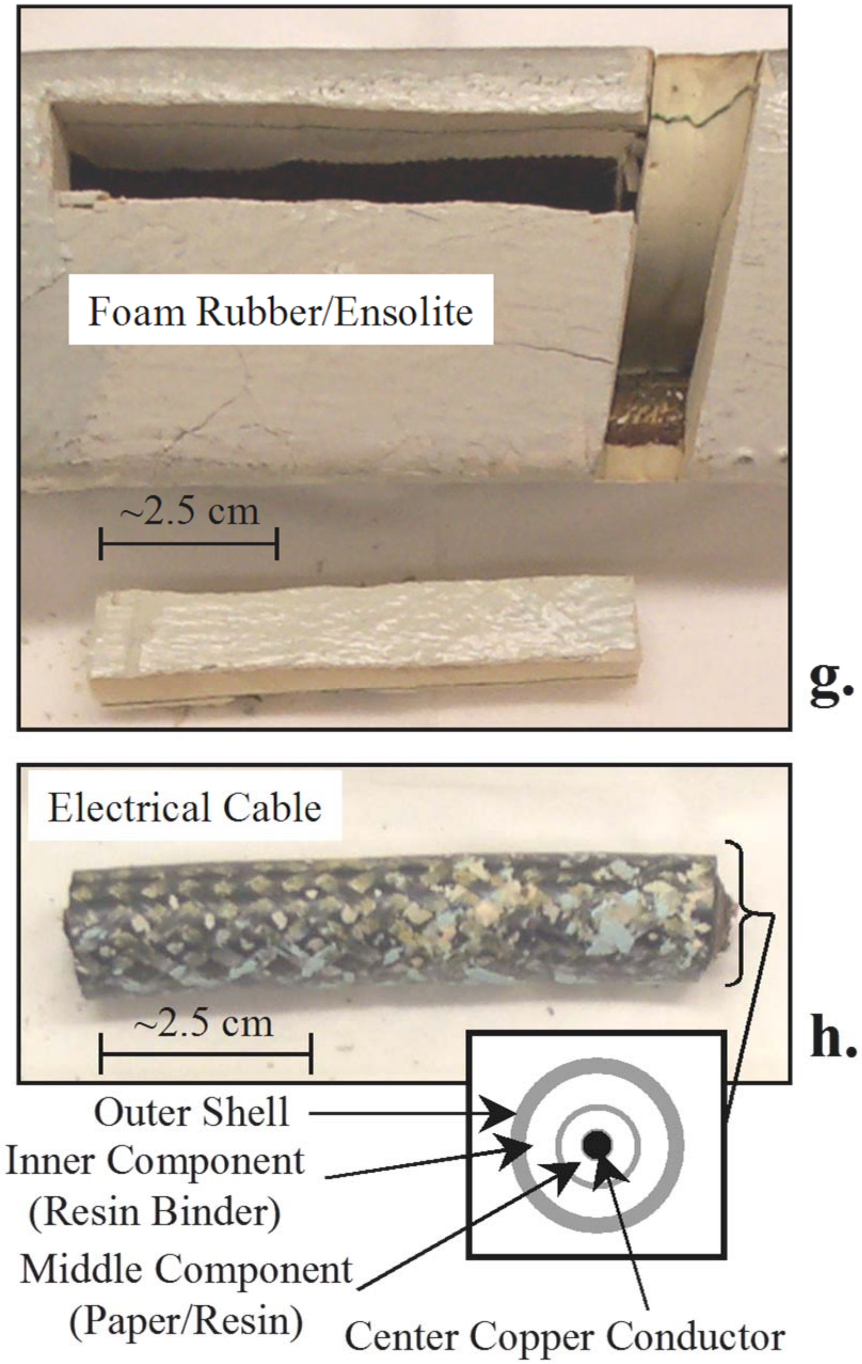


Figure 14 (a–h). Representative photos of shipboard solids before leaching: (a) Felt Gasket-Outer (FGO), (b) flange bottom edge where FGO was collected, (c) Felt Gasket-Inner (FGI) with flange collection site, (d) Black Rubber Pipe Hanger Liner (BRPHL)—subsample is shown in center, with remaining pieces of the ship sample on the left and right, (e) Bulkhead Insulation (BHI), (f) Aluminized Paint (AP), (g) Foam Rubber/Ensolite® (FRE), and (h) Electrical Cable (EC) with a schematic illustrating its internal components. The masses of each leached solid are reported in Subsection 3.4.

3.3. LEACHING DATA DESCRIPTION

Ideally, a leaching experiment would be performed by placing the solid into a large enough volume of ASW to avoid saturation with PCBs, and by avoiding dilution effects or other effects related to removal of the required volume of ASW leachate (~1 L) 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 did not exist. Indeed, this is the solid-specific property we sought to empirically determine in this effort 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 FGI as a representative test solid before 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 bench-top methodologies and SOPs were developed, evaluated, and optimized during this phase, before initializing experiments for which analytical results were collected and reported. Additionally, the approach developed and used in the study allowed for analytical data collection as a function of leaching time in known volumes of ASW leachate, while remaining below the saturation limit in the immediate volume of ASW leachate surrounding the solid at anytime during the leaching process. The process used to avoid saturation also allowed for leaching under completely advective conditions, a a more conservative condition unlikely to be the case within the vessel where PCBs-ISM reside. The practical concentration (saturation) limit for Aroclor® was empirically observed using neat Aroclor® standards as positive analytical controls for dissolution under conditions identical to the leaching conditions for shipboard solids. With these constraints and because the shipboard solids exhibited leaching at tPCB concentrations below these positive controls, the experimental leaching curves must reflect valid leach rates, including only the leaching suppression dictated by the shipboard solid matrix itself.

Each leaching experiment effectively simulated the ideal experiment described above using ASW exchange, *i.e.* by sequentially exposing a given shipboard solid to individual ~1-L aliquots of clean ASW at time intervals designed to avoid PCB saturation in each ASW leachate batch. 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 to detect PCB congeners by increasing the sampling time periods and analyzing 1-L aliquots from a very large leaching volume. These intervals or batch leaching experiments between ASW exchange points coincided with leachate sampling events and represent the sampling interval or time resolution between analyses of PCBs in the ASW leachate. The batch leaching/sampling experiments were continued until such a time that conventional chemical analysis of the ASW leachate indicated that leaching had stopped or had reached what appeared as a stable leaching condition subsequent to an empirically observed maximum leach rate. The mass normalized average leach rate (AvgLR) was then calculated as shown in Equation 5 (an extension of Equation 3) for ASW leachate samples that had previously contained the solid of interest 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 of exposure for the solid during the batch leaching experiment.

Equation 5 – Average leach rate for a shipboard solid (mass of PCB/mass of shipboard solid-time)

$$AvgLR = \frac{V}{M_S}\frac{[PCB]_f}{(t_f - t_i)},$$

where AvgLR (ng/g-shipboard solid-day) is the mass normalized average leach rate over the leaching interval, in which the expression on the right in Equation 5 corresponds to Equation 3 divided by M_S (g shipboard solid), the mass of the solid tested. Note that for all calculations of mass release using PCB concentration data, the calculated number is generally limited to two significant figures, a function of the reported sample analysis volume.

For each solid, a series of batch leaching experiments were plotted as a function of absolute leaching time and used to evaluate the AvgLR 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 batch leaching experiments, the PCB concentration was plotted versus absolute leaching time, reconstructing the ideal/classical experiment that the actual experiment was designed to simulate. This type of plot corresponds to the classical experimental concentration behavior versus time curve corresponding to the ideal 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 during the experiment, and as an inherent benefit, this analytically validated experimental protocol used an incremental volume that avoided a saturation condition. The classical concentration versus time curves are referred to as cumulative concentration curves and were prepared by calculating concentration using Equation 6 and plotting (C_i) as a function of leaching (exposure) time.

Equation 6 – cumulative concentration (mass of PCB/volume)

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

where C_i = PCB concentration for the ith data point in the cumulative concentration plot, C_j = PCB concentration (mass PCB/volume) for the jth incremental (batch) experiment, V_j = volume of ASW for the jth incremental experiment, V_k = incremental volume of ASW in the kth incremental experiment, and n = total number of incremental experiments in the test (total number of incremental ASW batch experiments, which is equal to the number of data points).

3.4. SHIPBOARD SOLID-SPECIFIC LEACHING DATA

Resources allowed evaluation of three leaching scenarios, which provided sufficient data for evaluating leaching dependence on both temperature and pressure. These three leaching study scenarios were:

a) all shipboard solids at low temperature/ambient pressure (4 ^{o}C/1 bar),

b) a subset of shipboard solids at low temperature/high pressure (4 ^{o}C/300 bar), and

c) all shipboard solids at warm temperature/ambient pressure (25 ^{o}C/1 bar) as previously reported (George et al., 2006).

The following subsections contain data and results applicable to scenarios a) and b) for each shipboard solid leaching experiment at a deep ocean temperature of 4 ^{o}C. Plots of cumulative PCB concentration in the total exposure volume versus leaching time (using Equation 6 to represent the classical experimental leaching curve) are presented here (Section 3.4), followed by the corresponding average PCB leach rates plotted versus absolute leaching time in Section 4. Comparisons of these leach rates were used to evaluate dependence on pressure at constant temperature (4 ^{o}C). Similarly, ambient pressure low temperature leach rates were compared to leach rates for data previously reported at 25 ^{o}C (scenario c) to illustrate differences in leach rate behaviors due to temperature, at a constant pressure of ~1 bar.

All cumulative concentration and average leach rate plots are presented according to level of chlorination (homolog groups), resulting in up to 10 homolog curves per shipboard solid, in addition to the target congeners detected during a given experiment. Detecting a target homolog group and failing to detect a target congener within that group is entirely possible because analyzing all congeners within the homolog groups was impractical. However, because a homolog group is the empirical quantitation of *all* congeners within that chlorination level, non-target congeners still contribute and can be captured in the homolog group value, even if the target congeners were not detected. In the following figures, the homolog groups detected during each solid leaching experiment are plotted, along with the corresponding target congeners detected in each homolog group. Homologs and target congeners not detected during the leaching experiment appear as a placeholder in the legends to provide a sense of how many homologs and target congeners were not detected (See Table 4 and Table 5 of Section 2 for reference while viewing these plots.) The homolog and congener detection levels can also be observed in the shipboard solid and leachate fingerprint plots that are included for for each leaching experiment.

For the concentration versus time plots, the slope of a line drawn between any two adjacent points on a curve is proportional to the AvgLR between those points, which can be calculated using Equation 5. Cumulative concentration curves that continue to increase reflect a leach rate greater than zero and continued leaching with time, while 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 increasing and horizontal curve regions (slopes > 0, then = 0, then > 0 again, etc.). While the cumulative concentration plots provide qualitative snapshot of leaching behaviors, AvgLR plots provide an unbiased quantitative evaluation of the leach rate behavior.

The distributions of PCBs released at various time intervals describe the temporal variability of PCB congener and homologs released from the diferent solids as a function of leaching time and were calculated and plotted as mass percent of total in each of the Aroclor® dissolution and shipboard solid-specific leaching behavior sections. For each Aroclor® and solid tested, homolog and congener distributions associated with the solid were compared with the distributions of total PCB released into the ASW leachate. Additionally, the results for four separate leachate samples (resulting in four sets of homolog and corresponding congener distributions) are presented across each entire leaching experiment, i.e., a series of batch leaching experiments for a solid as described above for the total leaching time. The leachate PCB distributions presented for each tested material corresponds to an initial or pre-maximum observed rate (iLR), the maximum observed rate (mLR), a post-maximum observed rate (pmLR), and the final distribution corresponds to the final empirical rate (fLR, at the end of the experiment). These are sufficient to demonstrate where temporal changes in material-specific leaching behavior occurred, illustrating the dynamic analyte-specific behavior that was observed.

The lower empirical limit of the leach rate range is bounded by results obtained for a negative control or procedural method-blank leaching experiments that did not contain PCBs. These negative controls were tested under conditions identical to shipboard solid leaching conditions, but with a cage only (without a shipboard solid sample matrix). Results from all negative controls analyzed during the leaching experiments are included in the Leaching Procedural Blank Data section of Appendix C.

The upper limit for the experimental leach rates of the shipboard solids was approximated by a positive analytical control curve corresponding to neat Aroclor® dissolution experiments. These are included for comparison with shipboard solid leaching results to provide a measure of the effective saturation limit in the experiments and as a reference point for the dissolution component of the PCBs-ISM leach rate.

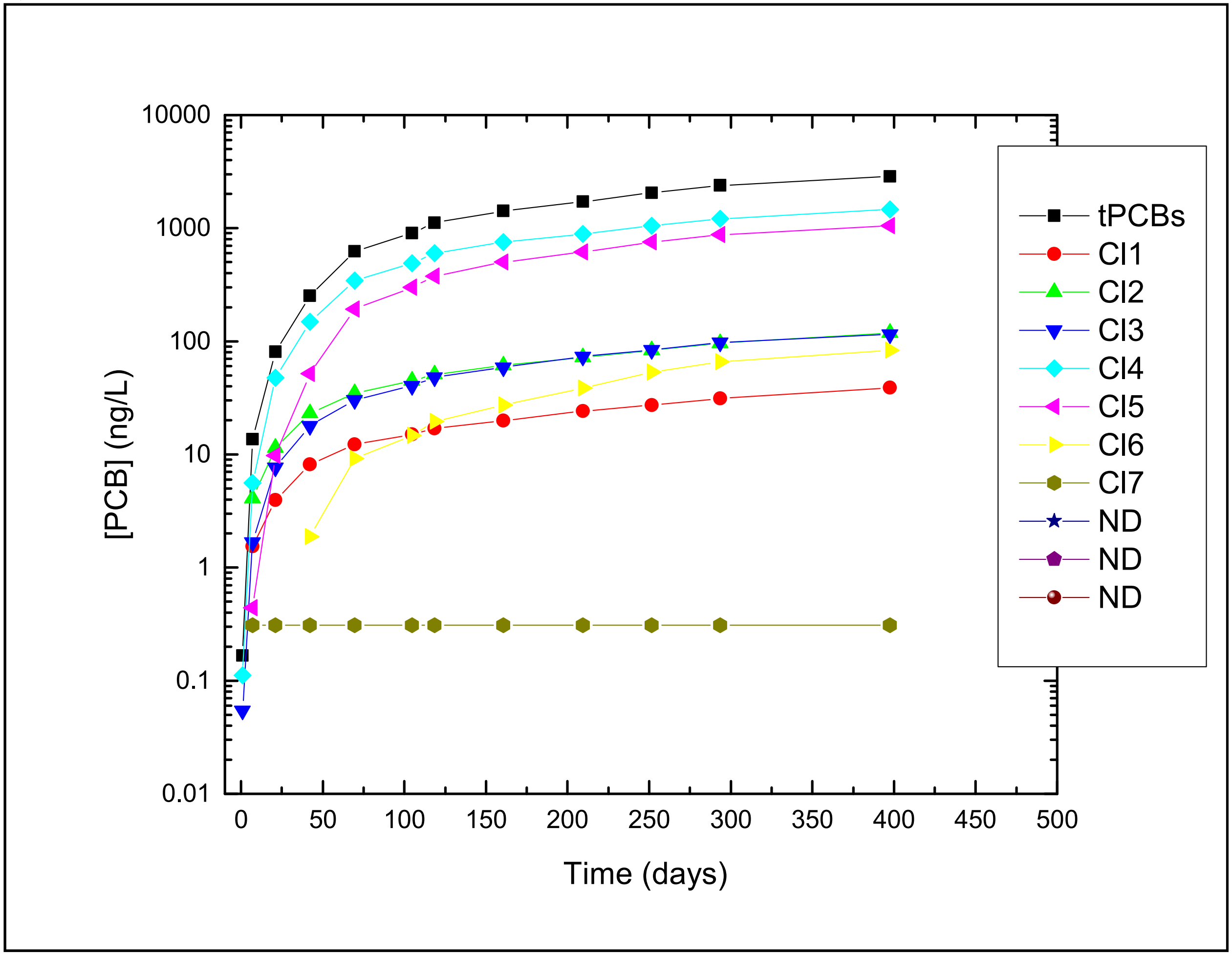
Representative solid analyses indicated that the following shipboard solids contained Aroclor® 1254 (A1254), but not Aroclor® 1268 (A1268): black rubber pipe hanger liner (BRPHL), electrical cable (EC), and foam rubber/Ensolite® (FRE). In the cumulative concentration plots and AvgLR plots, these data are related to the A1254 positive analytical control curves for maximum comparability. The remaining solids are presented in the context of the A1268 positive analytical control curves, as their representative solid analyses contained A1268, in some cases, with A1254: Bulkhead Insulation (BHI), Felt Gasket-Inner (FGI), Felt Gasket-Outer (FGO), and Aluminized Paint (AP).

3.4.1. Aroclor® 1254 (A1254) Analytical Control

Dissolution Behavior at 4°C/1 bar

Concentration behaviors are plotted for neat A1254 leached at 4 °C and ~1 bar as a function of dissolution time (exposure time). Homolog groups Cl1 through Cl7 were leached from A1254, and Figure 15 a) includes these homolog concentration curves (lower plot). The tPCB concentration curve is calculated as the sum of the homolog concentrations below it (upper curve in Figure 15 a) Curves for the detected target congeners are plotted below the homolog curves. As the tPCB curve shows, the long-term dissolution curve approaches 3 ppb (3,000 ng/L) over the nearly 400-day experiment for 18 mg of A1254 in a 12.05 L total leachate exposure volume. This correlates well with the PCB mass transfer into ASW that one would expect from a solubility experiment, i.e., if instead of the batch experiments described here, 18 mg of A1254 had been placed in 12 L of ASW and concentration monitored in situ over time.[10]

a)



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[10] The observed tPCB concentration approaches the solubility of A1254 given as 0.0025 – 0.003 mg/L (2500-3000 ng/L) in Mackay et al. (1992).

b)

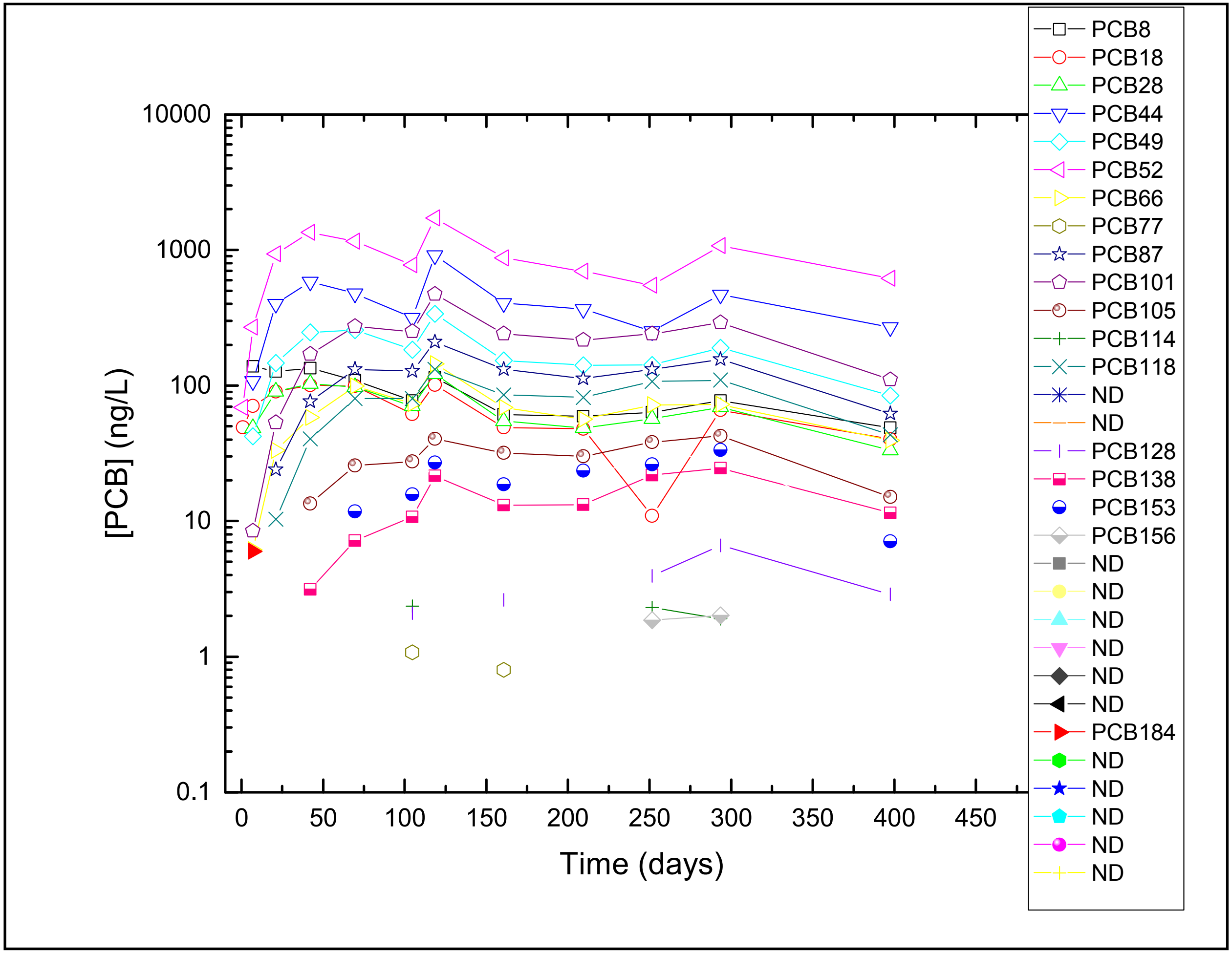


Figure 15. Cumulative PCB concentration versus exposure time for 18 mg of neat Aroclor® 1254 exposed to a total volume of 12.05 L of ASW leachate at 4 °C and 1 bar. Plot (a) shows tPCBs concentration and contributing homolog group concentrations versus exposure time, where the sum of the homolog curves is equal to the upper tPCB curve. Plot (b) corresponds to target congener concentrations within homolog groups Cl1 through Cl7 versus time.

Figure 16 shows the total released homolog and congener distributions, and compares these released PCB distributions to the initial PCB distributions determined for neat A1254 (Equation 6). All detected homologs and congeners were normalized and plotted as percent of total PCBs in each matrix (seawater versus “solid”), even though in many instances the percent contribution to total PCB level was <0.1% of the total amount of PCBs. These levels of homologs and congeners in “solids” can be significant if they release into seawater, as reflected in many seawater PCB distributions. The highest levels of release were from homolog groups Cl1 through Cl6, with relative magnitudes shown in Figure 16 (a, b) below.

PCB distributions, normalized as percent of total, for specific A1254 ASW samples at key intervals across the entire experiment (exposure time) are shown in Figure 17. The homolog and congener group distributions correspond to (a) the initial dissolution rate(iLR), (b) the maximum dissolution rate (mLR), (c) the post-maximum congener and homolog rate distributions (pmLR), and (d) the final empirical dissolution rate (fLR).

The 4 °C leaching experiments established an effective saturation limit for leaching of PCB analytes from shipboard solids that contain A1254. Similar results were reported from the previous ambient pressure/warm temperature study (George et al., 2006). This maximum concentration occurred in sample 212-147A-S-A-T38, over the leaching time interval from 294 to 398 days (also the longest time-interval in the experiment), at a tPCB concentration of 6360 pptr (ng/L). Contributions were observed from homolog groups Cl1 through Cl6, which also corresponded to maximum homolog concentrations observed in all A1254 leachate samples collected. Homolog group Cl7 was only detected in one sample very early on in the experiment, leaching interval from 1 to 7 days, at a concentration of 4 pptr. Homolog groups Cl8 through Cl10 were never detected in any leachate samples across the entire experiment and thus do not contribute to the effective saturation limit estimate. In addition, no single congeners exceeded the corresponding homologue group values.

The effective A1254 saturation limit was estimated as the sum of all observed maximum homolog group concentrations, or 6364 pptr and assumes that the solubility of any given homolog group is not significantly perturbed (suppressed) by the presence of other dissolved homolog groups at their maximum observed concentrations. The actual solubility for such a complex mixture is probably time-dependent, but should still be above the highest concentration observed experimentally (6360 pptr = 0.006360 ppm). Additionally, all PCB concentrations observed at warmer temperatures and ambient pressure (George et al., 2006), were higher by a factor of 2.5 (16200/6364) than these corresponding leaching concentrations at lower temperatures and ambient pressure. If this factor is applied to solubilities reported in the literature and compiled by Mackay, Shiu, and Ma (1992) for A1254 in freshwater, the low temperature solubility is in the range of 0.0039 to 0.117 mg/L (ppm), providing a reasonable assurance that we are below saturation across the 4 °C A1254 experiment. Additionally, these empirical A1254 data provide a positive control or upper limit for 4 °C leaching data that are described below for each of the shipboard solids tested.

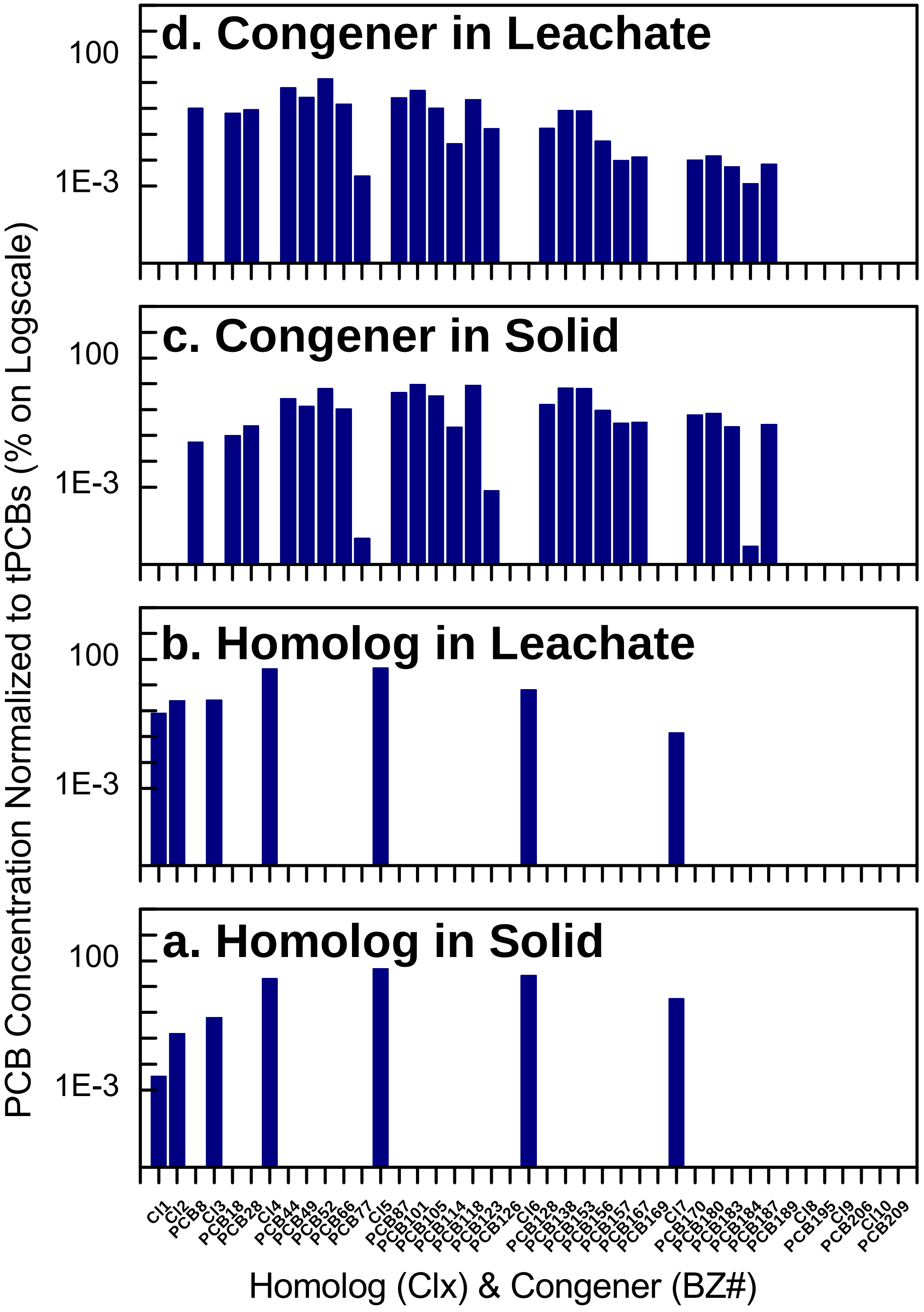


Figure 16 (a–d). Experimental homolog and congener PCB fingerprints for neat Aroclor® 1254 “solid” (a and c) compared with total homolog and congener distributions of PCBs released from A1254 into seawater (b and d) at 4 °C and ambient pressure (~1 bar). The latter distributions correspond to all PCBs released, also represented by the cumulative concentration endpoint for all analytes plotted in Figure 14. The solid distributions correspond to the pre-dissolution PCB content in the neat-solid A1254, derived from the mass balance performed at the conclusion of the experiment. Note the logscale used to make variances at very low levels visible.

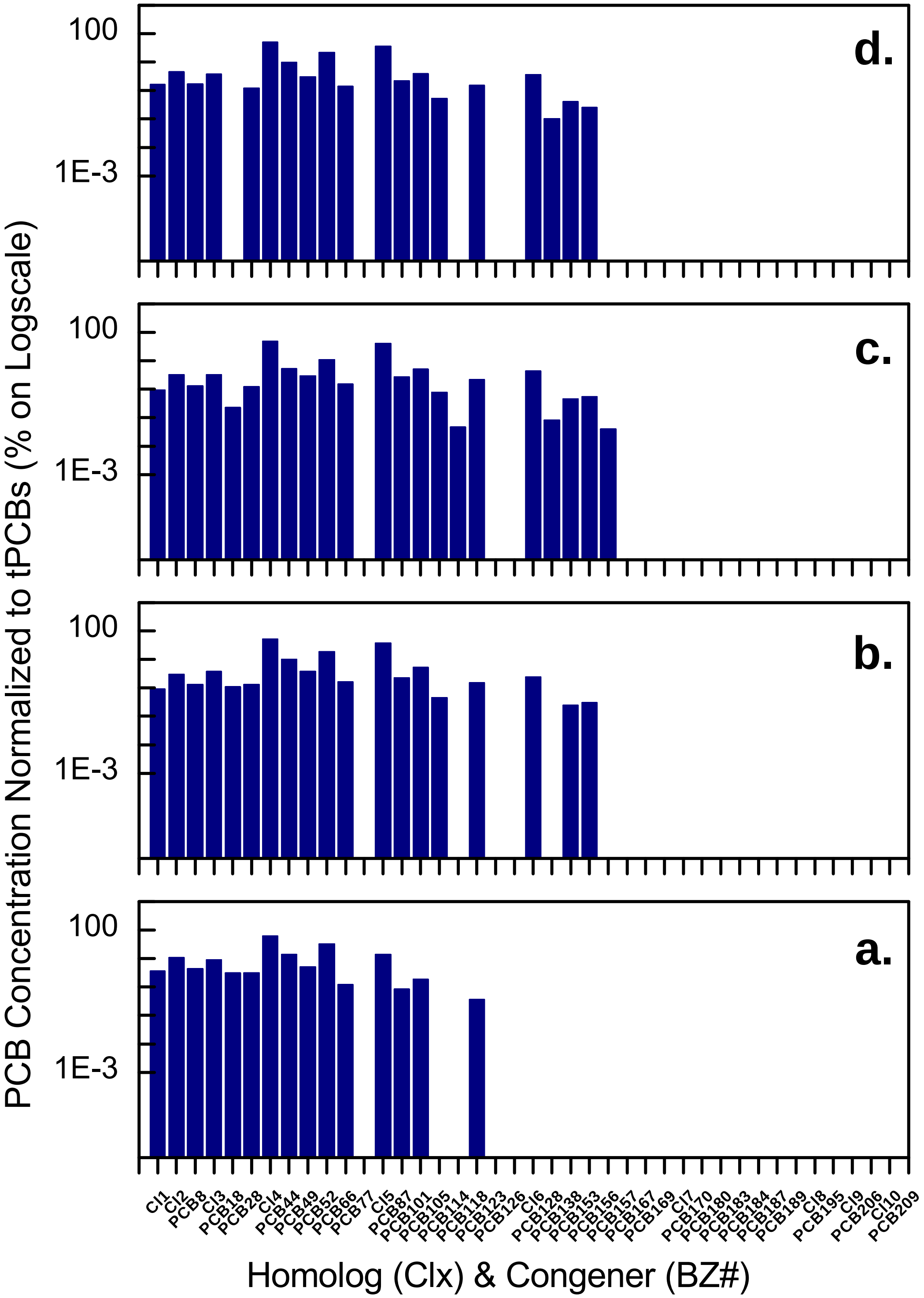


Figure 17 (a–d). Homolog and congener distributions during the neat Aroclor® 1254 experiment, normalized as percent of total, corresponding to the following intervals: (a) iLR – 21 d, (b) mLR – 119 d, (c) pmLR – 252 d, and (d) fLR – 398 d.

Appendix C contains the raw data for A1254 dissolution rate results. The concentration maxima of target congeners, if detected within each of these homolog groups, occurred in the same leachate samples as their corresponding homolog group maxima with the following exceptions: Cl4/PCB77 1.4 pptr (at 105 days, one of two detections during experiment), Cl5/PCB101&105 (at 322 days), PCB114 (at 252 days), and Cl6/PCB153&156 (at 322 days). These exceptions indicate that solubility of individual congeners in ASW leachate may not be the only factor contributing to the dissolution, i.e., insoluble PCBs in the Aroclor® matrix may be retarding the fundamental congener solvation. Note that in some cases the occurrence of different maxima in different (sequential) leachate samples over time is possibly 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-42, day-70, day-105, day-161, day-210, day-252, and day-294 are 60 ng/L, 64 ng/L, 59 ng/L, 56 ng/L, 63 ng/L, 58 ng/L, and 69 ng/L, respectively (Appendix C). All of these concentrations, except for the 69 ng/L value, are within expected analytical precision of each other. The Relative Standard Deviation (RSD) for the seven similar values was 7%, while the RSD for the corresponding PCB8 blank spike (BS) and PCB 8 blank spike duplicate (BSD) sample results was 13% and 15% respectively. Similar concentrations are also observed for the Cl2 group in all six of these samples. The RSD was 10%, which could have had contributions from as many as 12 congeners. Clearly, the variability in PCB8 leachate sample results for these seven leaching time periods was comparable to that from analysis of standard materials, and if one assumes that all of the contributing dichloro-congeners in the Cl2 homolog 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. Therefore, while determining the exact maximum concentration for all congeners in these empirical studies may not be possible, the range can be determined from a comparison of measured congeners and corresponding homolog group.

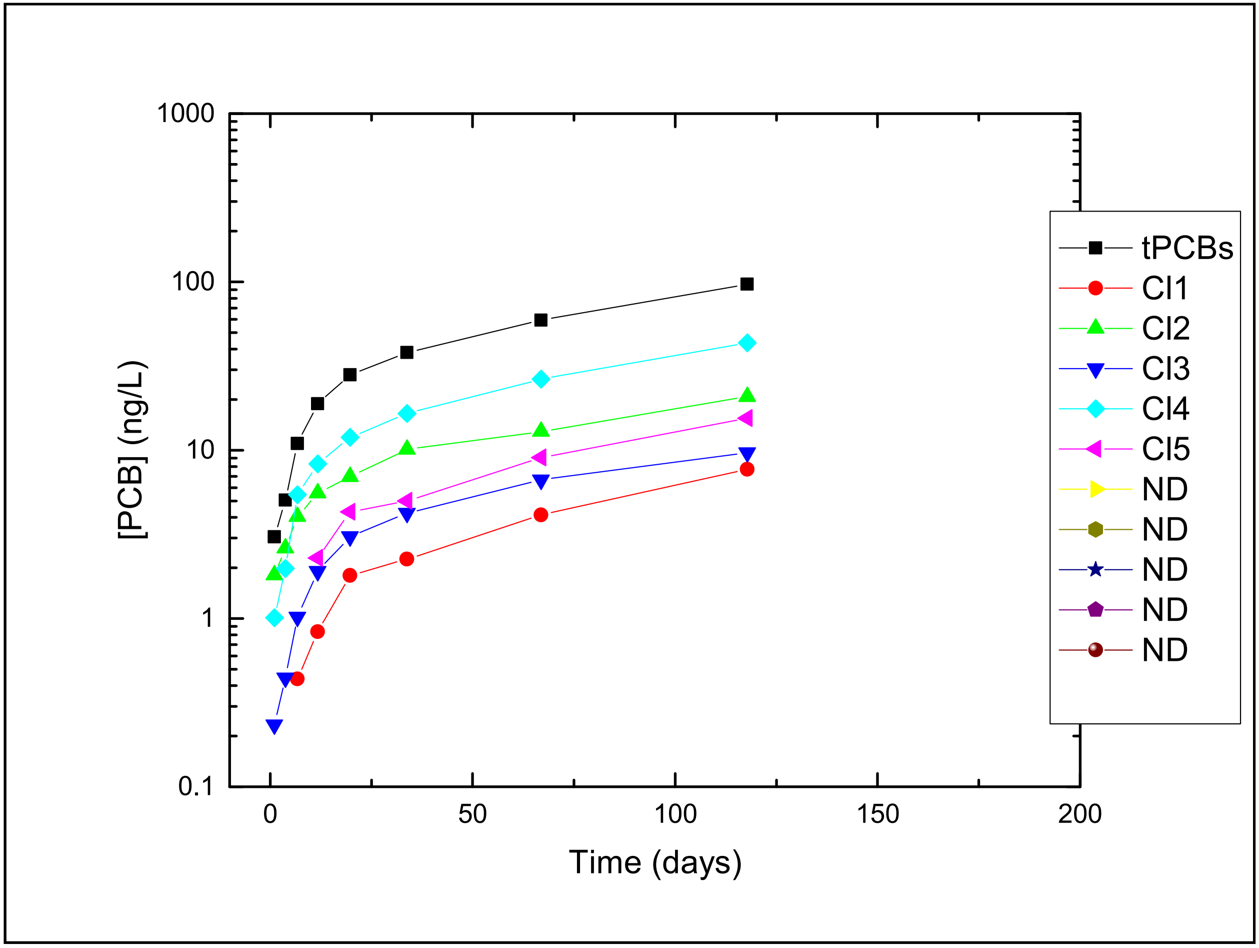
Finally, if one considers that the maximum concentration observed was 6,360 pptr (meaning all other A1254 leachate concentrations lie below this value), the A1254 saturation limit based on the sum of observed homolog maxima was estimated at 5,855 pptr, and the concentration in the total experimental leaching volume was 2,865 pptr (as indicated by the final concentration value in Figure 14a and in the cumulative concentration table in Appendix D, Aroclor® 1254 (A1254) Results), then the observed dissolution behavior must indeed be limited by the neat 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 as possible in a leaching sample, i.e., 6,360 pptr, or up to the estimated saturation limit of 5,855 pptr. These combined observations demonstrate that this leaching experiment defines an upper limit for Aroclor® 1254 PCB release from the most closely related solid matrix possible, itself, in the form of a mixture of solid PCBs.

Dissolution Behavior at 4 °C/300 bar

The leaching experiment results at 4 °C and 300 bar are shown below (Figure 18) for 20.7 mg of A1254 in 16.16 L of seawater over a leaching time of nearly 120 days. Because high pressure/low temperature experiments were resource- and hardware-limited to three concurrent experiments on select shipboard solids (bulkhead insulation, felt gasket-inner, and electrical cable, selected based partly on leach rates observed at ambient pressure/low temperature and partly on shipboard removal/mitigation considerations), the high pressure/low temperature A1254 experiment was initiated only after one of those shipboard solid experiments was terminated. The relatively short 120 day leaching time was sufficient to observe a stable steady-state leach rate.

The distributions plotted in Figure 18 correspond to all PCBs released, also represented by the cumulative concentration endpoint for all analytes plotted in Figure 19. The solid distributions correspond to the pre-dissolution PCB content in the neat-solid A1254, derived from the mass balance performed at the conclusion of the experiment. The log scale was used to make variances at very low sub-percentage levels visible**.**

a)



b)

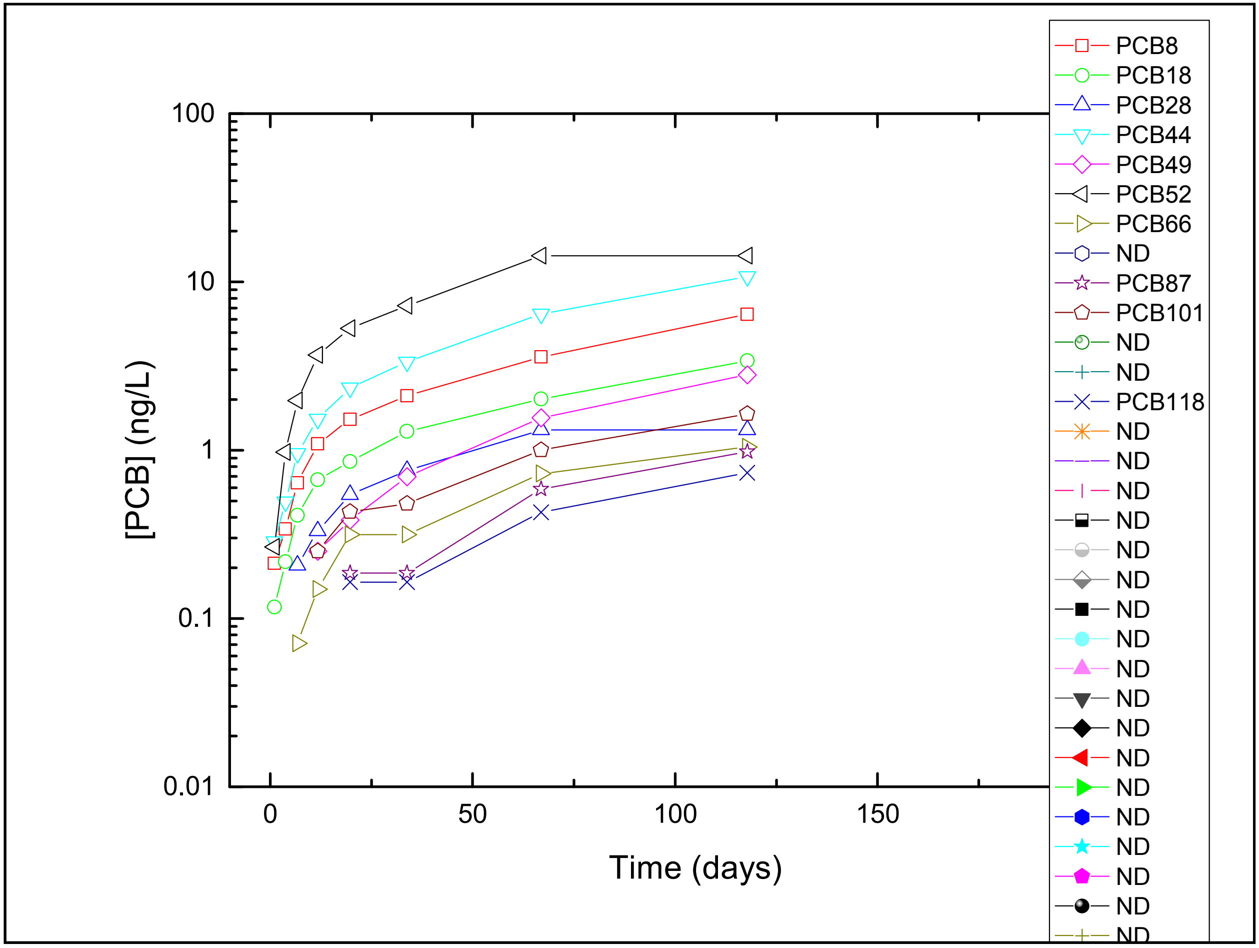


Figure 18. Cumulative PCB concentration versus exposure time for 20.7 mg of neat Aroclor® 1254 exposed to a total volume of 16.2 L of ASW leachate at 4 °C and 300 bar for ~120 days. Plot (a) shows tPCBs concentration and contributing homolog group concentrations versus exposure time, where the sum of the homolog curves is equal to the upper tPCB curve. Plot (b) corresponds to target congener concentrations within homolog groups Cl1 through Cl5 versus time.

Note that the congener and homolog fingerprints in A1254 tested at 4 °C/300 bar exhibit slight differences and contain a Cl8 component when compared with the congener and homolog fingerprints in A1254 tested at 4 °C/1 bar (Figure 15 a&c). These differences are related to the use of two A1254 SRM sources with different lot numbers and demonstrate a potential source of variance in shipboard solid PCB content. It was fortunate that a Cl8 signature was present in the A1254 tested at 4 °C/300 bar, since some of the shipboard solids tested under these conditions also exhibited an A1268 signature, which is known to contain Cl8.

PCB distributions, normalized as percent of total, for specific A1254 ASW samples at key intervals across the entire experiment (exposure time) are shown in Figure 20. The homolog and congener group distributions correspond to (a) the initial dissolution rate (iLR), (b) the maximum dissolution rate (mLR), (c) the post-maximum congener and homolog rate distributions (pmLR), and (d) the final empirical dissolution rate (fLR).

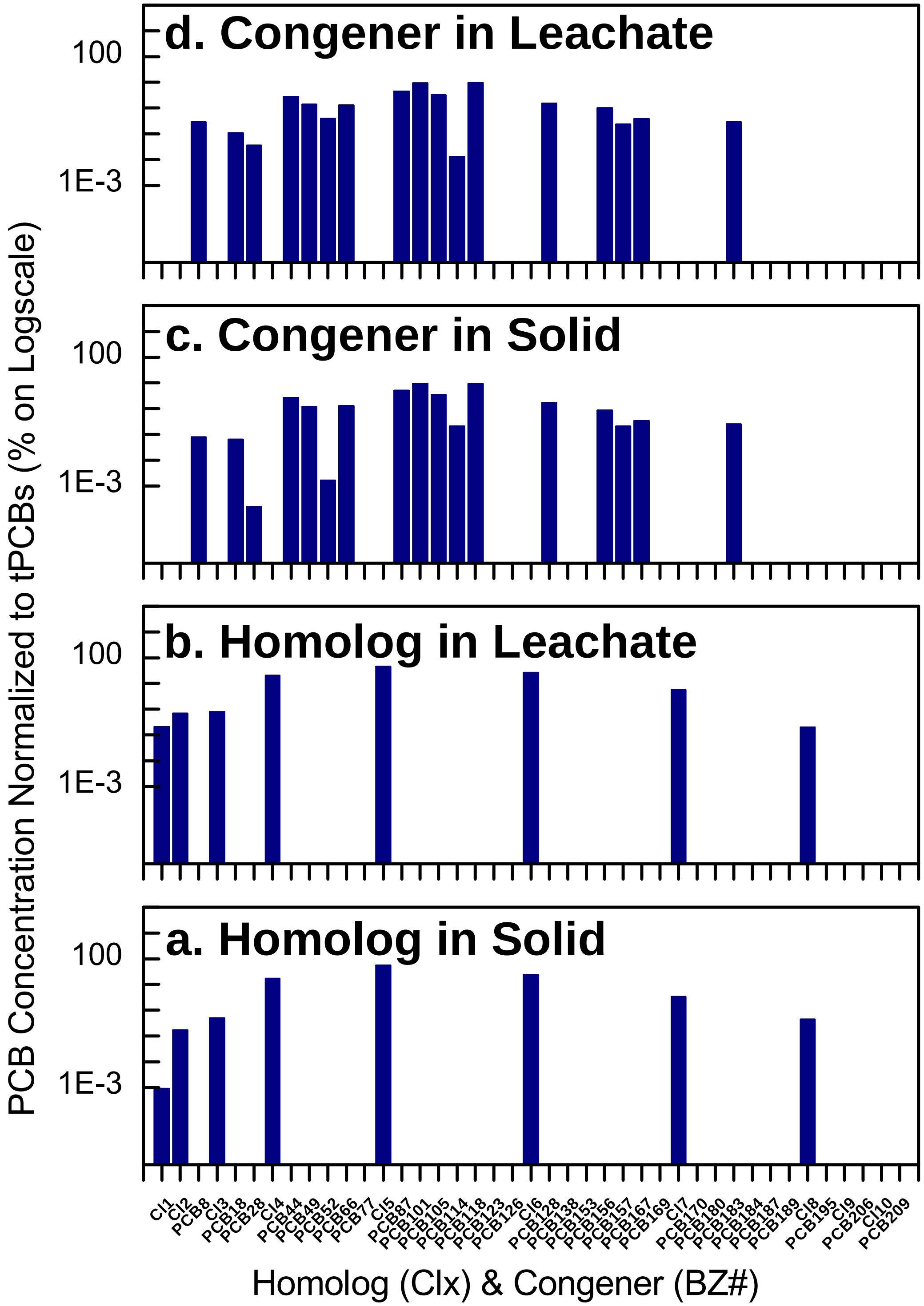


Figure 19 (a–d). Experimental homolog and congener PCB fingerprints for neat Aroclor® 1254 "solid" (a and c) compared with total homolog and congener distributions of PCBs released from A1254 into seawater (b and d) at 4 °C and high pressure (300 bar).

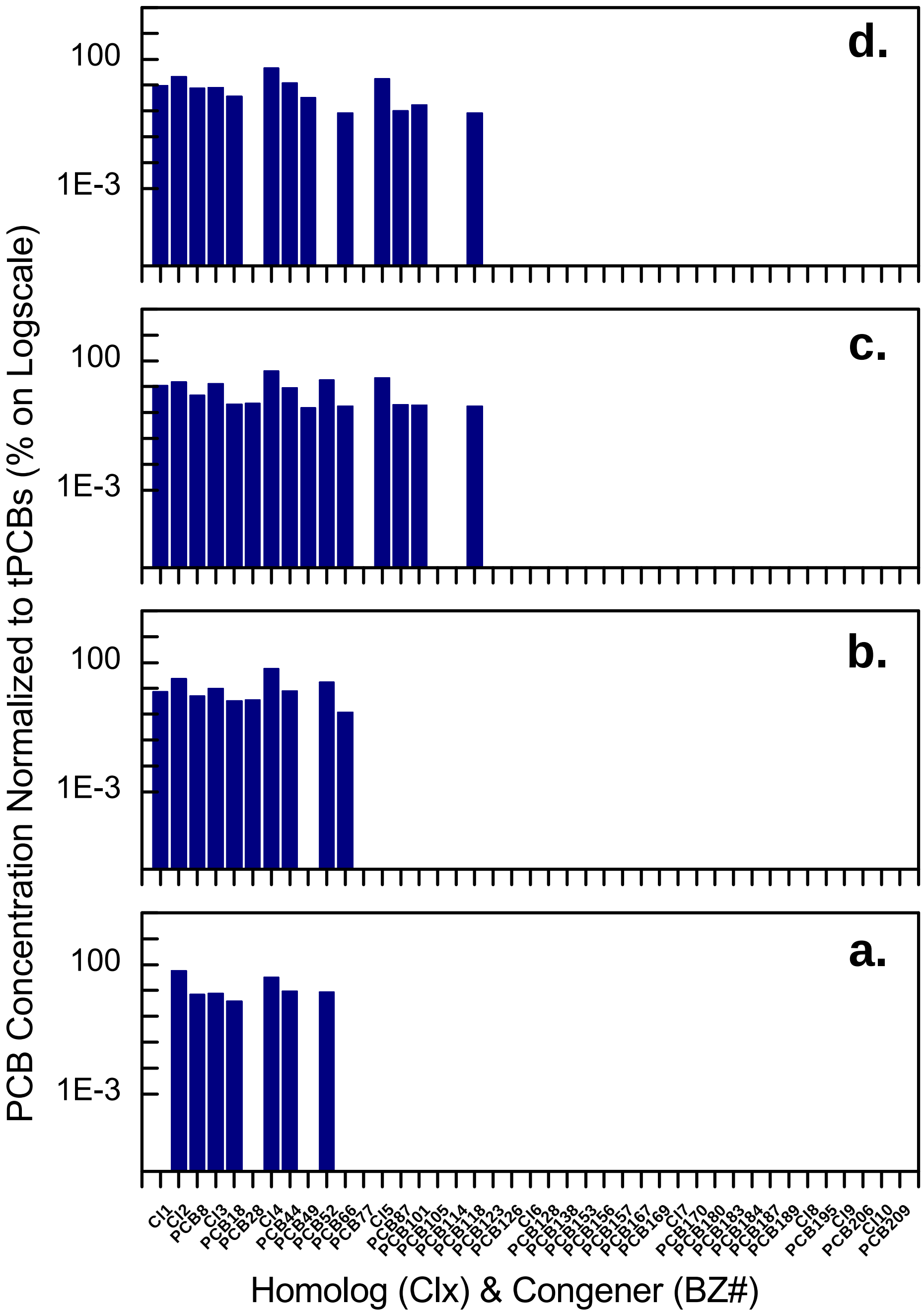
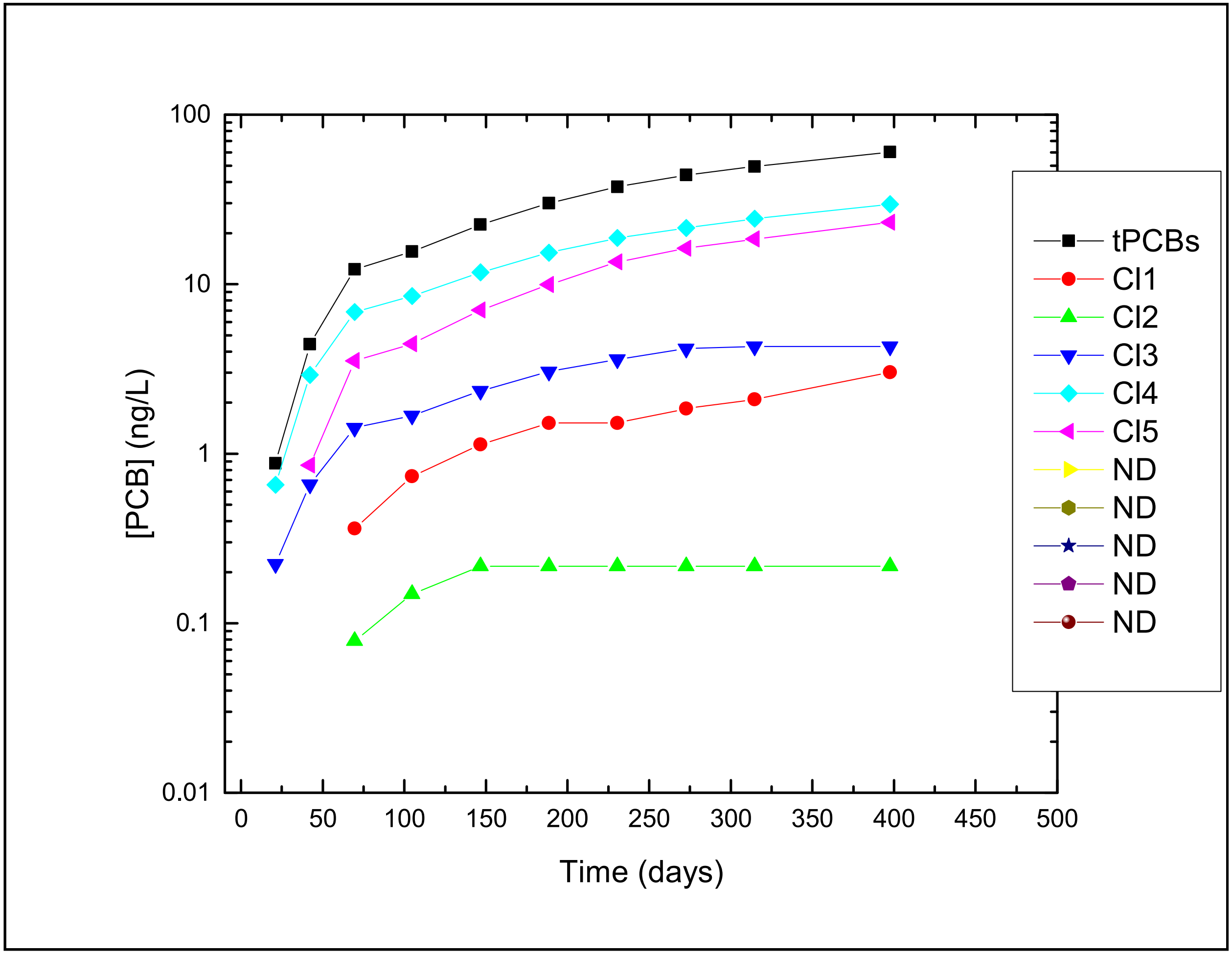


Figure 20 (a–d). Homolog and congener distributions during the 4 ^{o}C/300bar neat Aroclor® 1254 experiment, normalized as percent of total, corresponding to intervals ending on days: (a) 1, (b) 7, (c) 20, and (d) 118.

3.4.2. Black Rubber Pipe Hanger Liner (BRPHL) Leaching Behavior

Leaching concentration behaviors for BRPHL leached at 4 °C and ~1 bar are plotted for tPCBs and homolog groups Cl1 through Cl5 and Cl7 (Figure 18a). Plots for homolog groups and target congeners within each homolog group are shown in Figure 21 (a–b). The BRPHL subsample (2.113 g) containing 4.10 mg (0.194 wt%) tPCB was exposed over a leaching time of nearly 500 days to a total leachate volume of 14.82 L.

a)



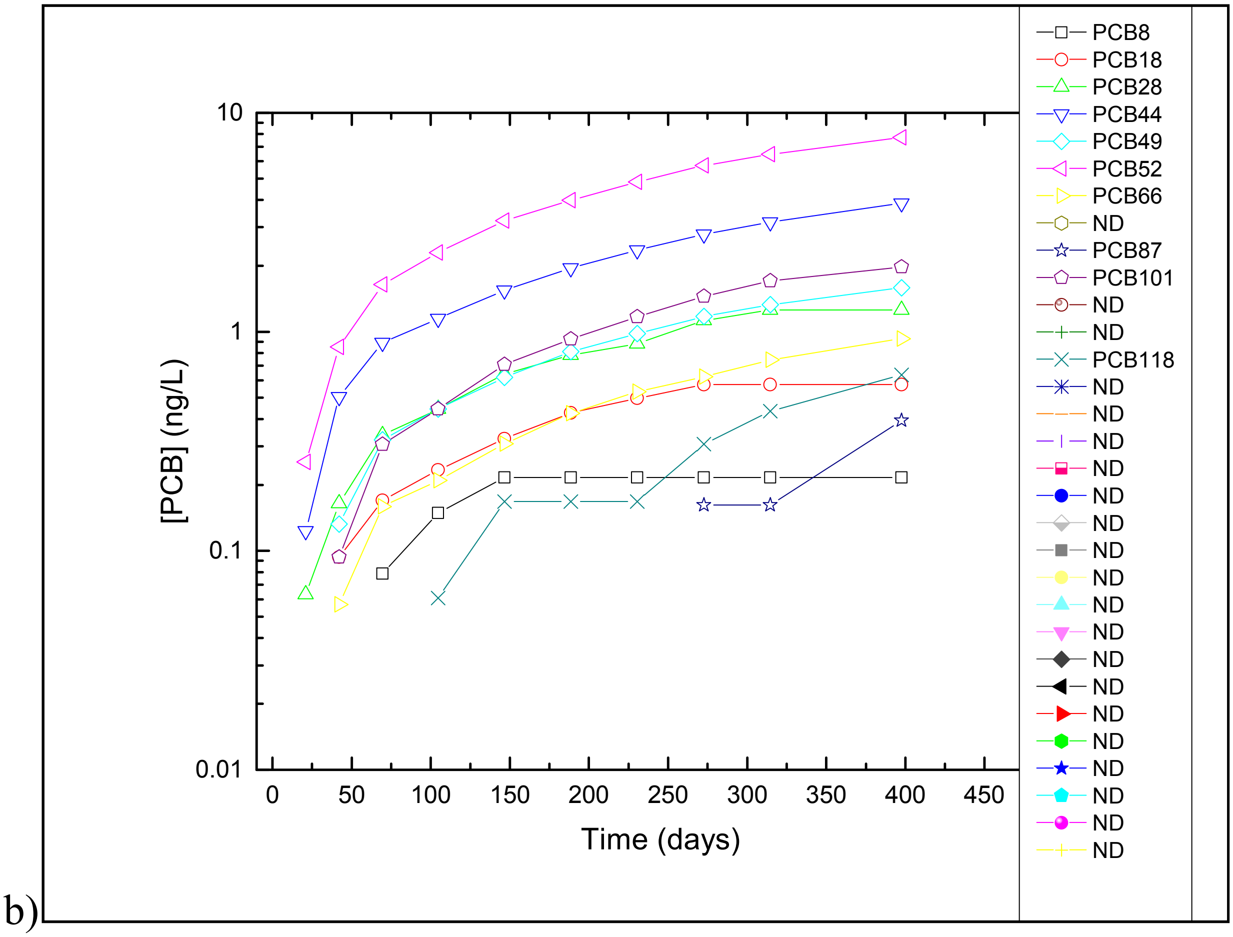


Figure 21 (a–b). Experimental PCB concentration versus leaching time for BRPHL at 4 °C and ~1 bar containing 0.19 wt% (4.1 mg) tPCBs exposed to a total volume of 12.07 L of ASW leachate for a period of 400 days. Plot (a) shows tPCBs concentration and contributing homolog group concentration versus leaching time, where the sum of the homolog curves is equal to the upper tPCB curve. Plot b shows target congener concentrations within homolog groups Cl1 through Cl5 versus leaching time.

Figure 22 shows total released homolog and congener distributions or distributions compared with the initial PCB distributions determined for BRPHL solid. All homologs and congeners detected are normalized and plotted as percent of measured tPCBs in each matrix (leachate versus solid). The solid distributions correspond to the pre-leaching PCB content in BRPHL solid, derived from the mass balance performed for the leaching experiment. 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 distributions. The highest levels of release from BRPHL were from homolog groups Cl1 through Cl5 (Cl4 > Cl5 > Cl3 > Cl1 > Cl2).

Fingerprints for specific BRPHL leachate samples are plotted at key intervals across the entire leaching experiment (exposure time). Figure 23 corresponds to the homolog group and congener distributions in samples at (a) an initial pre-maximum leach rate (iLR), (b) the maximum leach rate (mLR), (c) a post-maximum leach rate (pmLR), and (d) the final empirical leach rate (fLR).

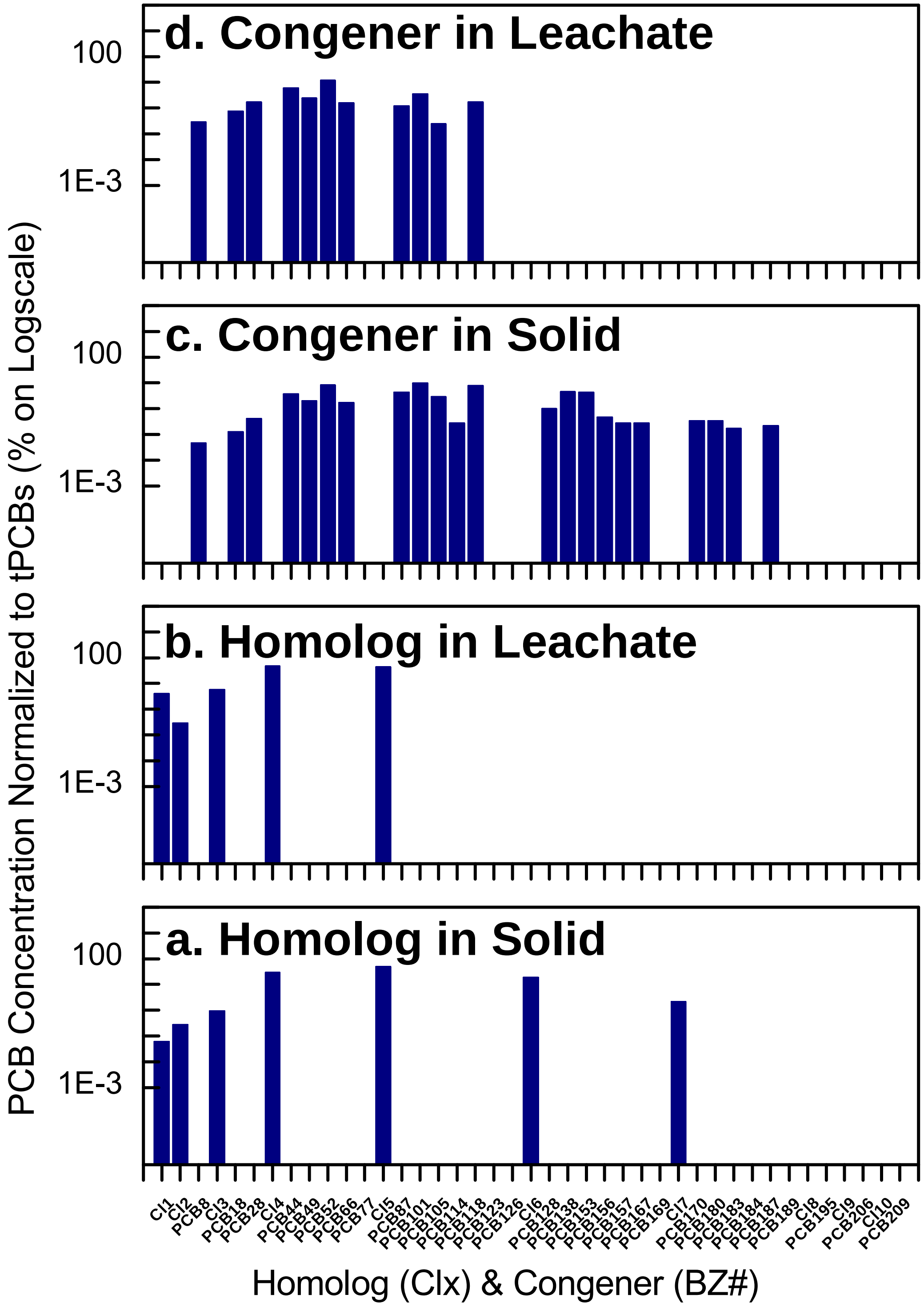


Figure 22 (a–d). Experimental homolog and congener PCB distributions at 4 °C and ~1 bar for BRPHL solid (a and c) compared with total homolog and congener distributions of PCBs leached from BRPHL into seawater (b and d). The leachate distributions are derived from all PCBs released, also depicted as the cumulative leachate concentration endpoint for detected analytes in Figure 21.

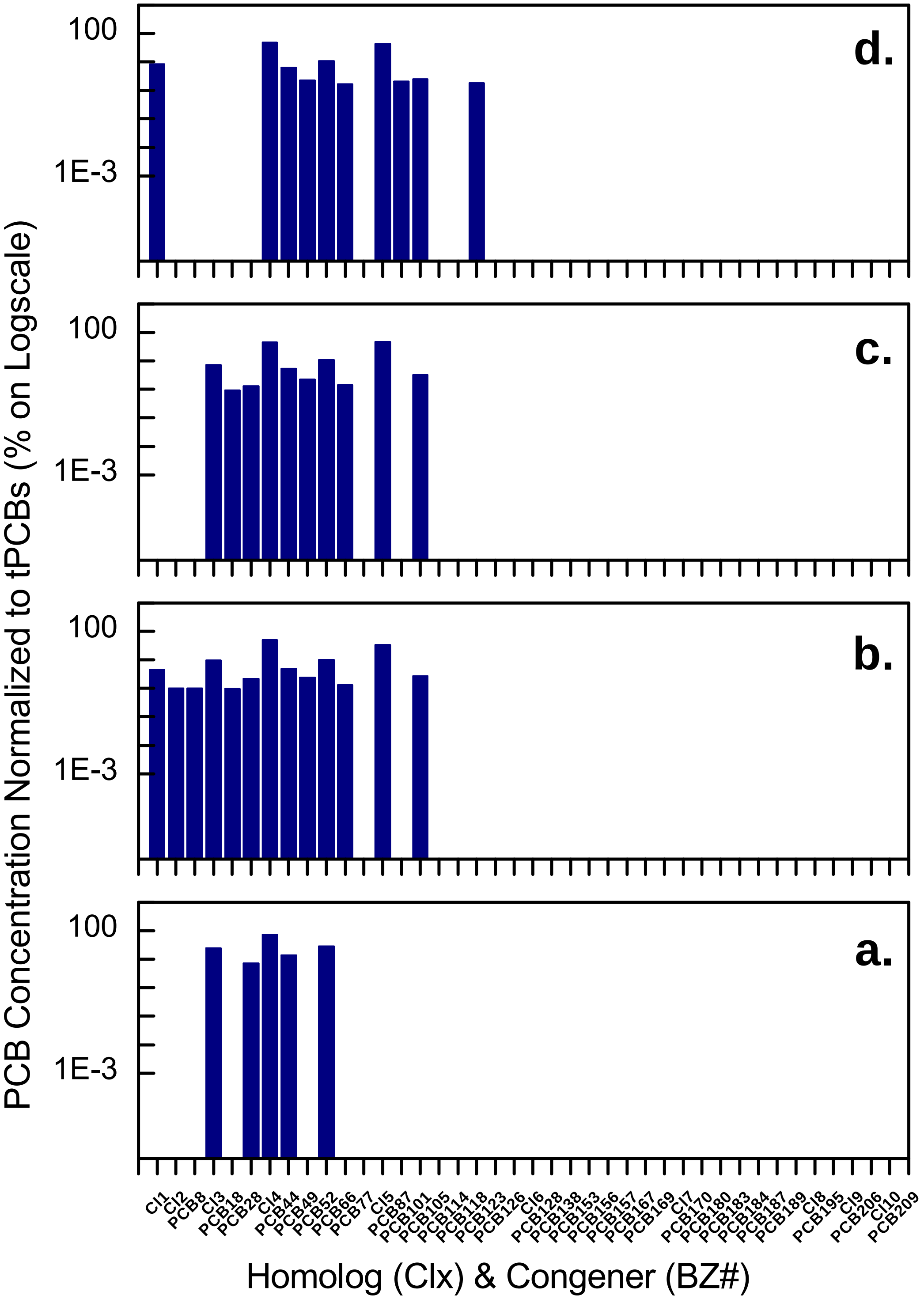


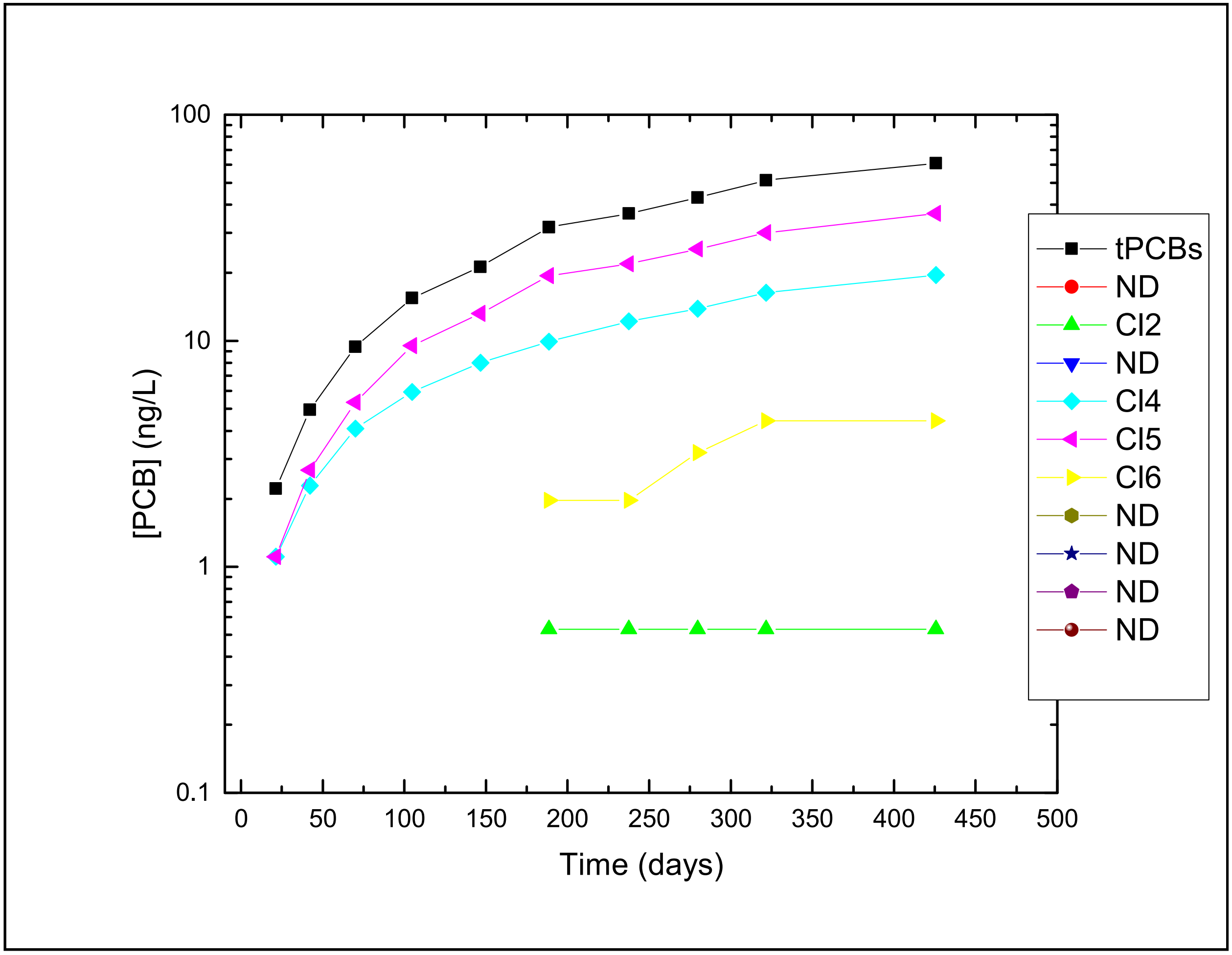
Figure 23 (a–d). Homolog and congener distributions during the 4 °C and ~1 bar BRPHL leaching experiment, normalized as percent of total, corresponding to leaching intervals: (a) iLR – 21 d, (b) mLR – 70 d, (c) pmLR – 231 d, and (d) fLR – 398 d.

3.4.3. Electrical Cable (EC) Leaching Behavior

Leaching Behavior at 4°C/1 bar

Leaching concentration behaviors for EC leached at 4 °C and ~1 bar includes contributions from homologs Cl2 and Cl4 – Cl6, as shown in Figure 24 (a). Each of these homolog groups and contributions from target congeners are plotted in Figure 24 (b). The total exposure volume of seawater leachate was 12.02 L for EC (27.64 g) containing 30.6 mg tPCBs (0.111 wt%). Note also significant attenuation exists for homologue groups Cl2 and Cl6 that initially released (horizontal line behavior). Leaching from EC was dominated by Cl5 where Cl5 > Cl4 >> Cl6 >> Cl2. Most abundant congeners leached from EC were 101 > 44 = 118 > 87 with detectable levels 5 other congeners.

a)



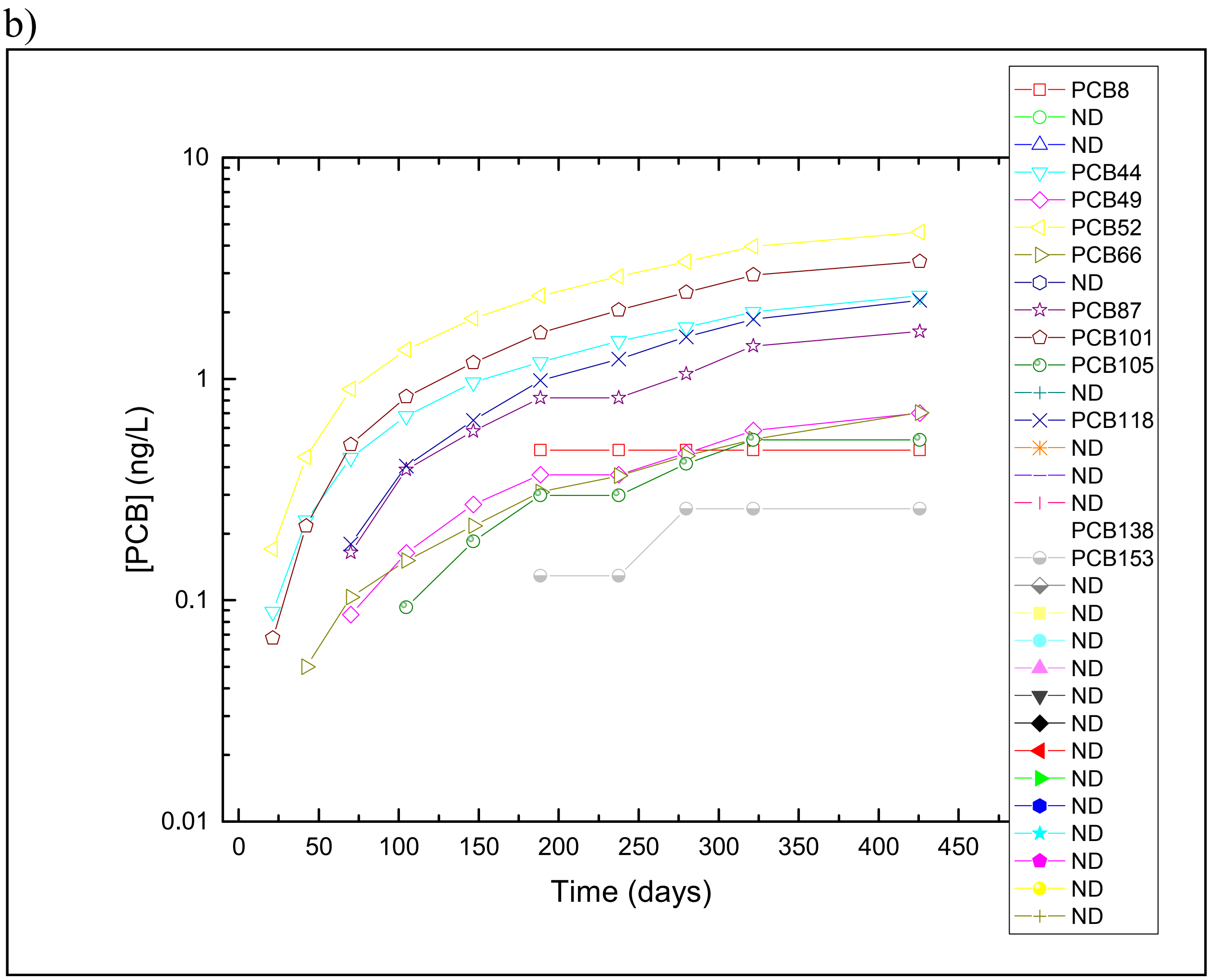


Figure 24 (a–b). Cumulative PCB concentration versus leaching time for EC containing 0.11 wt% (30.6 mg) tPCBs exposed to a total volume of 12.02 L of ASW leachate. Plot (a) shows the tPCBs concentration and contributing homolog group concentrations versus leaching time for EC, where the sum of the homolog curves is equal to the upper tPCB curve. Plot (b) corresponds to target congener concentrations within homolog groups Cl2 and Cl4-Cl6 versus leaching time.

Total released homolog and congener distributions or distributions are compared with the initial PCB distributions determined for EC solid in Figure 25. All detected homologs and congeners were normalized and plotted as percent of measured tPCBs in each matrix (leachate versus solid). 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. 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 distributions. The highest levels of release from EC solid were from homolog groups Cl4 and Cl5.

Normalized distributions for specific EC leachate samples are presented below at key intervals across the entire leaching experiment (exposure time). Figure 26 shows the homolog group and congener distributions corresponding to (a) an initial pre-maximum leach rate (iLR), (b) the maximum leach rate (mLR), (c) a post-maximum leach rate (pmLR), and (d) the final empirical leach rate (fLR).

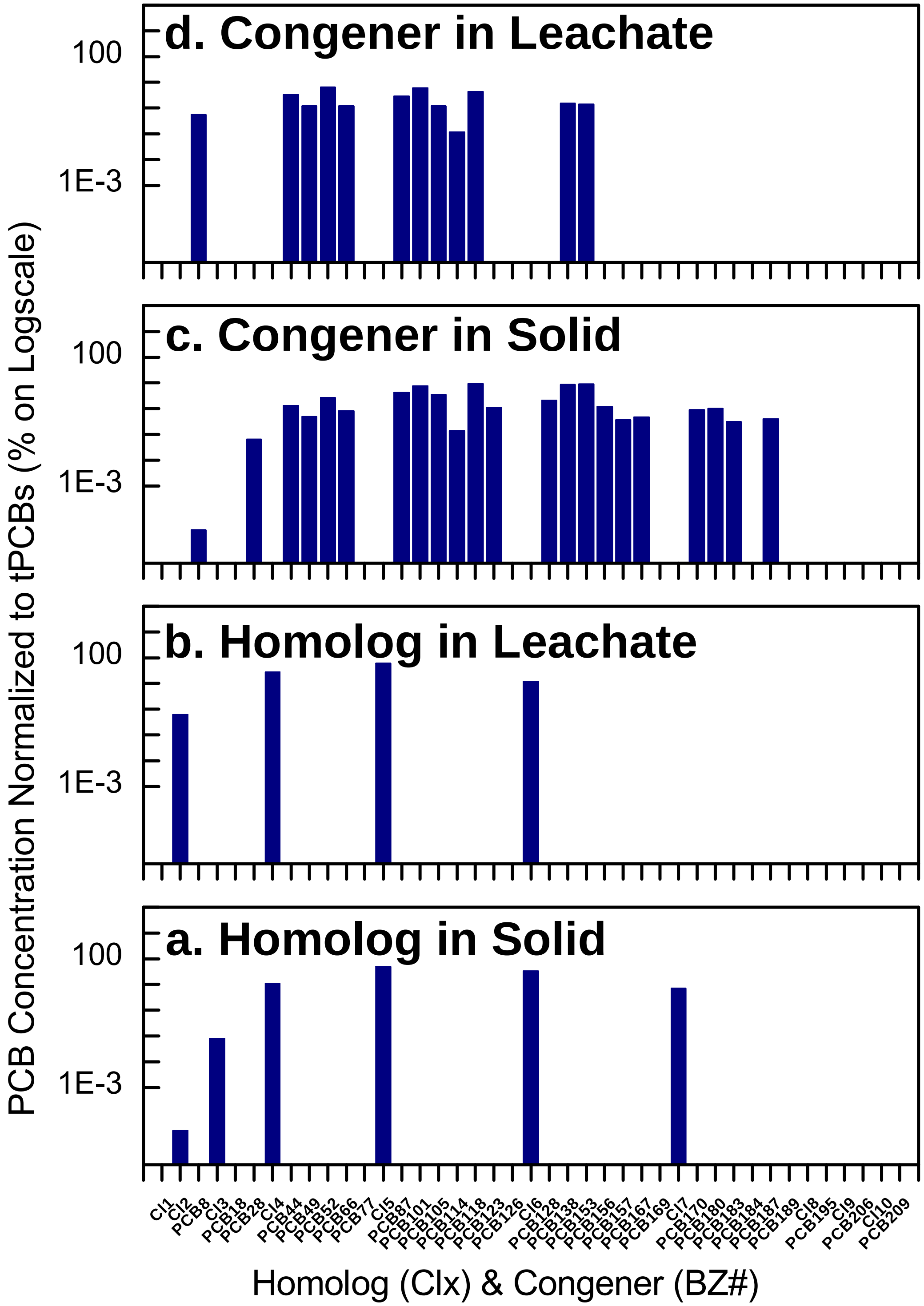


Figure 25 (a–d). Experimental homolog and congener PCB distributions at 4 °C and ~1 bar for EC solid (a and c) compared with total homolog and congener distributions of PCBs leached from EC into seawater (b and d). Leachate distributions are derived from all PCBs released, which also corresponds to the cumulative leachate concentration endpoint for analytes plotted in Figure 24.

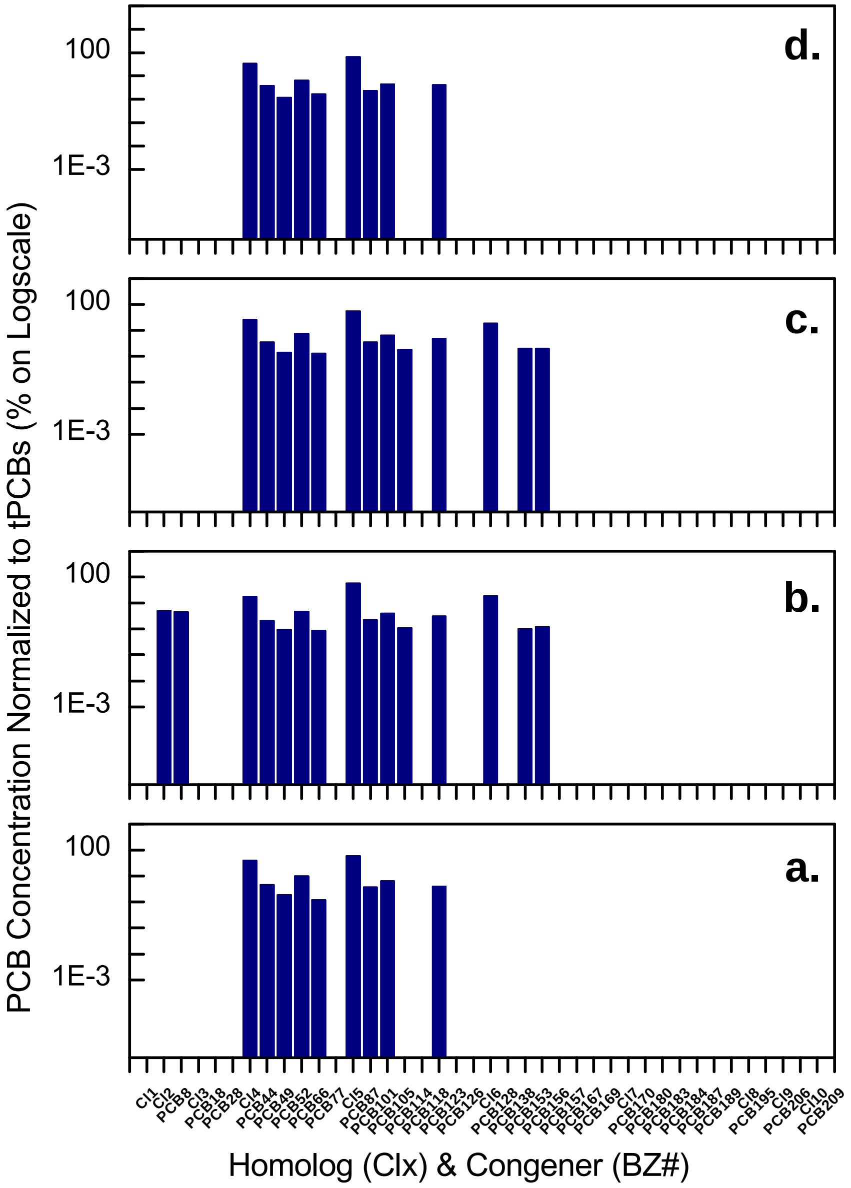
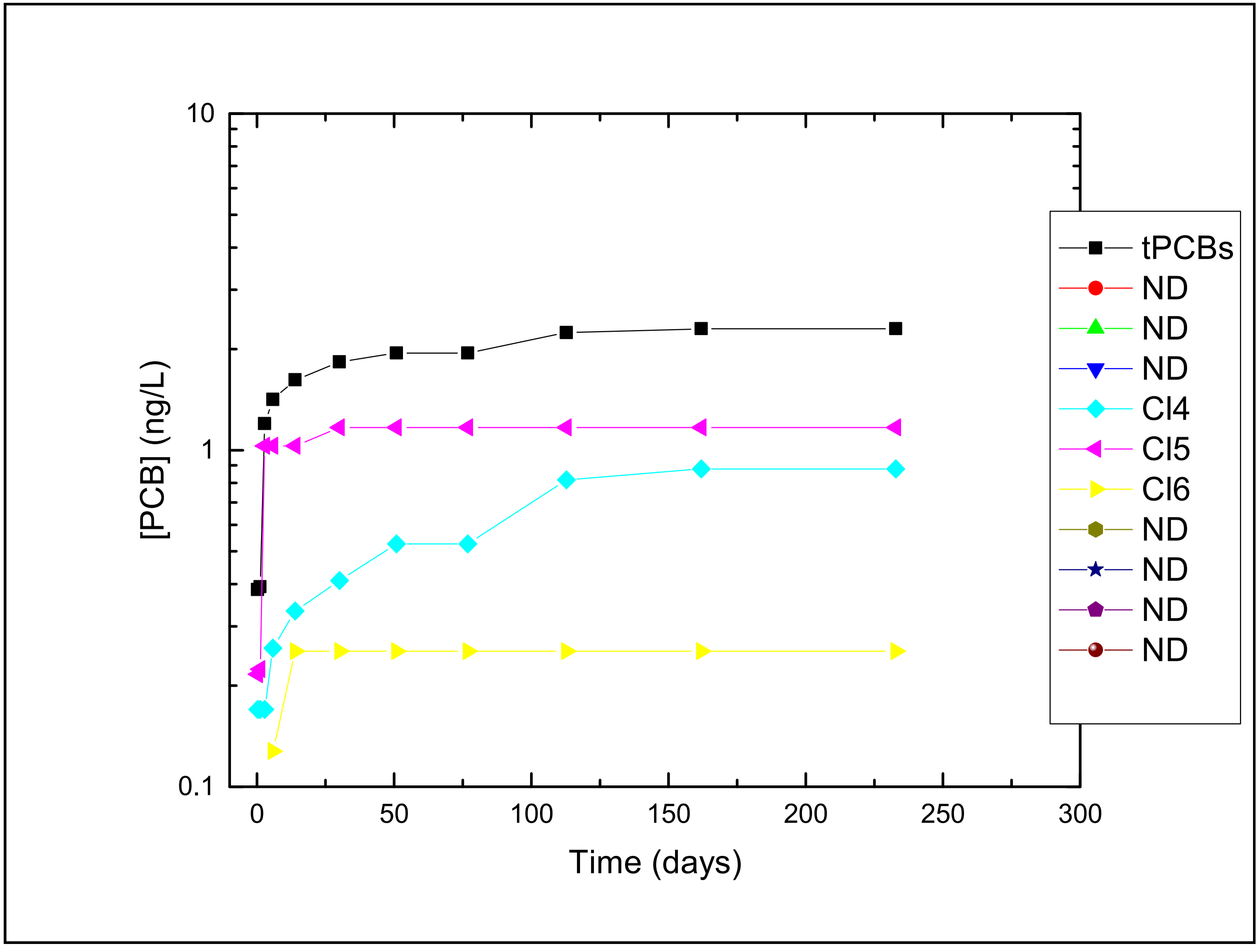


Figure 26 (a–d). Homolog and congener distributions during the 4 °C and ~1 bar EC leaching experiment, normalized as percent of total, corresponding to the following leaching interval: (a) iLR – 70 d, (b) mLR – 189 d, (c) pmLR – 280 d, and (d) fLR – 426 d.

Leaching Behavior at 4 ^{o}C/300 bar

Electrical cable was also tested at at 4 °C and 300 bar, for which 28.065g of EC was evaluated in a total volume of 10.9 L. Homolog and congener concentration plots are included below (Figure 27), followed by PCB fingerprints in the solid and leachate at various leaching times throughout the experiment (Figures 28 and 29). 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. The logscale was used to make variances at very low sub-percentage levels visible**.** Detections were only observed for groups Cl5 > Cl4 >> Cl6 , while other homolog groups were not detected over the course of the experiment.

a)


10
1
0.1
[PCB] (ng/L)
0
50
100
150
200
250
300
Time (days)
tPCBs
ND
ND
ND
Cl4
Cl5
Cl6
ND
ND
ND
ND

b)

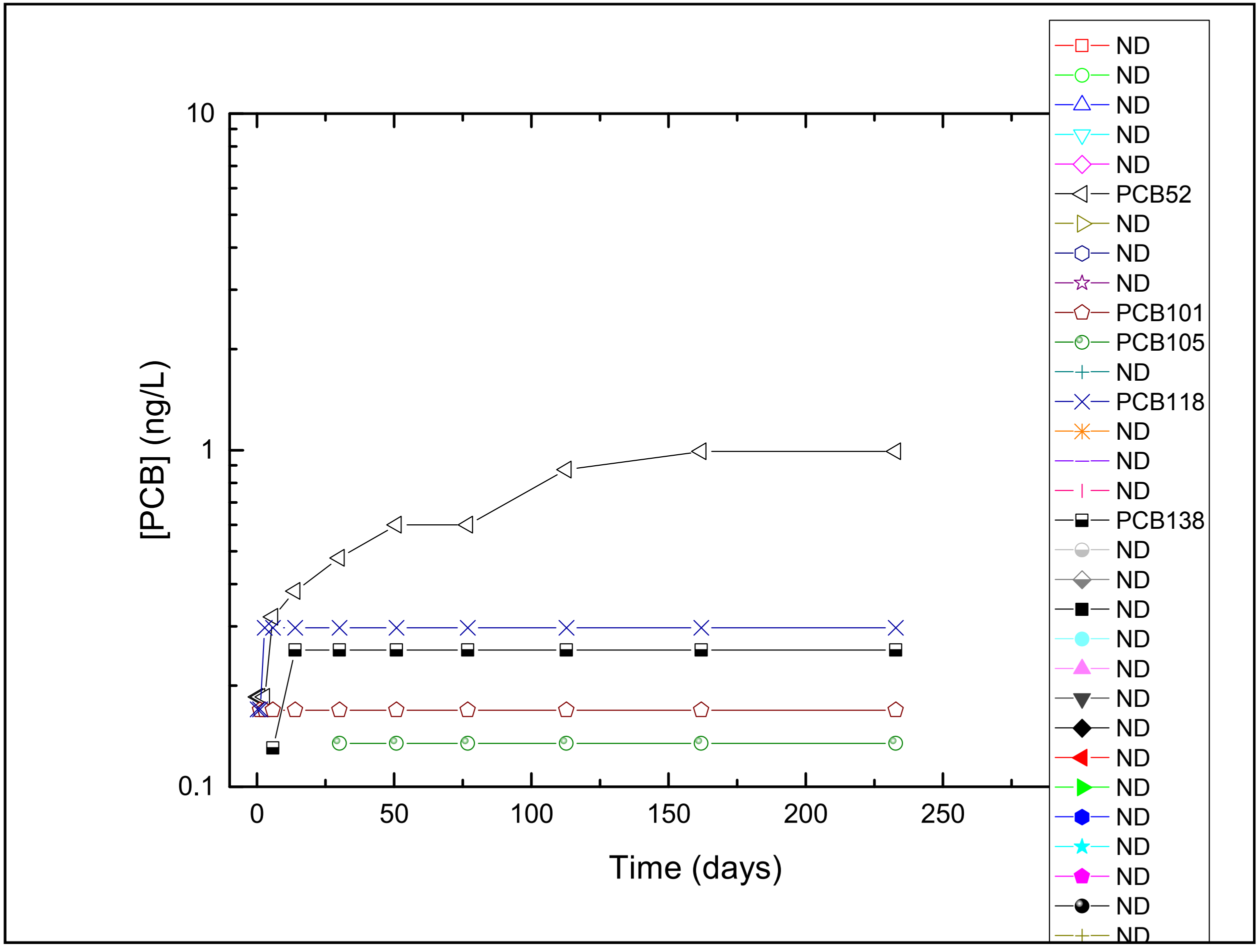


Figure 27 (a–b). Cumulative PCB concentration versus leaching time for EC containing 0.0865 wt% (24.3 mg) tPCBs exposed to a total volume of 10.9 L of ASW leachate for 240 days. Plot (a) shows the tPCBs concentration and contributing homolog group concentrations versus leaching time for EC, where the sum of the homolog curves is equal to the upper tPCB curve. Plot (b) corresponds to target congener concentrations within homolog groups Cl4-Cl6 versus leaching time.

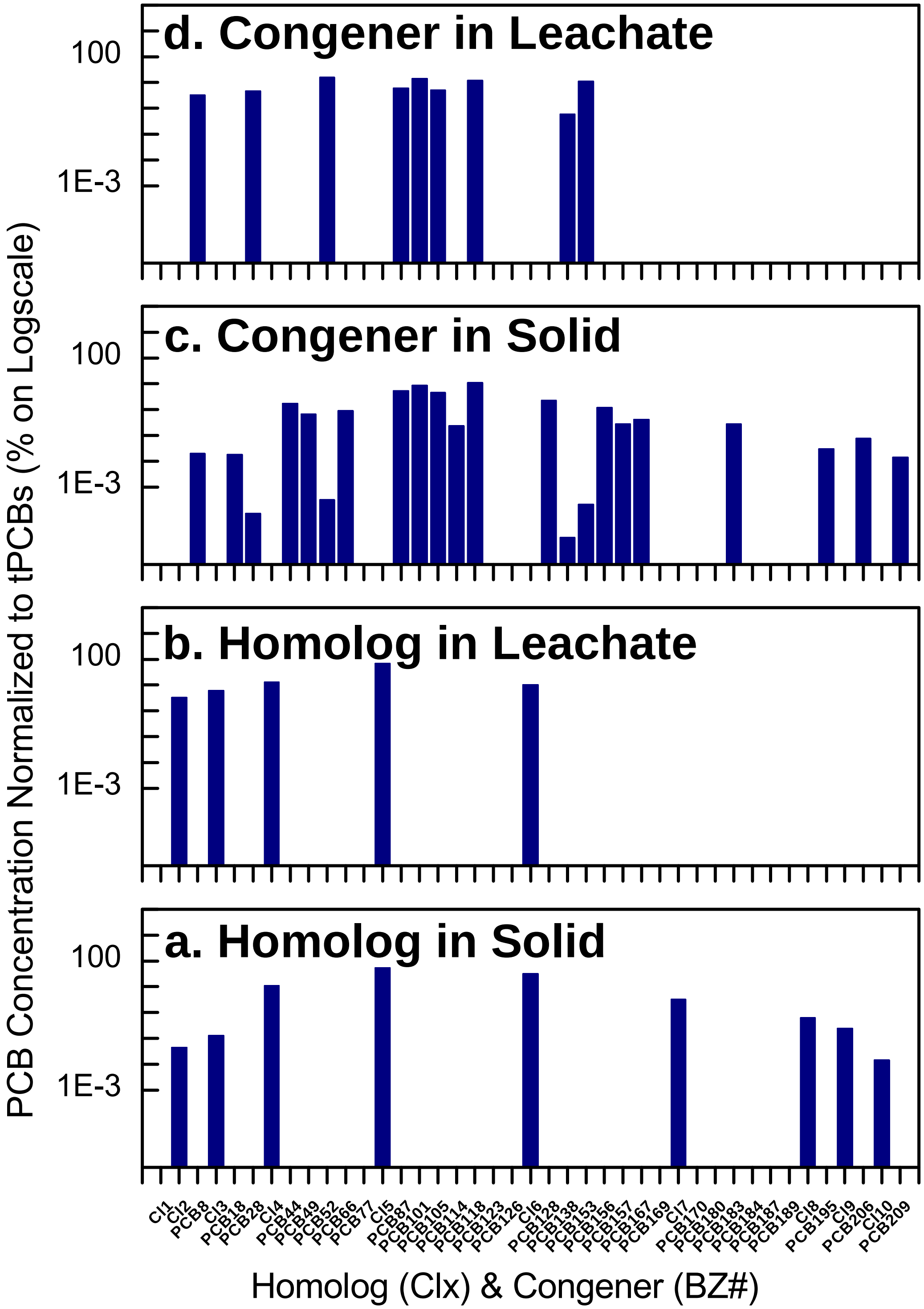


Figure 28 (a–d). Experimental homolog and congener PCB distributions at 4 °C and 300 bar for EC solid (a and c) compared with total homolog and congener distributions of PCBs leached from EC into seawater (b and d). Leachate distributions are derived from all PCBs released, which also corresponds to the cumulative leachate concentration endpoint for analytes in Figure 27.

These EC results showed a different solid fingerprint pattern than EC tested at ambient pressure, with the observation of more Cl7 congeners in the latter, but the presence of Cl8, Cl9, and Cl10 homologues & congeners in the former. Despite these solid differences, congeners and homologs detected measured in leachate were quite similar, meaning the EC matrix appeared to hold onto the higher MW congeners more tightly.

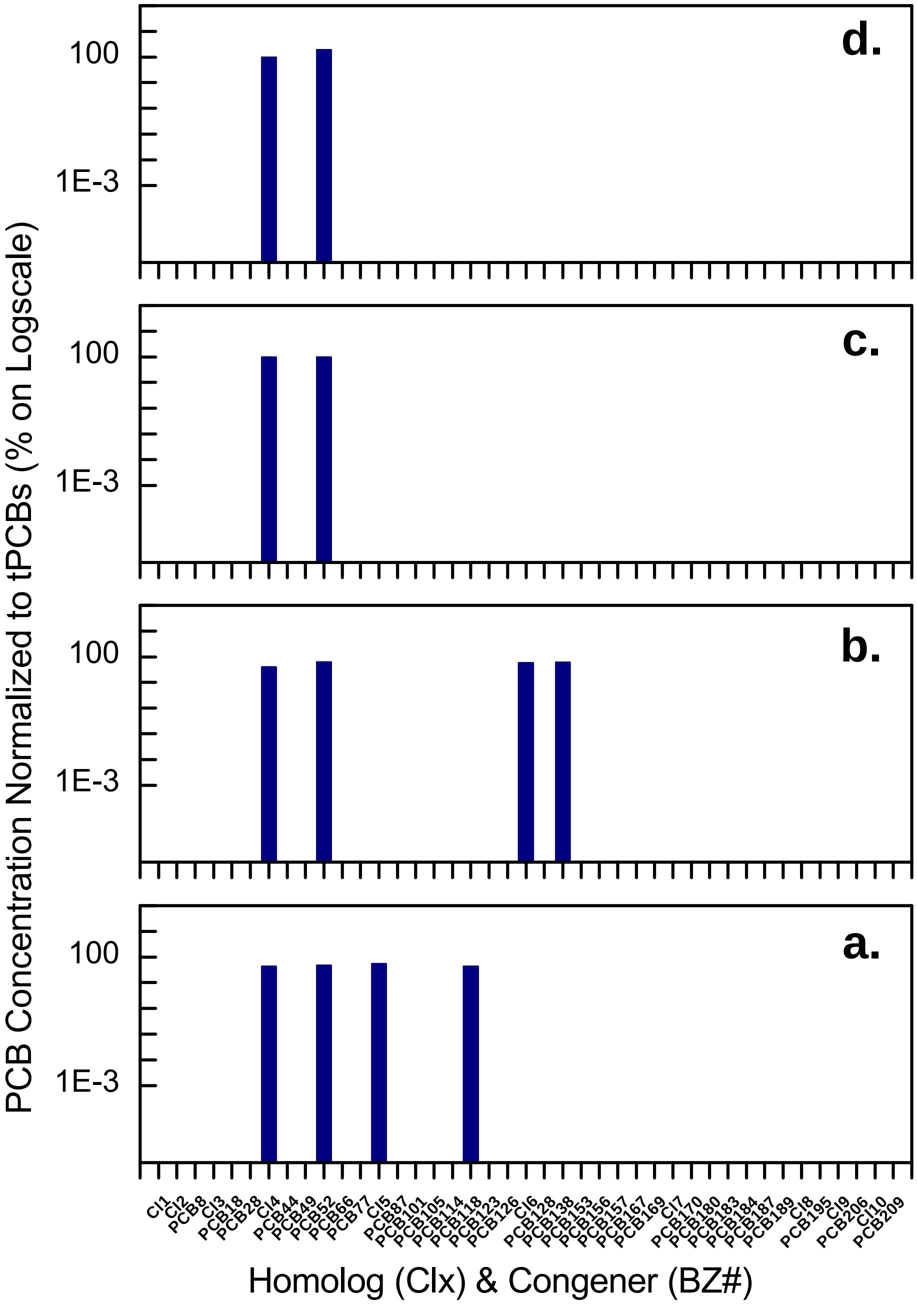
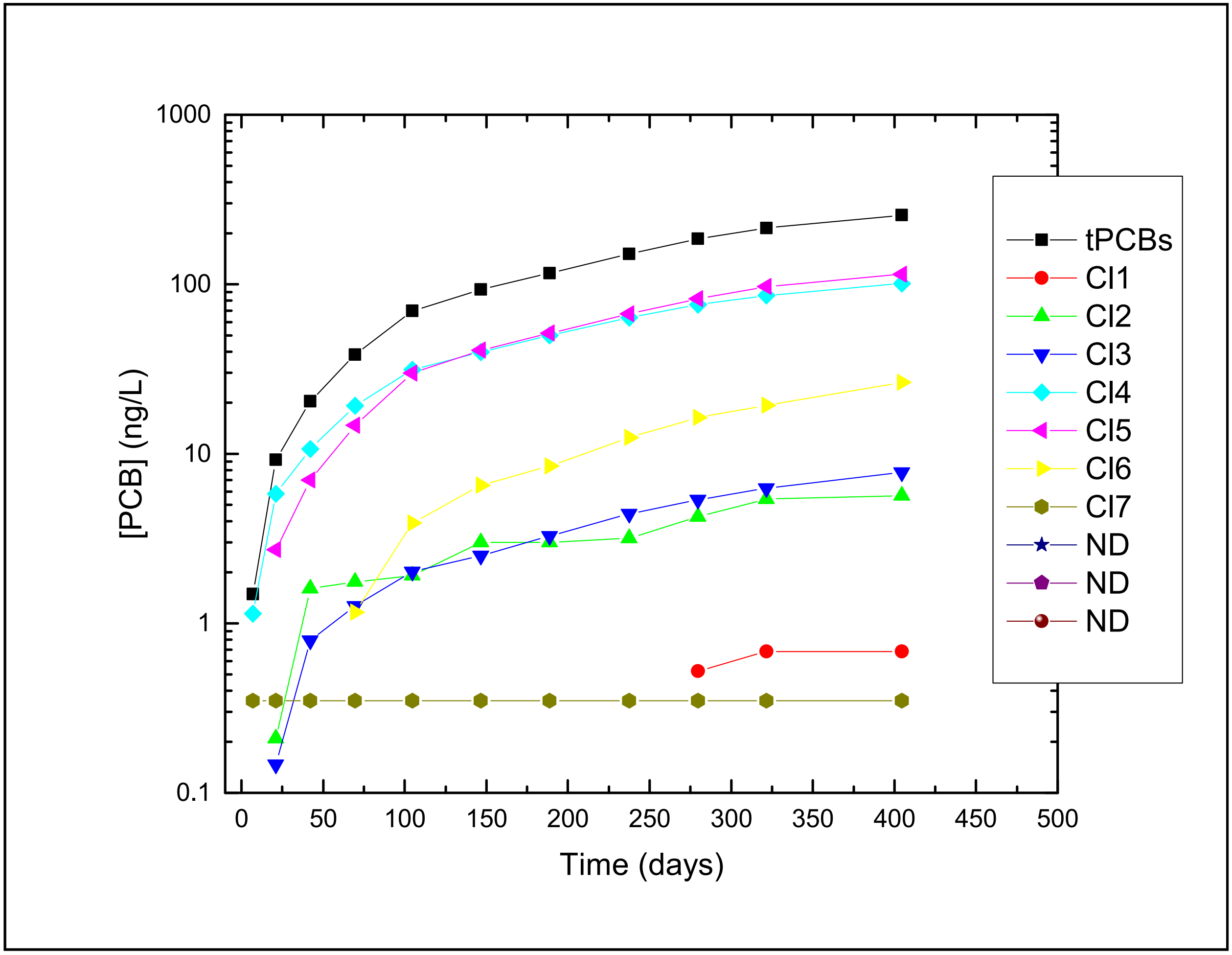


Figure 29 (a–d). Homolog and congener distributions during the 4 °C and 300 bar EC leaching experiment, normalized as percent of total, corresponding to leaching intervals: (a) iLR & mLR – 0.25 d, (b) pmLR – 5.8 d, (c) pmLR – 51 d, and (d) fLR – 162 d.

3.4.4. Foam Rubber/Ensolite® (FRE) Leaching Behavior

Figure 30 (a) includes contributions from homologs Cl2 through Cl7 to the tPCB concentration behavior for FRE leached at 4 °C and ~1 bar. The FRE solid (2.44 g) contained 17.9 mg tPCBs (0.732 wt%) and was exposed to a total volume of 12.11 L of ASW leachate over the leaching period of 405 days. Target PCB congener concentration curves that contribute to each of these homolog group behaviors are shown in Figure 30 (b). Homologues were dominated by Cl 5 ~ Cl4 >> Cl6 > Cl3 ~ Cl2 and the congeners were dominated by PCB52 > PCB44 ~ PCB101 > PCB118 ~ PCB87 ~ PCB49 with relatively minor contributions from other congeners.

a)



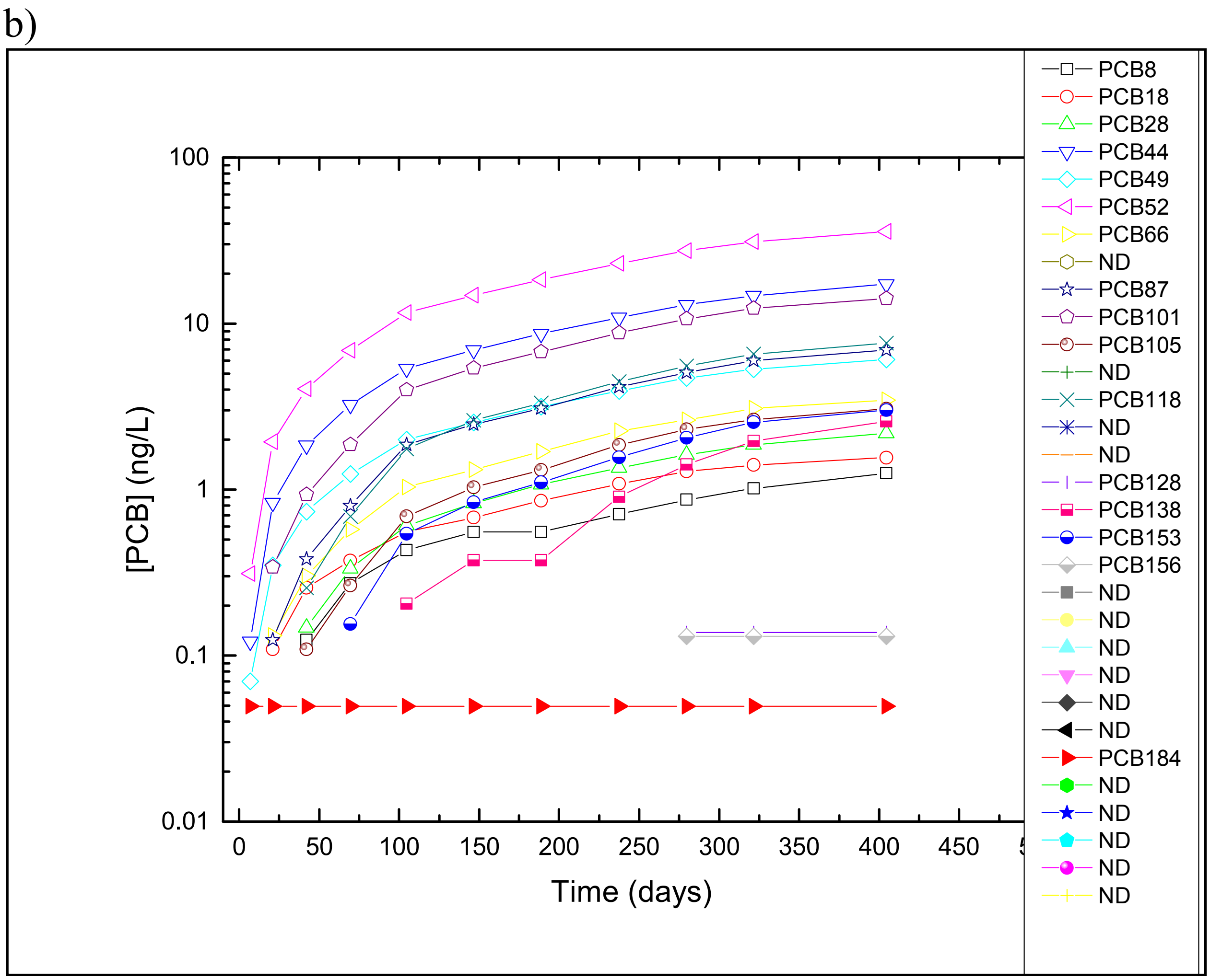


Figure 30 (a–b). Cumulative PCB concentration versus leaching time for FRE containing 0.732 wt% (17.9 mg) tPCBs exposed to a total volume of 12.11 L of ASW leachate over 405 days. Plot (a) shows the tPCBs concentration and contributing homolog group concentrations versus leaching time, where the sum of the homolog curves is equal to the upper tPCB curve. Plots (b) are the corresponding target congener concentrations within homolog groups Cl2 through Cl7 versus leaching time.

Figure 31 shows total released homolog and congener distributions or distributions compared with the initial PCB distributions determined for FRE solid. Detected homologs and congeners were normalized and plotted as percent of measured tPCBs in each matrix (leachate versus solid). The solid distributions correspond to the pre-leaching PCB content in FRE solid, determined from the leaching experiment mass balance. 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 distributions. The highest levels of release from FRE were from homolog groups Cl2 through Cl6. Cl5 and Cl6 dominated in the solid while Cl4 and Cl5 were highest in leachate, and Cl1, Cl2, and Cl3 made up a higher percentage in the leachate than solid, while Cl7 was detected both in the solid and the leachate.

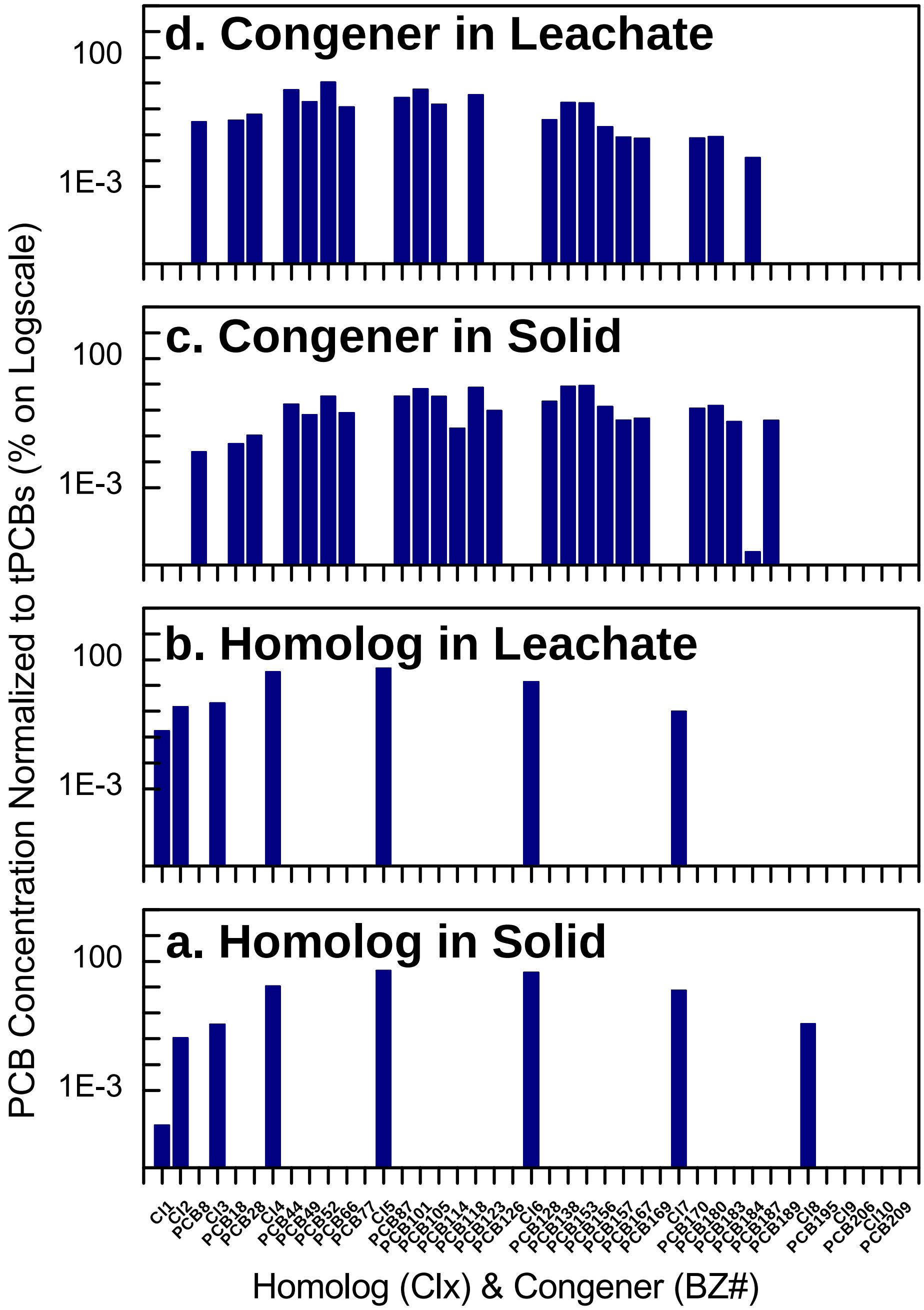


Figure 31 (a–d). Experimental homolog and congener PCB distributions for FRE solid (a and c) compared with total homolog and congener distributions of PCBs leached from FRE into ASW (b and d). The leachate distributions correspond to all PCBs released over the leaching experiment, also represented by the cumulative leachate concentration endpoint for analytes plotted in Figure 30.

Normalized distributions corresponding to specific FRE leachate samples are presented below at key intervals across the entire leaching experiment (exposure time). Figure 32 corresponds to the homolog group and congener distributions at (a) the initial leach rate (iLR), (b) the maximum leach rate (mLR), (c) the post maximum leach rate (pmLR), and (d) the final empirical leach rate (fLR).

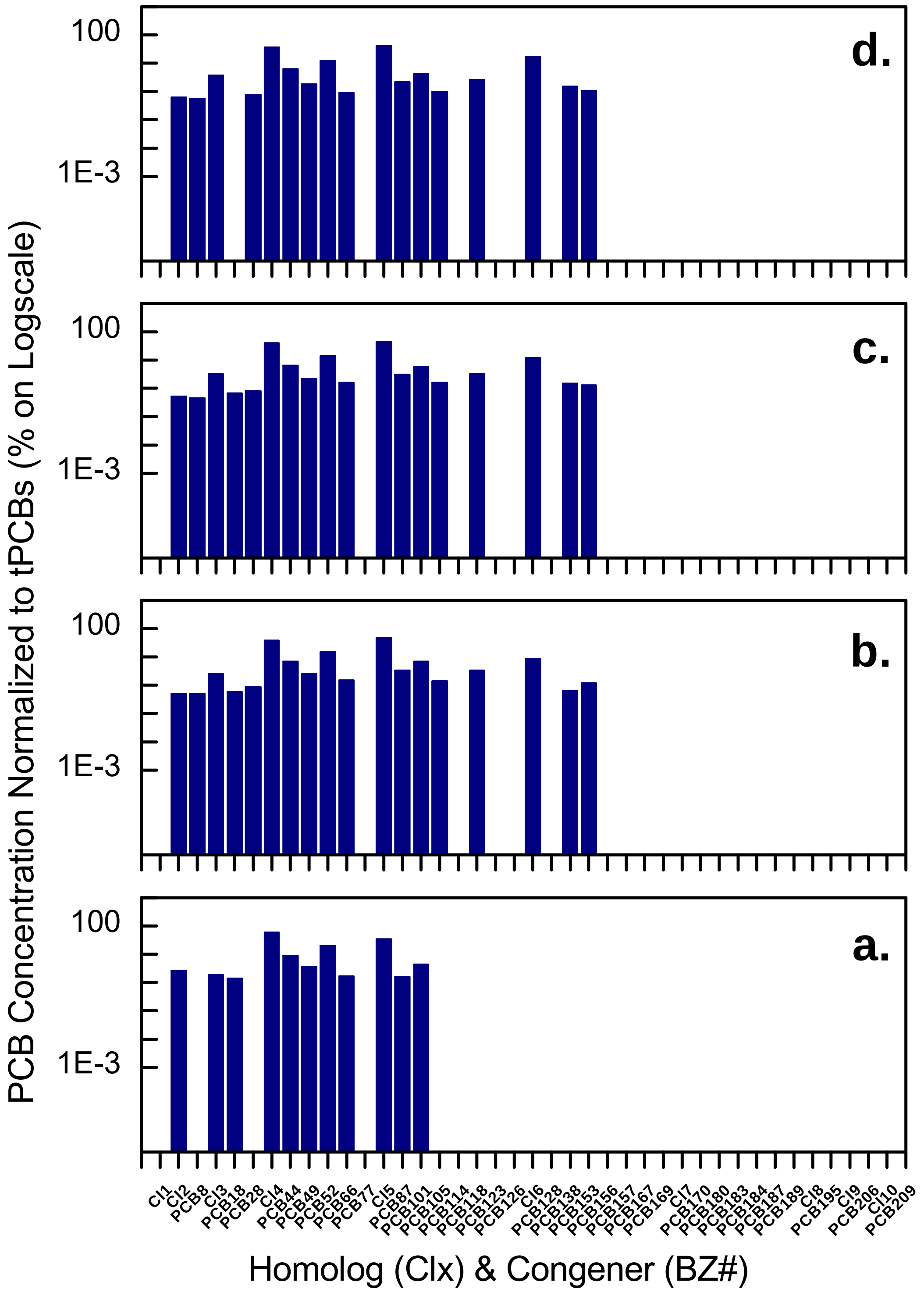
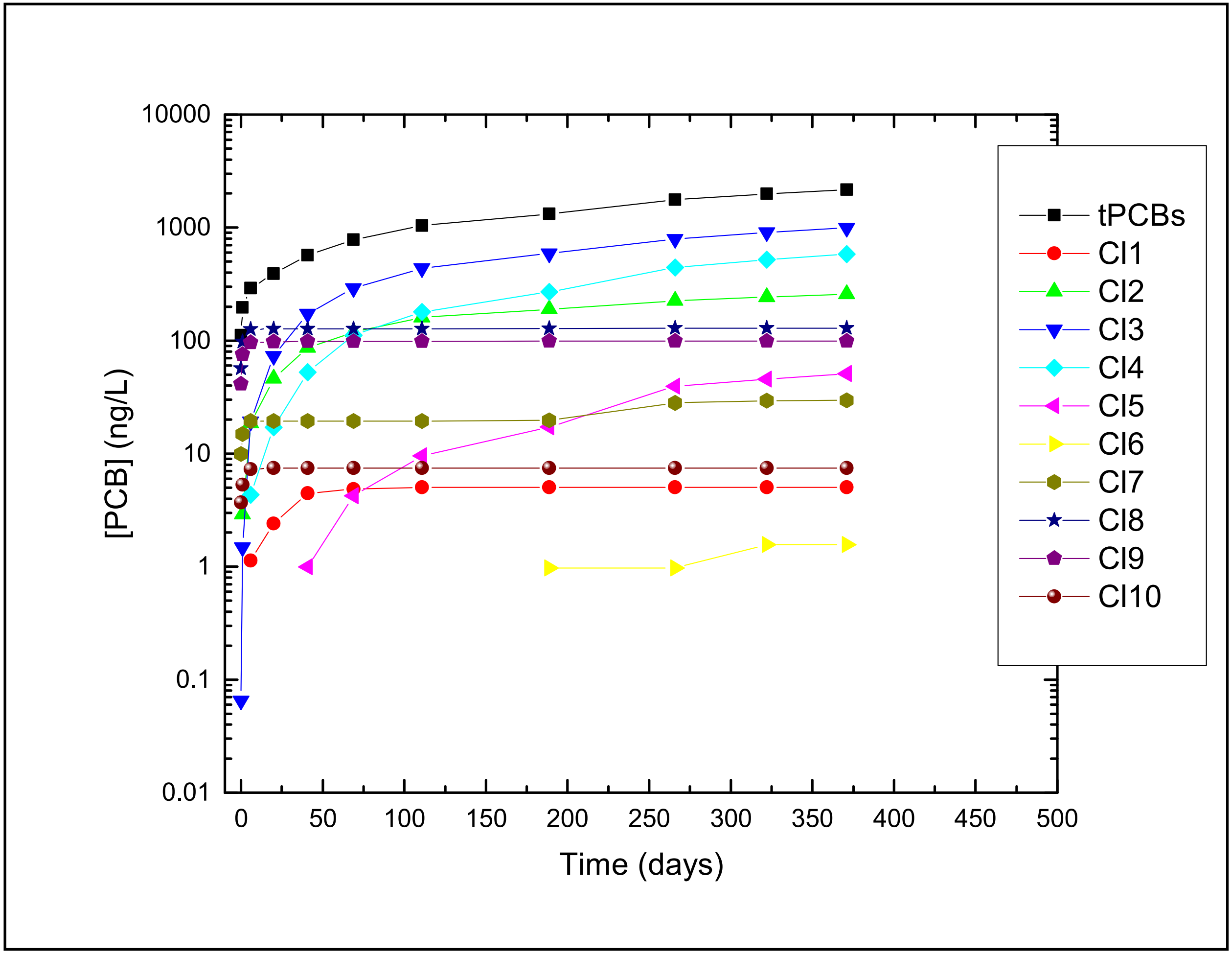


Figure 32 (a–d). Homolog and congener distributions during the FRE leaching experiment, normalized as percent of total, for the following leaching intervals: (a) iLR – 21 d, (b) mLR – 105 d, (c) pmLR – 238 d, and (d) fLR – 405 d.

3.4.5. Aroclor® 1268 (A1268) Analytical Control Dissolution Behavior

The 4 °C/~1 bar results for this positive analytical control, 20.1 mg exposed to a total of 10.25 L of ASW over the nearly 400-day experiment, is shown in Figure 33 (a), and includes contributions to the tPCB concentration from all homolog groups, Cl3 > Cl4 > Cl2 > Cl8 ~ Cl9 > Cl5 > Cl7 > Cl10 ~ Cl1 > Cl6. The corresponding target congeners are plotted in Figure 33 (b), dominated by PCB18 > PCB28 > PCB8 > PCB52 ~ PCB44 > PCB206 (only twice early on) > PCB49 ~ PCB66, with others only minimally contributing. 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 14.

a)



b)

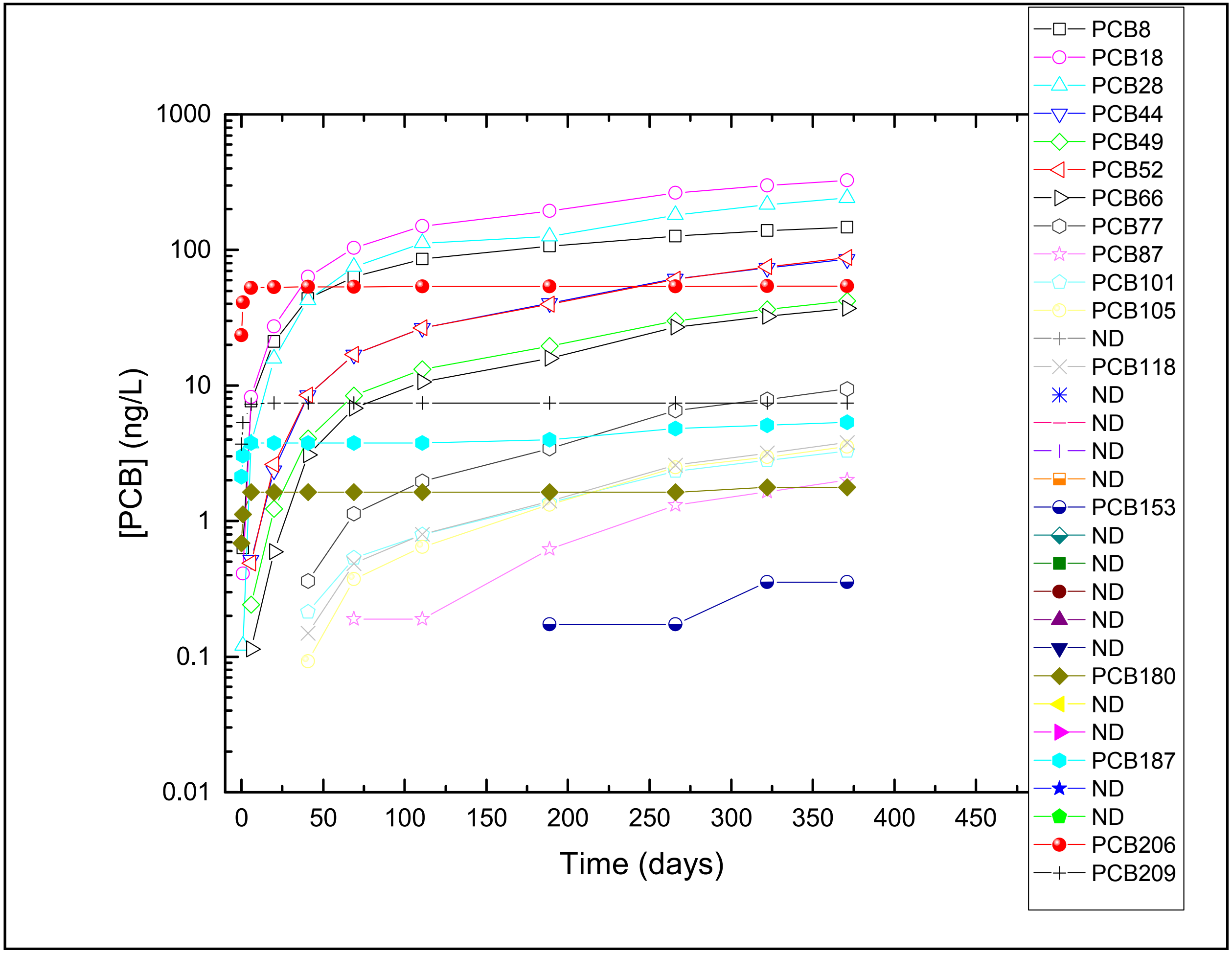


Figure 33 (a–j). Cumulative PCB concentration versus exposure time for 20.1 mg of A1268 in a total volume of 10.25 L of seawater for ~375 days. Plot (a) shows experimental tPCBs concentration and contributing homolog group concentrations versus time, where the sum of the homolog curves is equal to the upper tPCB curve. Plots (b) are target congener concentrations within homolog groups Cl1 through Cl10 versus time.

Figure 34 shows total released homolog and congener distributions compared with the initial PCB distributions determined for neat A1268 "solid." All homologs and congeners detected are normalized and plotted as percent of measured tPCBs in each matrix (ASW versus solid). Solid distributions correspond to the initial pre-exposure PCB content in A1268 solid, determined from the experiment mass balance. 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 distributions. All homolog groups were detected in the neat A1268 and leachate, with the highest levels of release from neat A1268 in homolog groups Cl2 through Cl5 and Cl7, even though the highest percentages of homologs in th eneat A1268 were in Cl8, Cl9, and Cl10. A similar pattern was evident in the congener fingerprints, with PCB18 and PCB128 highest in the leachate, while PCB206 and PCB209 were highest in the neat A1268.

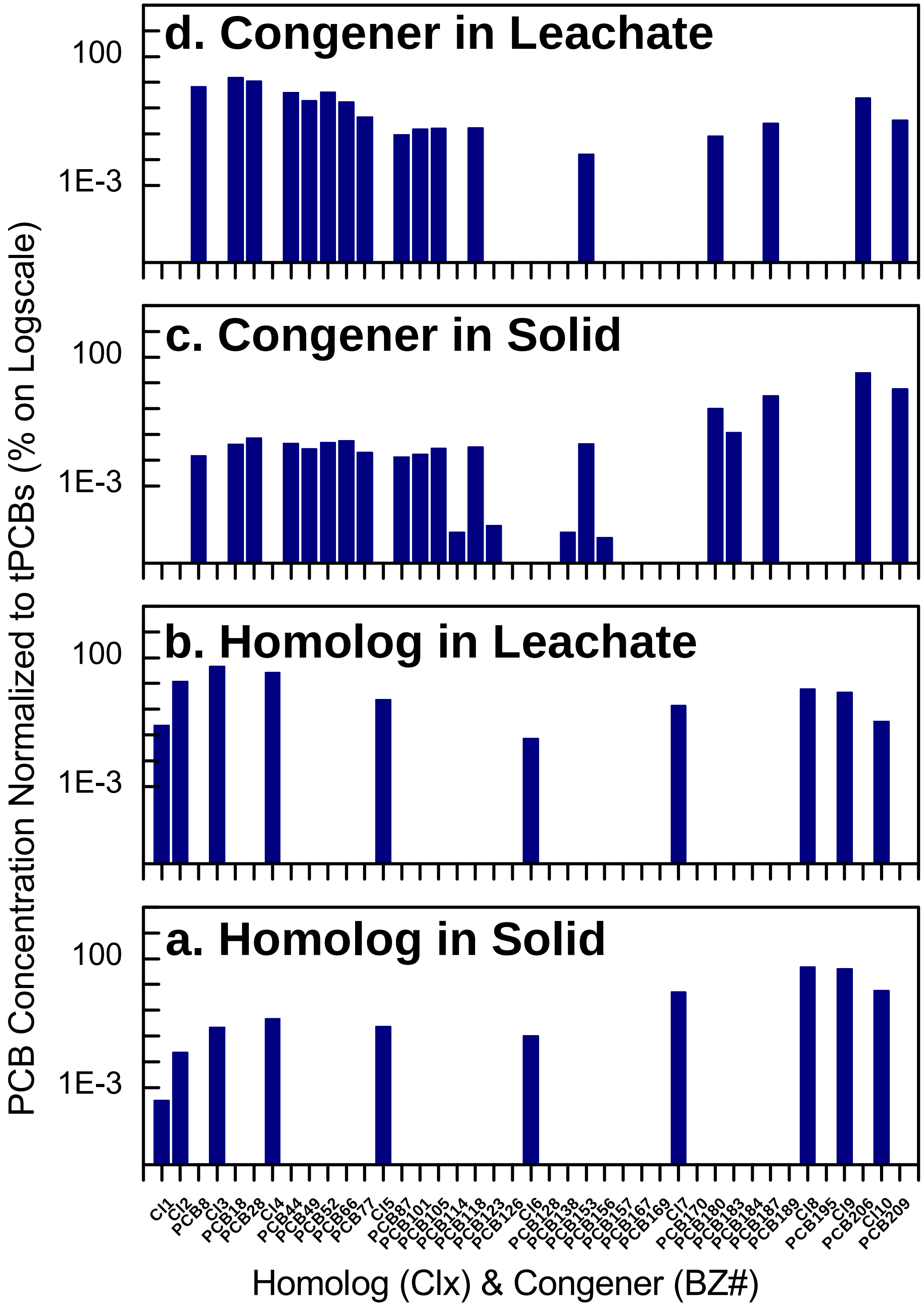


Figure 34 (a–d). Experimental homolog and congener PCB distributions for neat A1268 solid (a and c) compared with total homolog and congener distributions of PCBs released from neat A1268 into seawater (b and d). ASW distributions correspond to all PCBs released from A1268 during the experiment and also to the cumulative concentration endpoint for analytes plotted in Figure 33.

Fingerprints for specific A1268 seawater samples are included at key intervals across the entire experiment (exposure time). Figure 35 shows homolog groups corresponding to (a) the initial and maximum observed dissolution rate (iLR and mLR) and narrowest distribution of congeners and homologs, (b) the post maximum leach rate appearance of Cl1, Cl4, and Cl5 homolog contributions (pmLR1), (c) the broadest homolog and congener distributions with additional post maximum leach rate appearance of Cl6-Cl8 contributions (pmLR2), and (d) the final empirical dissolution rate (fLR).

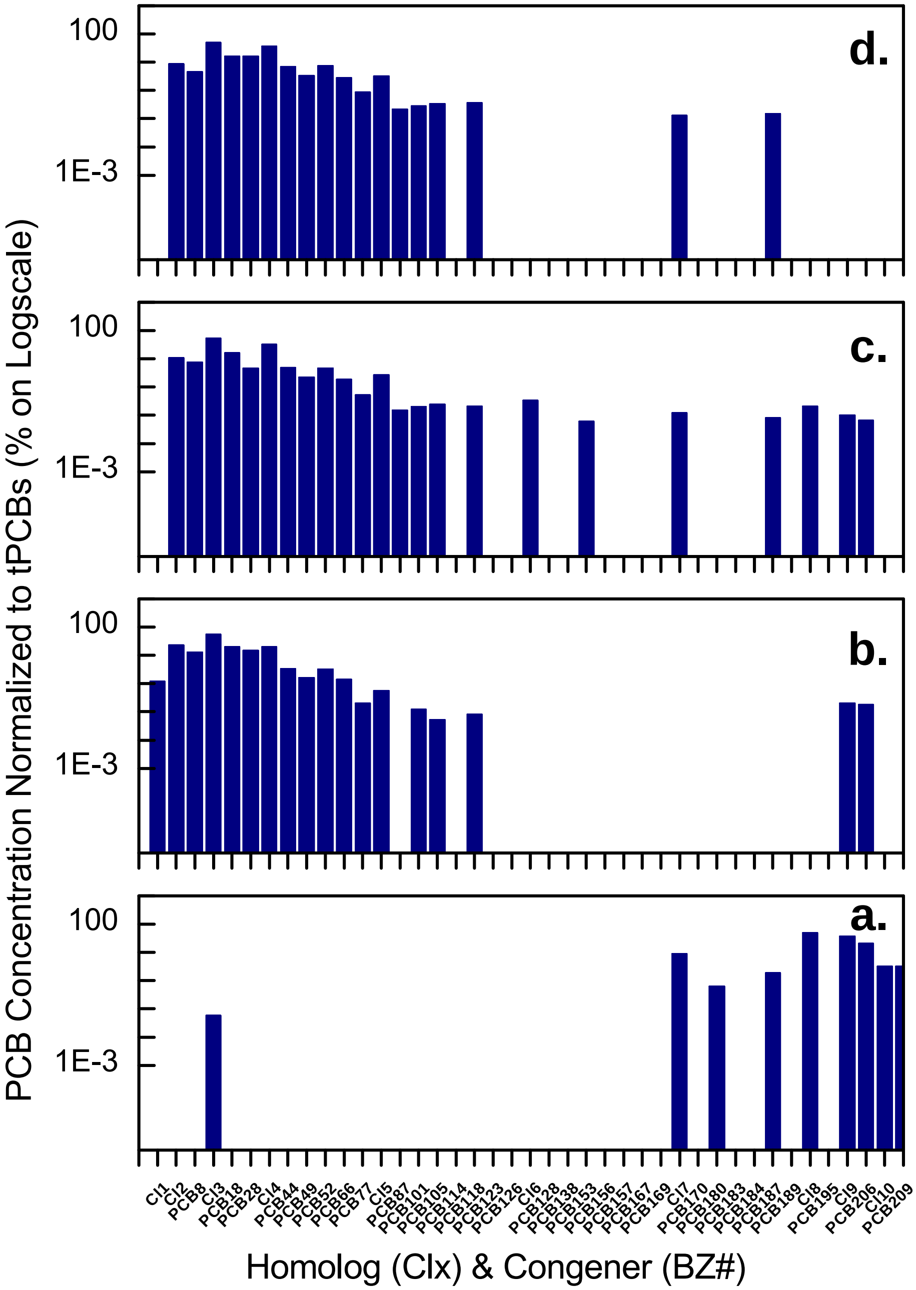


Figure 35 (a–d). Homolog and congener distributions during the A1268 dissolution experiment, normalized as percent of total, for the following exposure intervals: (a) iLR and mLR – 0.035d, (b) pmLR1 – 41 d, (c) pmLR2 – 189 d, and (d) fLR – 371 d.

The most concentrated ASW 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-S2-T24) occurred over the interval 188 to 265 days, nearly (1 day less than) the longest time-interval in the experiment, with a maximum tPCB concentration of 6384 pptr (ng/L), and contributions from homolog groups Cl2-Cl5 and Cl7-Cl8. However, this particular sample contained only the maxima for Cl3 – Cl5 homologs (2900, 2500 and 320 pptr, respectively) across the entire A1268 experimental series. The following were maxima observed across the entire experiment for Cl1 (in sample 214-59B-S2-T10 at day 41, 29 pptr), Cl2 (in sample 214-59B-S2-T18 at day 111, 590 pptr), Cl6 (in sample 214-59B-S2-T22, day 189, 14 pptr), and Cl7-Cl10 (in sample 214-59B-S2-T1, at 5 minutes, 140, 800, 580, and 52 pptr, resepctively). The effective A1268 saturation limit is estimated as the sum of all maximum homolog concentrations observed (7,925 pptr) and assumes that the solubility of any given homolog group would not be significantly affected (suppressed) by the presence of other dissolved homolog groups at their maximum observed concentrations. The true solubility for such a complex mixture is probably time-dependent, but as postulated for A1254, A1268, should exhibit a solubility value above the highest concentration observed (6384, but below the effective saturation limit 7925 pptr, or between 0.006384 and 0.007925 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 homolog solubilities compiled by Mackay, Shiu , and Ma (1992). Applying the homolog distribution for A1268 in this study to these values, the solubility range is estimated as 0.000182 to 0.00119 mg/L (ppm). However, as demonstrated for A1254, the estimation based on homolog solubilities was severely underestimated relative to empirical observed solubilities. If we assume that this would also be the case for A1268, the adjusted range for A1268 becomes 0.00070 to 0.0199 mg/L, giving reasonable assurance that we are below saturation in samples across the A1268 leaching experiment. Again, as for A1254, the solubility of A1268 should be suppressed slightly in seawater.

The observed concentration maxima of target congeners, if detected within each of these homolog groups, occurred in the same samples as homolog maxima, with the exception of PCB153 (single detection at day 322), and two equivalent detections for PCB8 at day 41 and day 111 (Cl2 maximum). 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., insoluble PCBs in the Aroclor® matrix are likely impeding the solvation of other congeners.

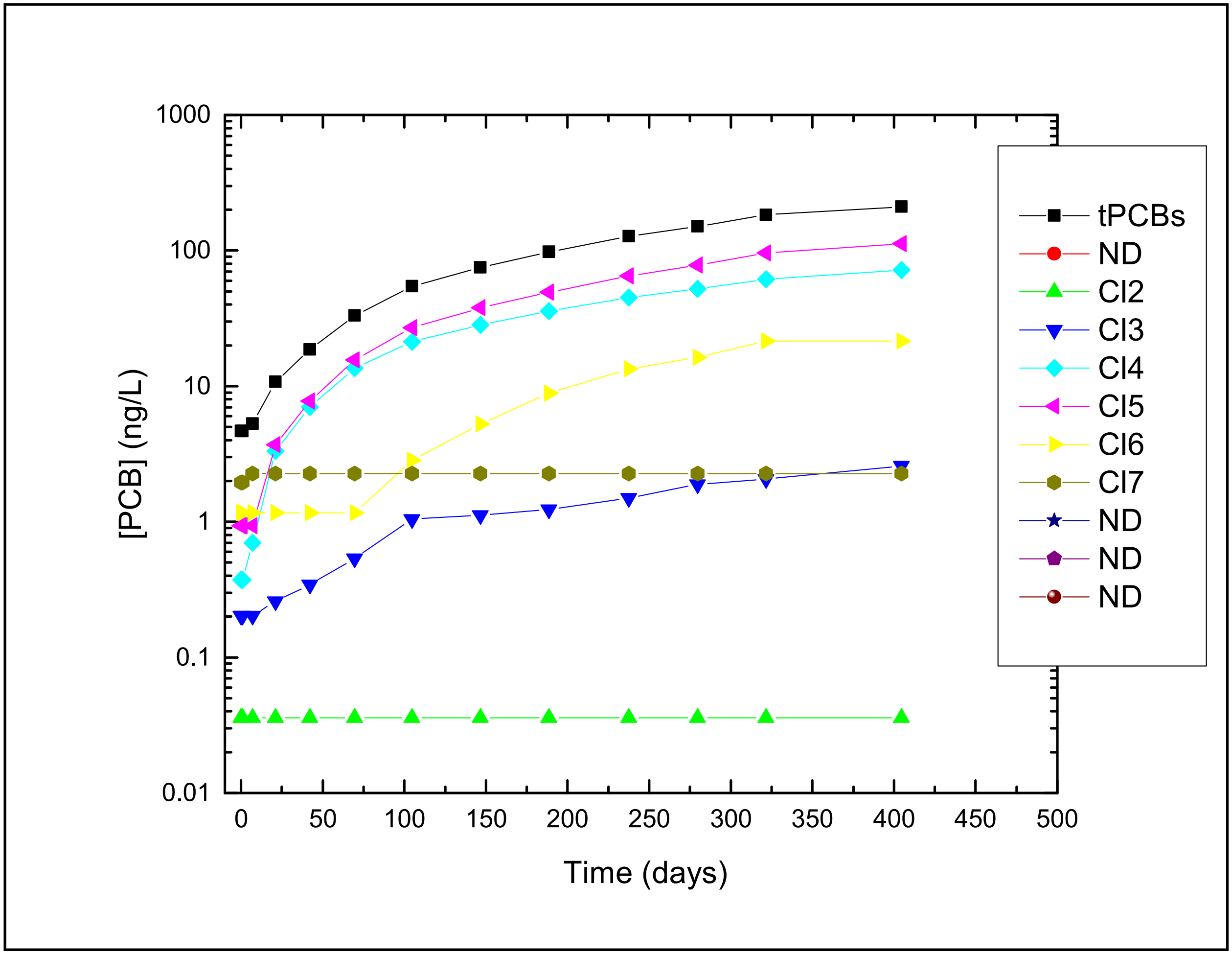
If one considers that the maximum empirical concentration observed was 6,384 pptr (all other leachate concentrations were below this value), an effective A1268 PCB saturation limit of 7,925 pptr was calculated per above, and the concentration in the total experimental volume was 2,791 pptr (as indicated by the final concentration value in Figure 33 and in the cumulative concentration table in Appendix D), then the observed dissolution behavior must be limited by the neat 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 as possible in an experimental A1268 ASW sample, i.e., 6,384 pptr, and likely up to the estimated saturation limit of 7,925 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, neat Aroclor® 1268 itself, a mixture of PCBs.

3.4.6. Bulkhead Insulation (BHI) Leaching Behavior

Leaching Behavior at 4 ^{o}C/1 bar

Figure 36 (a) shows the leaching concentration curves for BHI at 4 °C/~1 bar for tPCBs and contributing homolog groups Cl2 through Cl7, for which target congeners are separately plotted in Figure 36 (b). BHI (0.42 g), containing 0.172 mg (0.041 wt%) tPCBs, was exposed to a 12.08 L total volume of ASW leachate over a leaching time of ~400 days and exhibited the maximum leach rate for all shipboard solids tested under these conditions. It also approached the leach rate for both positive control curves to within three orders of magnitude. The very open/porous nature of this solid and corresponding high surface area, combined with the likelihood that PCBs are primarily coating the inorganic nature of the solid surfaces (rather than PCBs incorporated into an organic/polymer matrix), would result in an increased solvent accessible surace area (SASA) and greater PCB transport out of the matrix. Such behavior would lead to an increase in observed PCB "leaching" similar to what was observed for neat Aroclor® PCB matrices in results presented in this study.

a)



b)

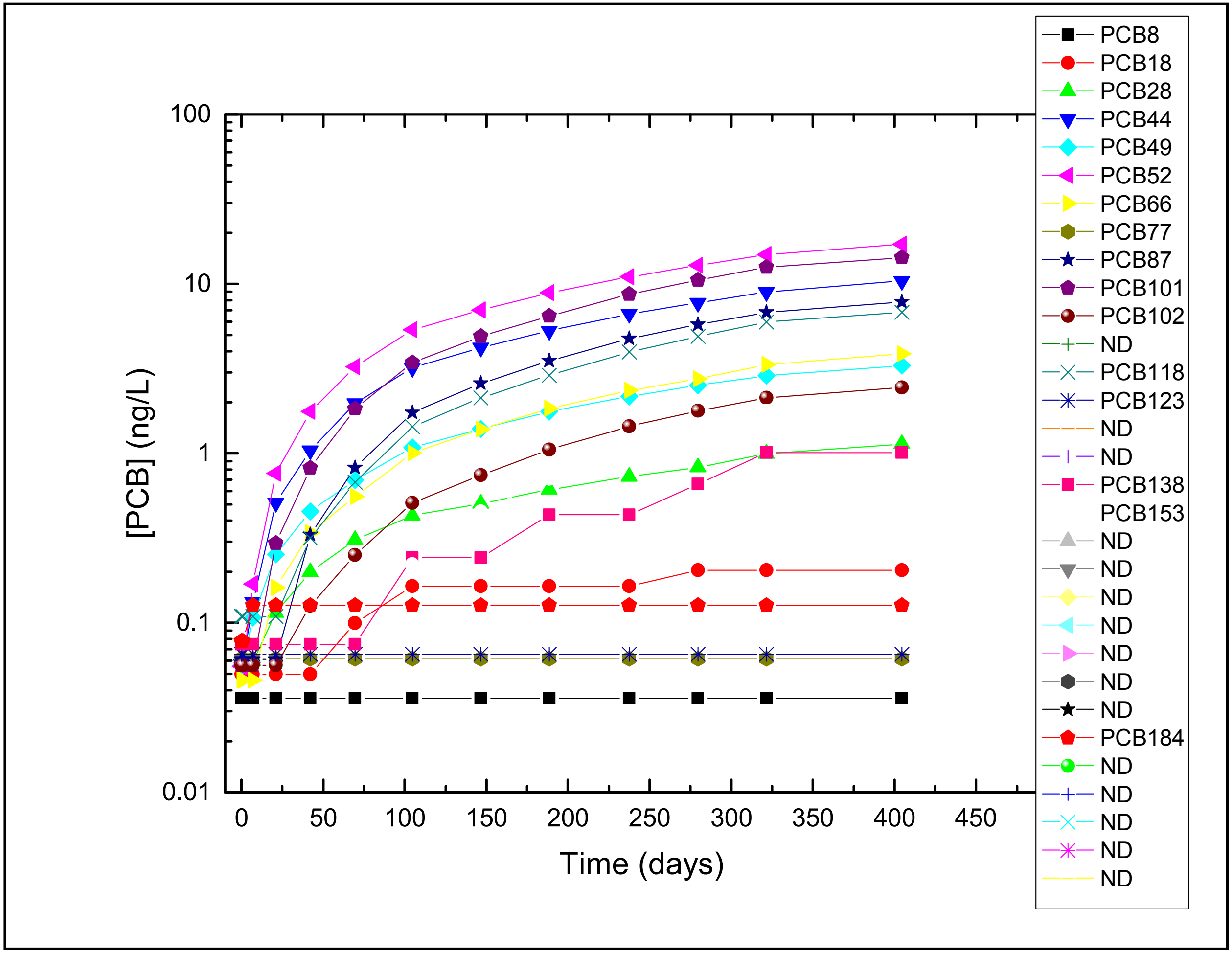


Figure 36 (a–b). Experimental PCB concentration versus leaching time for BHI containing 0.17 mg (0.041 wt%) tPCBs exposed to a total volume of 12.08 L of seawater leachate. Plot (a) shows the tPCBs concentration and contributing homolog group concentrations versus leaching time, where the sum of the homolog curves is equal to the upper tPCB curve. Plots (b) are target congener concentrations within homolog groups Cl2 through Cl7 versus leaching time.

The molecular fingerprints associated with the BHI solid and leachate are shown below (Figure 37). 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. The leaching was dominated by homologs Cl5 > Cl4 >> Cl6 > Cl3 ~ Cl7. While for the congeners PCB52 > PCB101 > PCB44 > PCB87 ~ PCB118 > PCB66 ~ PCB49 > PCB28 ~ PCB138 dominated and the others were only detected in samples relatively early in the experiment. In general, higher MW congeners (> Cl7) were not observed in the leachate even though they were present in the BHI solid.

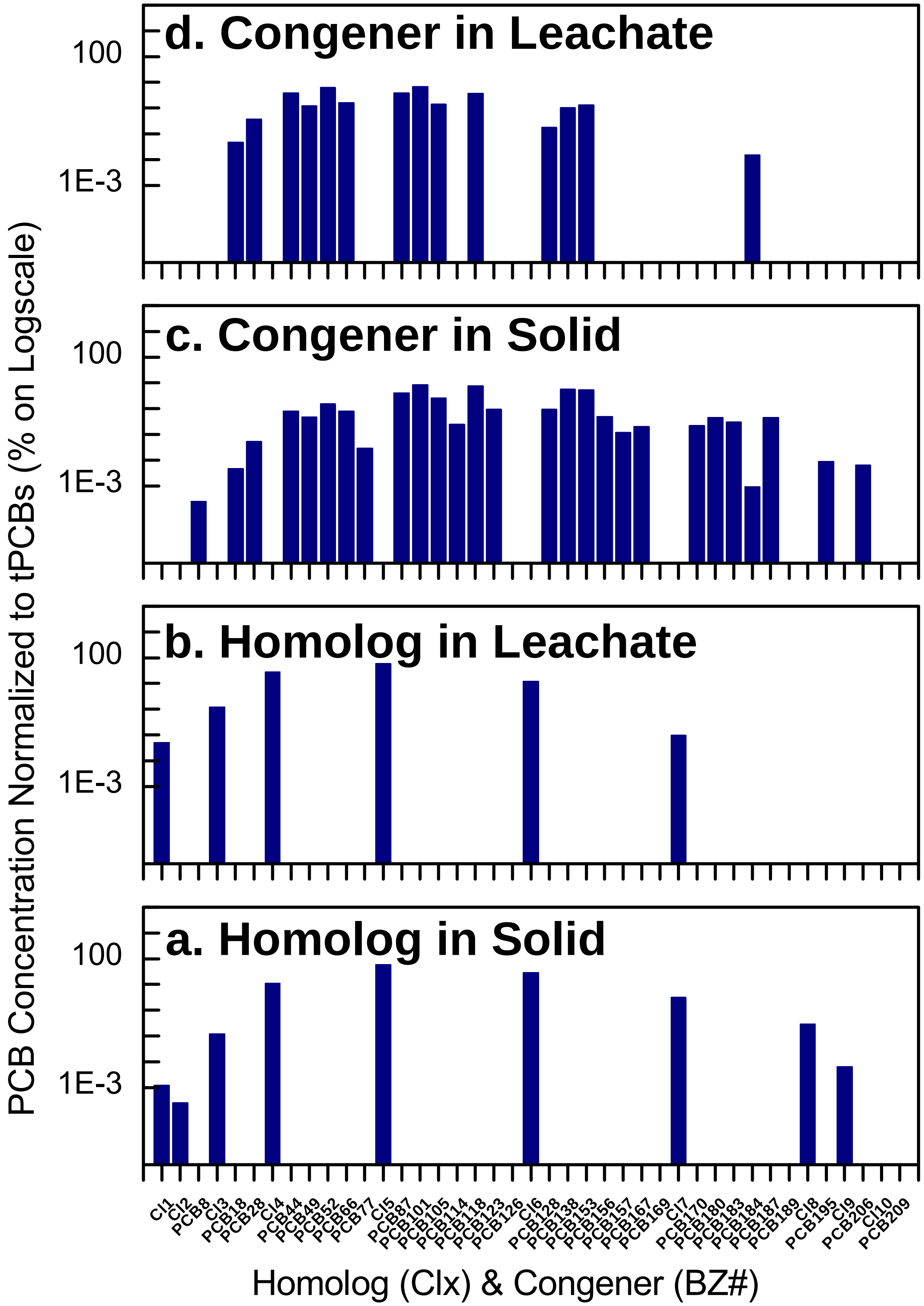


Figure 37 (a–d). Experimental homolog and congener PCB distributions for BHI solid (a and c) compared with total homolog and congener distributions of PCBs leached into seawater from BHI (b and d). The leachate distributions correspond to all released PCBs, which is also the cumulative leachate concentration endpoint for analytes presented in Figure 36.

Fingerprints for specific samples of BHI leachate are shown at key intervals across the entire leaching experiment (exposure time). Figure 38 homolog group and congener distributions correspond to (a) the initial and maximum leach rate (iLR and mLR), (b) the observed post-maximum increase in tetrachlorobiphenyl and decrease in dichlorobiphenyl groups (pmLR1), (c) the post-maximum signature showing broadest homolog and congener distributions (pmLR2), and (d) the final empirical leach rate (fLR), which was also the narrowest homolog and congener distributions observed.

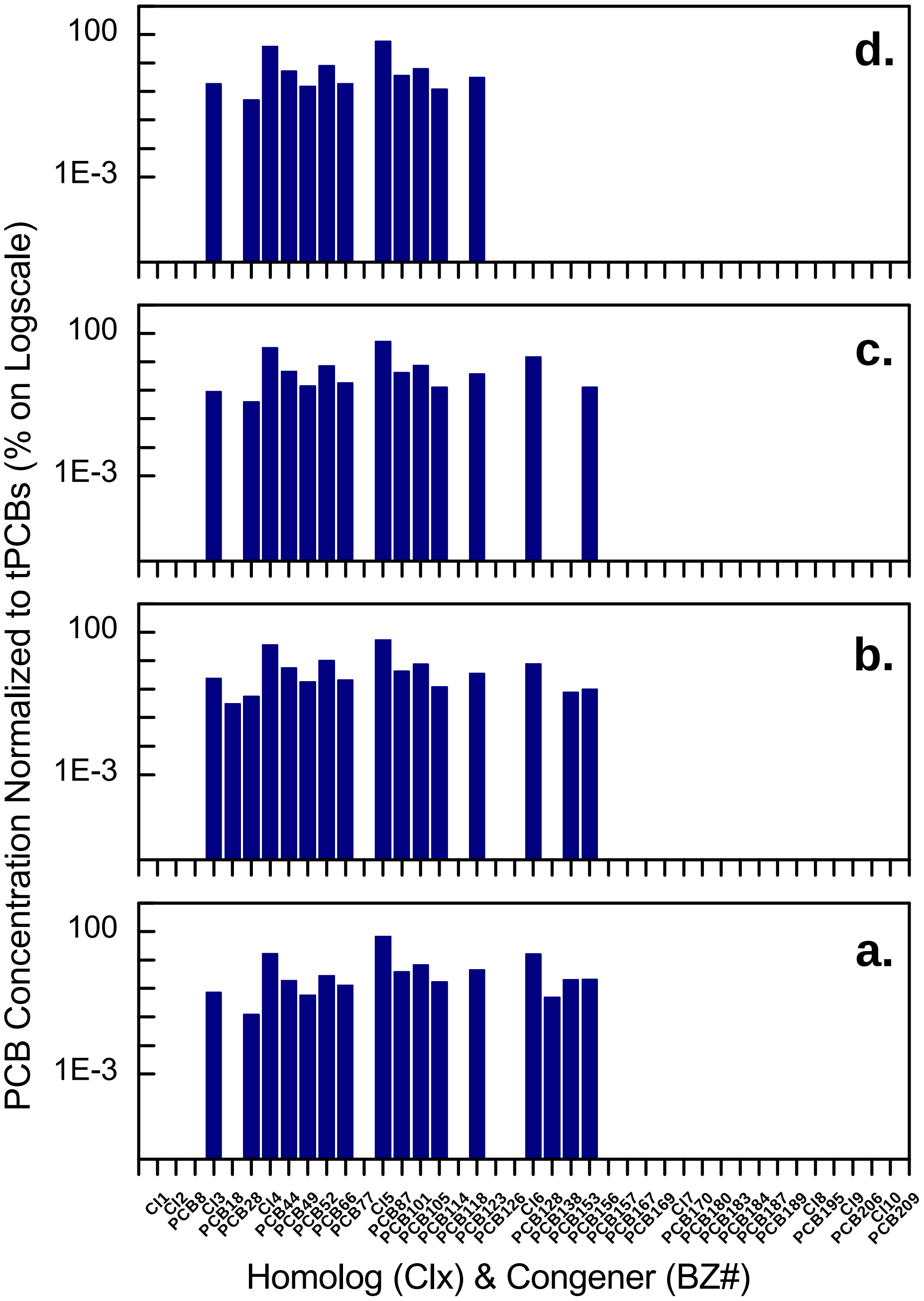
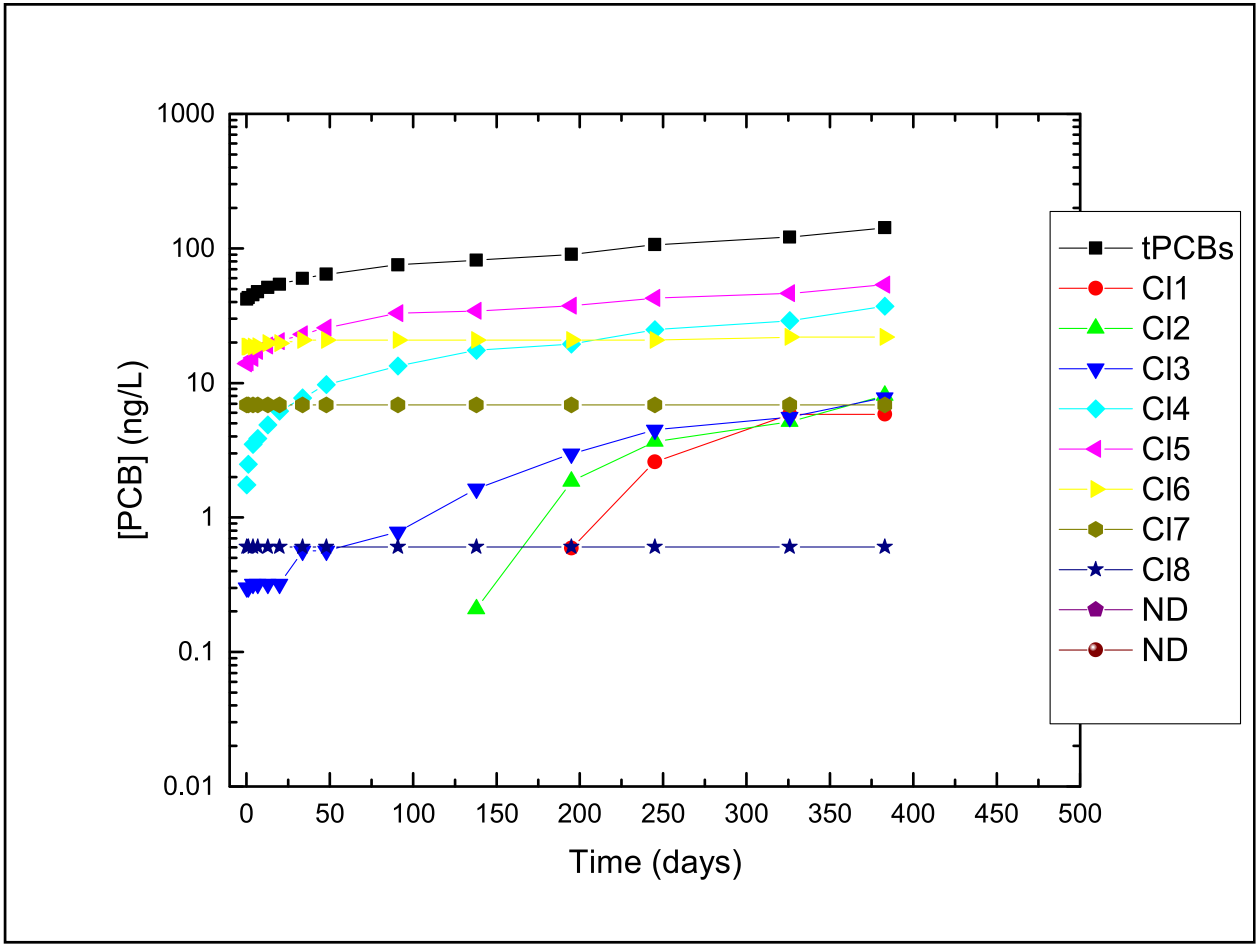


Figure 38 (a–d). Homolog and congener distributions during the BHI leaching experiment, normalized as percent of total, corresponding to selected leaching intervals: (a) iLR and mLR – 0.0028d (4 minutes), (b) pmLR1 – 105 d, (c) pmLR2 – 238 d, and (d) fLR – 405 d.

Leaching Behavior at 4°C/300 bar

This shipboard solid was also tested at 4°C and 300 bar, for which 0.395g of BHI was evaluated in a total volume of 13.95 L. Homolog and congener concentration plots are included below (Figure 39), followed by PCB fingerprints in the solid and leachate at various leaching times throughout the experiment (Figures 40 and 41). Detections were observed for groups Cl1–Cl8 over the course of the experiment.

a)



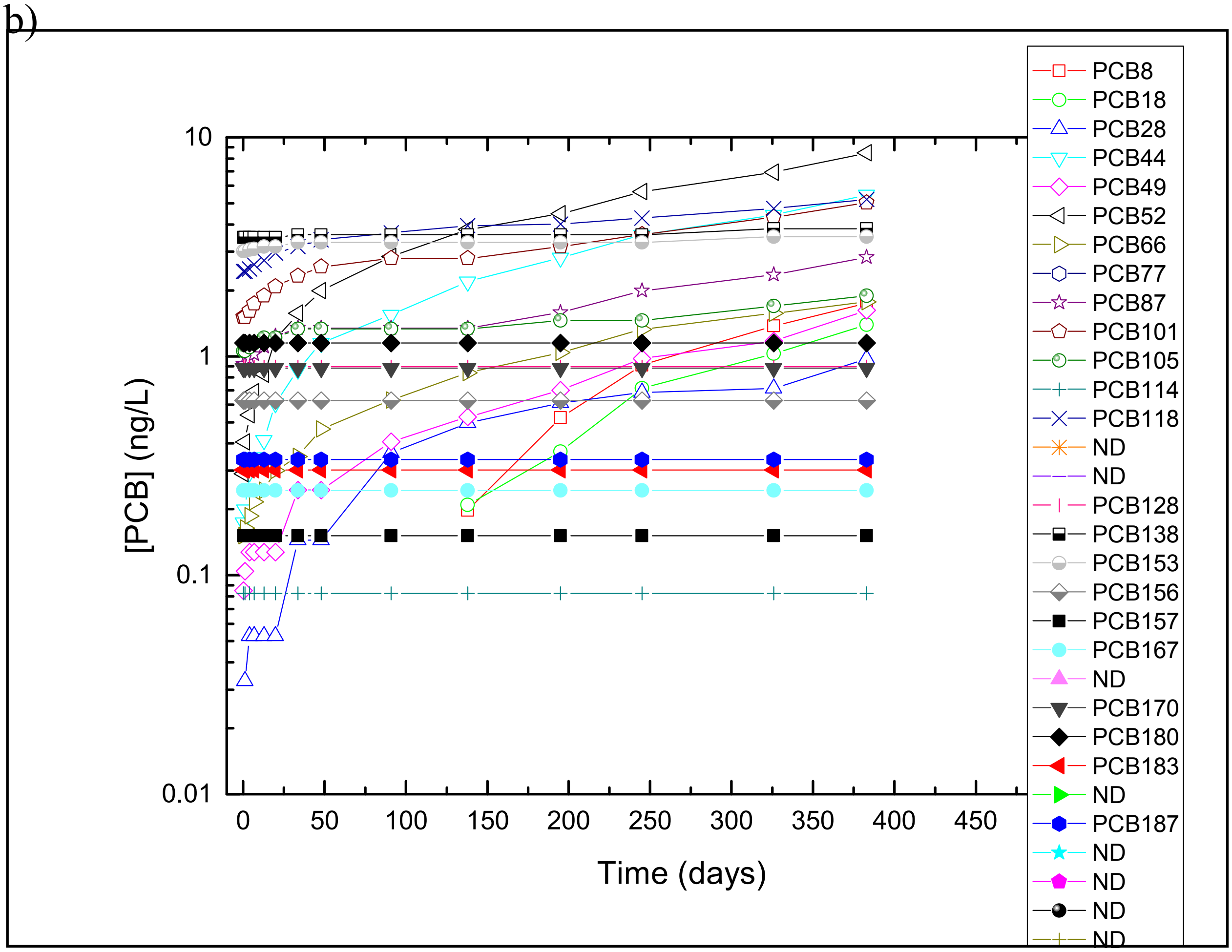


Figure 39. Cumulative PCB concentration versus leaching time for BHI containing 0.106 wt% (0.419 mg) tPCBs exposed to a total volume of 13.95 L of ASW leachate at 4 ^{o}C/300 bar over nearly 400 days. Plot (a) shows the tPCBs concentration and contributing homolog group concentrations versus leaching time for EC, where the sum of the homolog curves is equal to the upper tPCB curve. Plot (b) corresponds to target congener concentrations within homolog groups Cl1–Cl8 versus leaching time.

The molecular fingerprints associated with the BHI solid and leachate are shown below (Figure 40). 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. The logscale was used to make variances at very low sub-percentage levels visible. Leaching was dominated by homologs Cl5 > Cl4 > Cl6 > Cl3 ~ Cl ~ Cl1, while for the congeners PCB52 > PCB118 ~ PCB101 ~ PCB44 > PCB87 > PCB105 ~ PCB8 ~ PCB66 ~PCB105 ~ PCB49 > PCB28 dominated and the others were only detected in samples relatively early in the experiment. While similar to the 4^{o}C/1 bar experiments across most of the homologue and congeners, Cl8 was observed early in the 4^{o}C/300 bar experiment, unlike at 4^{o}C/1 bar wherer higher MW congeners (> Cl7) were not observed in the leachate even though they were present in the BHI solid.

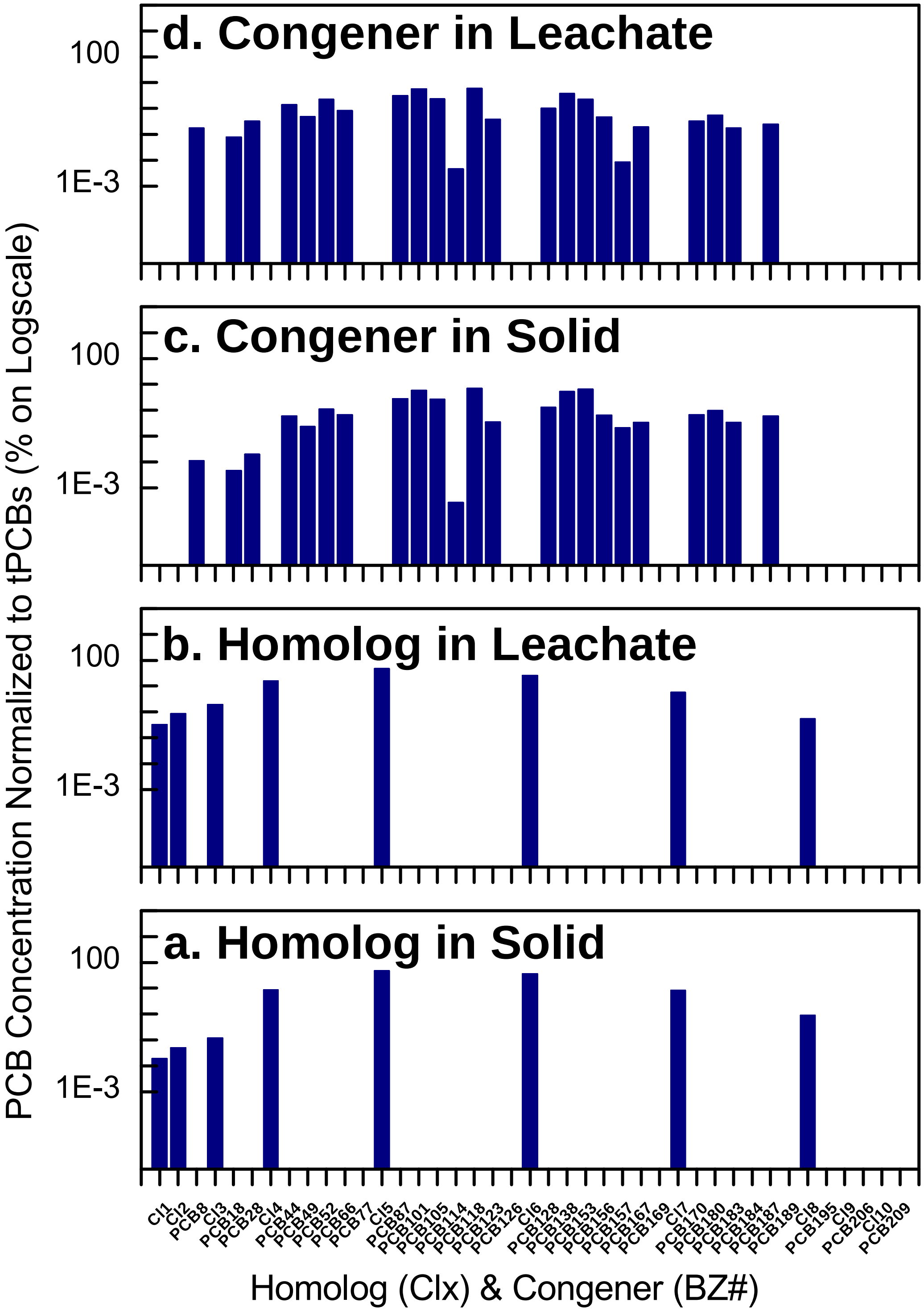


Figure 40 (a–d). Experimental homolog and congener PCB distributions at 4 °C and 300 bar for BHI solid (a and c) compared with total homolog and congener distributions of PCBs leached from BHI into seawater (b and d). Leachate distributions are derived from all PCBs released, which also corresponds to the cumulative leachate concentration endpoint for analytes in Figure 39.

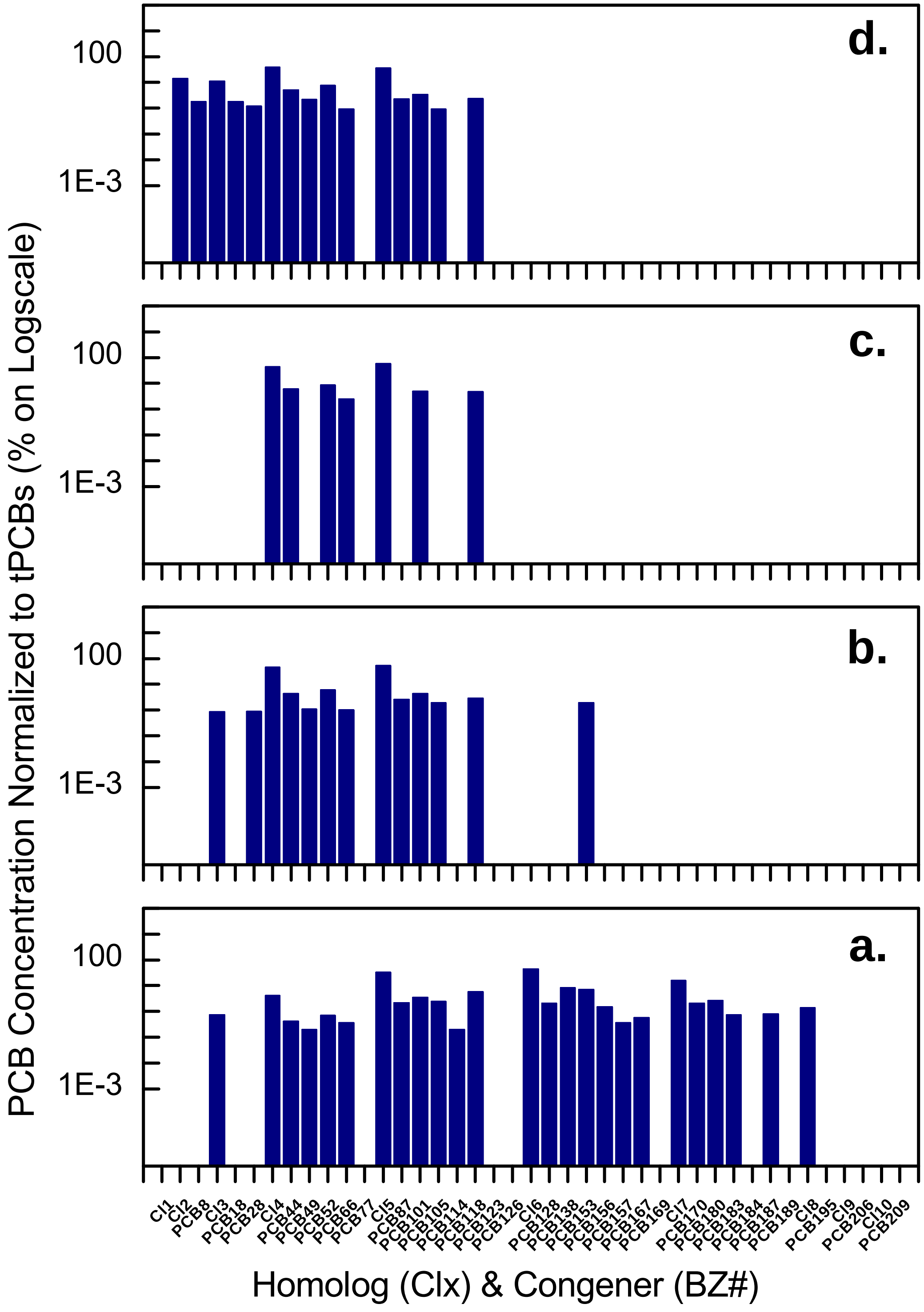


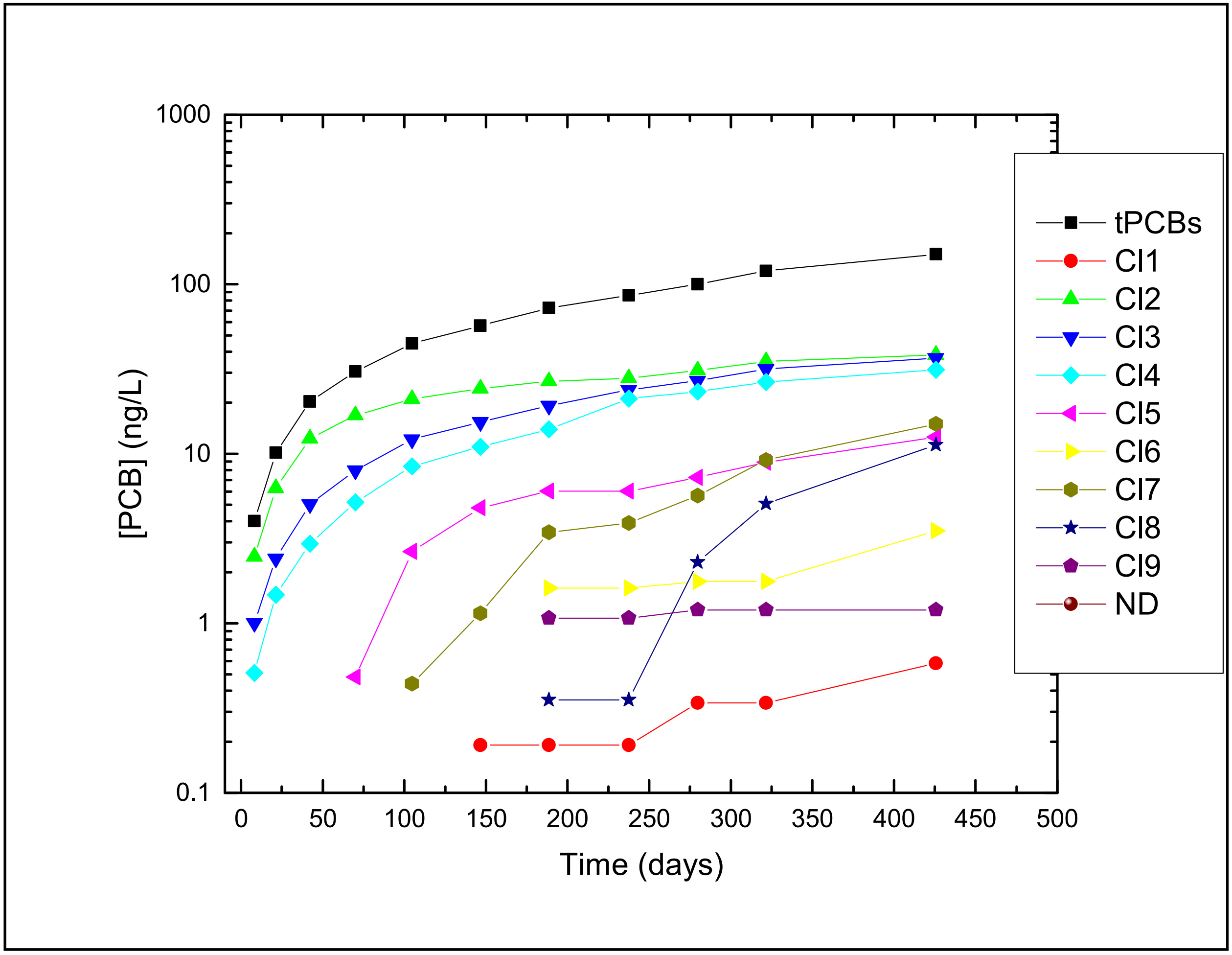
Figure 41 (a–d). Homolog and congener distributions during the 4 °C and 300 bar BHI leaching experiment, normalized as percent of total, corresponding to the following leaching intervals: (a) iLR and mLR – 0.21 d, (b) pmLR1 – 4 d, (c) pmLR2 – 48 d, and (d) fLR – 383 d.

3.4.7. Felt Gasket/Inner (FGI) Leaching Behavior

Leaching Behavior at 4^{o}C/1 bar

PCB concentration behaviors for FGI (2.783 g), containing 474 mg (17.0 wt%) tPCBs exposed to a total leaching volume of 12.01 L at 4 ^{o}C/~1 bar for nearly 430 days are shown in Figure 42 (a), for which all 9 homolog groups (Cl1 through Cl9) contributed to the tPCB concentration curve behavior as a function of leaching time. Curves for each of the target congeners in these homolog group is plotted in Figure 42 (b). This sample exhibited some leaching of nearly all possible homolog 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 contains 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.

a)



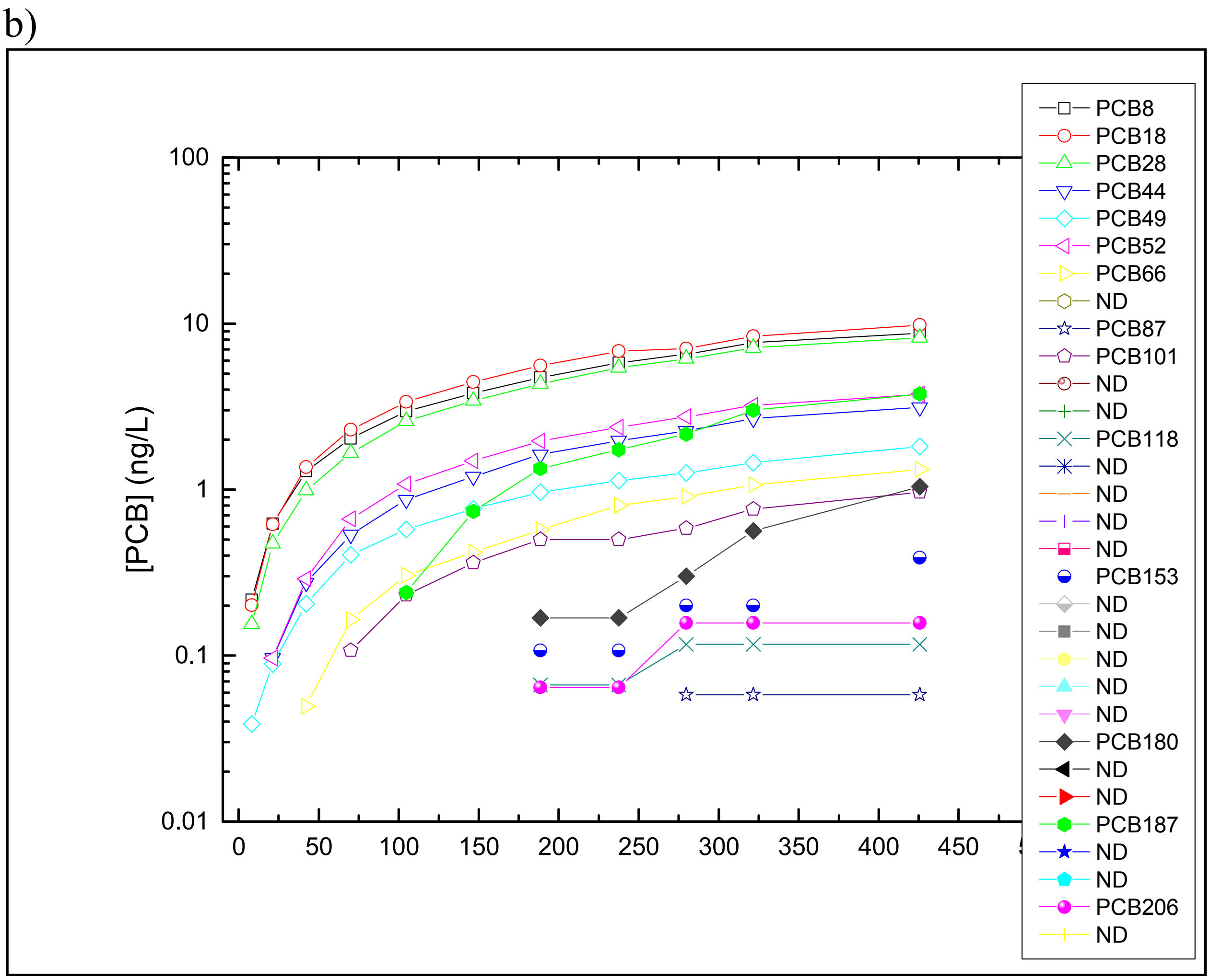


Figure 42 (a–b). Cumulative PCB concentration versus leaching time at 4 °C/1bar for FGI containing 474 mg (17.0 wt%) tPCBs exposed to a total volume of 12.01 L of ASW leachate. Plot (a) shows tPCBs concentration and contributing homolog group concentrations versus leaching time, where the sum of the homolog curves is equal to the upper tPCB curve. Plots (b) are target congener concentrations within homolog groups Cl1 through Cl9 versus leaching time.

Figure 43 shows total released homolog and congener distributions compared with the initial PCB distributions for FGI solid. All detected homologs and congeners are normalized and plotted as percent of measured tPCBs in each matrix (leachate versus solid). 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. The highest levels of release from FGI were from homolog groups Cl2 through Cl8. It is interesting that FGI exhibits much high contributions from the higher MW homologs and congener (Cl7 – Cl10), whereas lower weight PCBs dominate in the leachate homologs and congeners (Cl2 – Cl7), with some appearance of higher MW homologs and congeners at later leaching times. In fact, Cl2 – Cl4 homologs and congener are all that are released in the first 2 mos of the leaching experiment. This behavior is a clear example that even for very low (<0.1%) contributions of an analyte to tPCBs in the solid can still be significant if the analyte leaches into seawater.

Normalized distributions for specific FGI leachate samples are presented below at key intervals across the entire leaching experiment (exposure time). Figure 44 homolog group and congener distributions correspond to (a) the initial and maximum leach rate (iLR and mLR), (b) the narrowest homolog and congener post-maximum leach rate (pmLR1), (c) broader homolog and congener post-maximum leach rate (pmLR2), and (d) the final empirical leach rate (fLR), showing disappearance of the nonachlorobiphenyl group. Unlike results at 25 ^{o}C (George at al., 2006), PCB209 (Cl10) was not observed to release during this experiment.

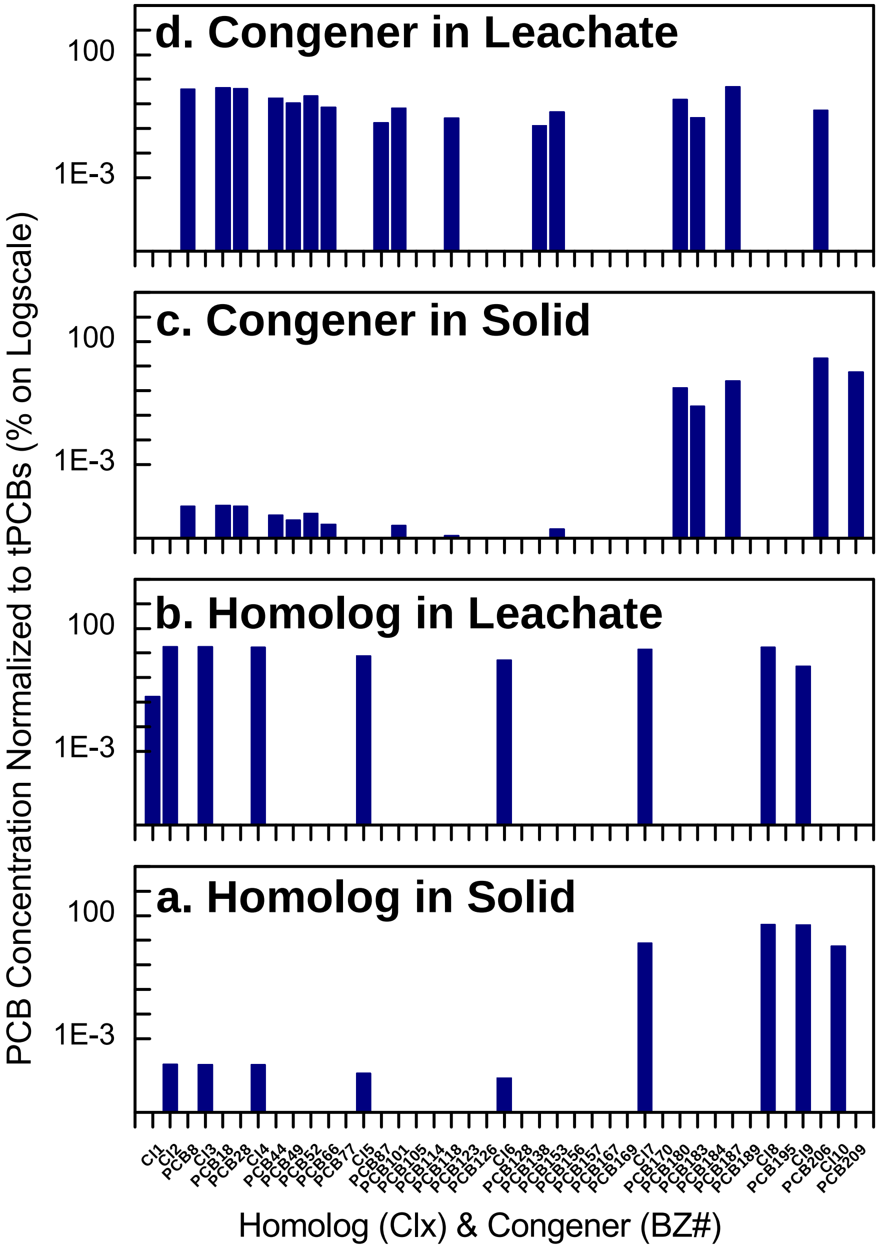


Figure 43 (a–d). Experimental homolog and congener PCB distributions for FGI solid (a and c) compared with total homolog and congener distributions of PCBs leached from FGI into seawater (b and d). The leachate distributions correspond to all PCBs released at 4 ^{o}C/1 bar during the experiment and are derived from the cumulative leachate concentration endpoints plotted in Figure 42.

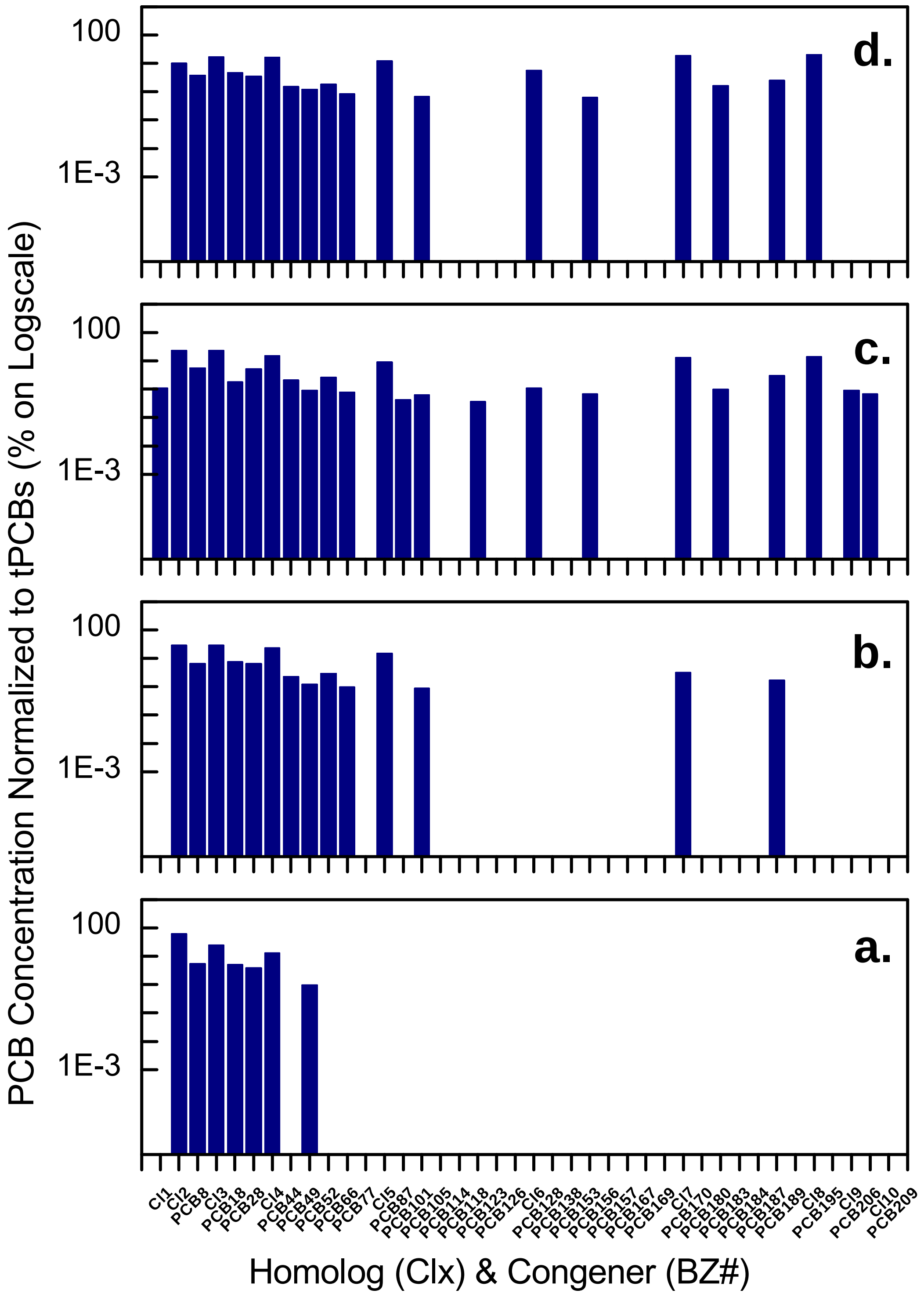
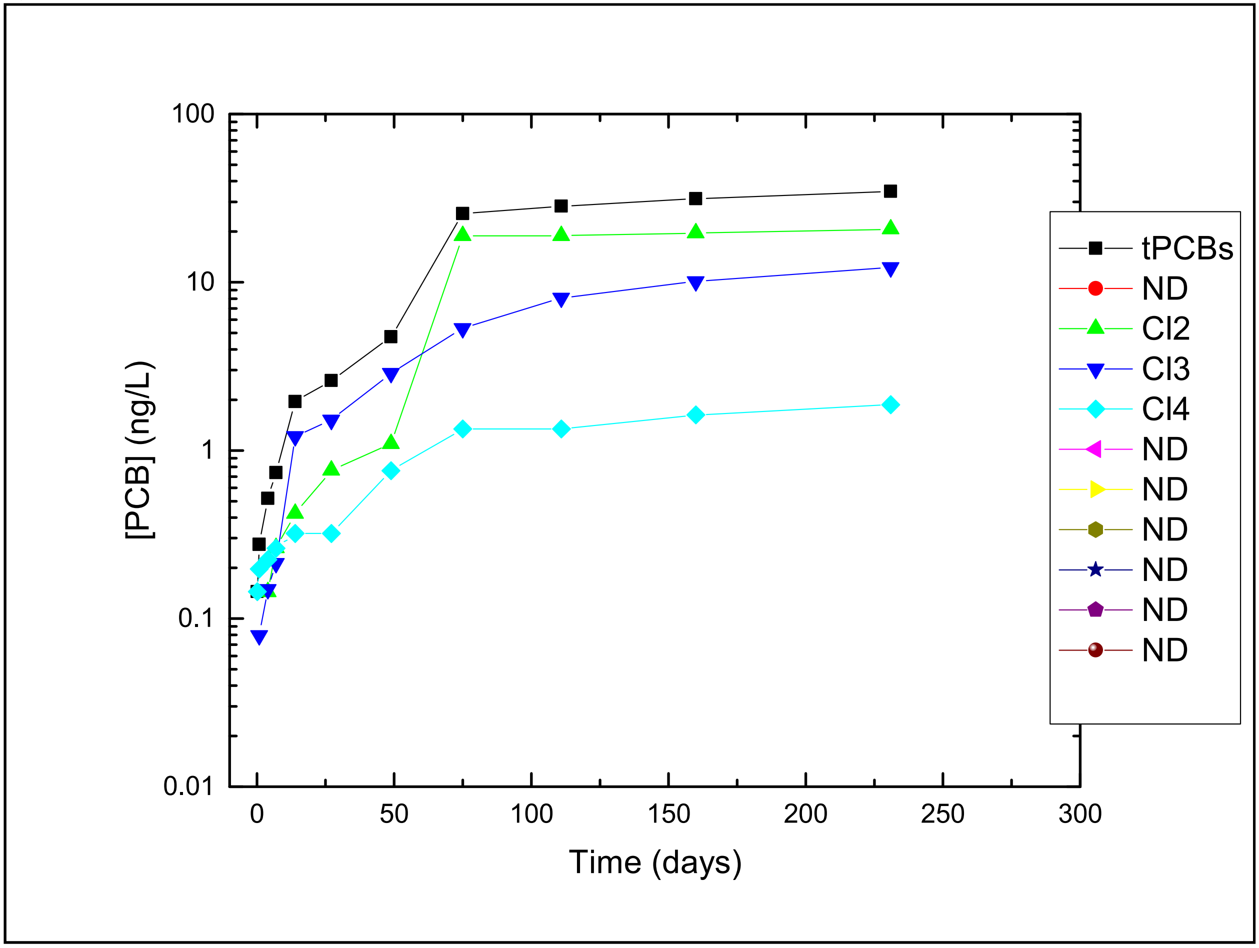


Figure 44 (a–d). Homolog and congener distributions during the FGI leaching experiment at 4 °C/1 bar, normalized as percent of total, for selected leaching intervals as follows: (a) iLR and mLR – 8 d, (b) pmLE1 – 105 d, (c) pmLR2 – 280 d, and (d) fLR – 426 d.

Leaching Behavior at 4 ^{o}C/300 bar

This shipboard solid was also tested at 4 ^{o}C and 300 bar, for which 2.298g of FGI was evaluated in a total volume of 10.7 L of ASW. Homolog and congener concentration plots are included below (Figure 45), followed by PCB fingerprints in the solid and leachate at various leaching times throughout the experiment (Figures 46 and 47). Detections were observed for groups Cl2 – Cl4 over the course of the experiment, with Cl2 > Cl3 >> Cl4 and PCB18 ~ PCB8 > PCB28 > PCB52 > PCB44. This behavior is much different than what was observed above at 1 bar, in that higher MW homologs and congeners are not observed here from 2 mos out to ~8 mos, where this leaching experiment ends.

a)



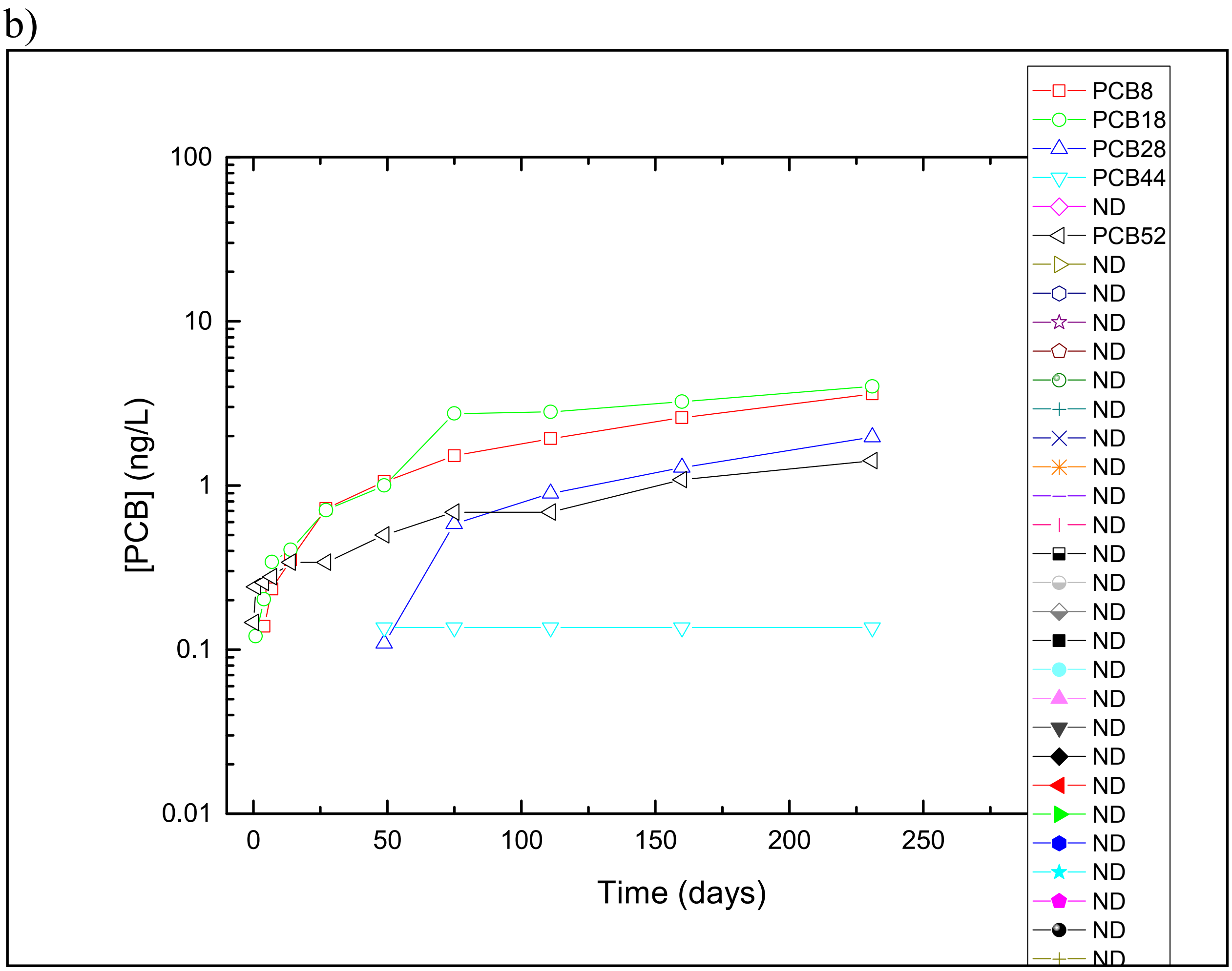


Figure 45. Cumulative PCB concentration versus leaching time at 4°C and 300 bar for FGI containing 12.62 wt% (290 mg) tPCBs exposed to a total volume of 10.7 L of ASW leachate over 231 days. Plot (a) shows the tPCBs concentration and contributing homolog group concentrations versus leaching time for FGI, where the sum of the homolog curves is equal to the upper tPCB curve. Plot (b) corresponds to target congener concentrations within homolog groups Cl2-Cl4 versus leaching time.

Homolog and congener distributions are shown in Figure 46 for shipboard solid FGI and for the total leachate fingerprint (all released PCBs). Solid distributions correspond to the initial PCB content in FGI solid, from the leaching experiment mass balance performed at the end of the leaching experiment. The logscale was used to make variances at very low sub-percentage levels visible**.**

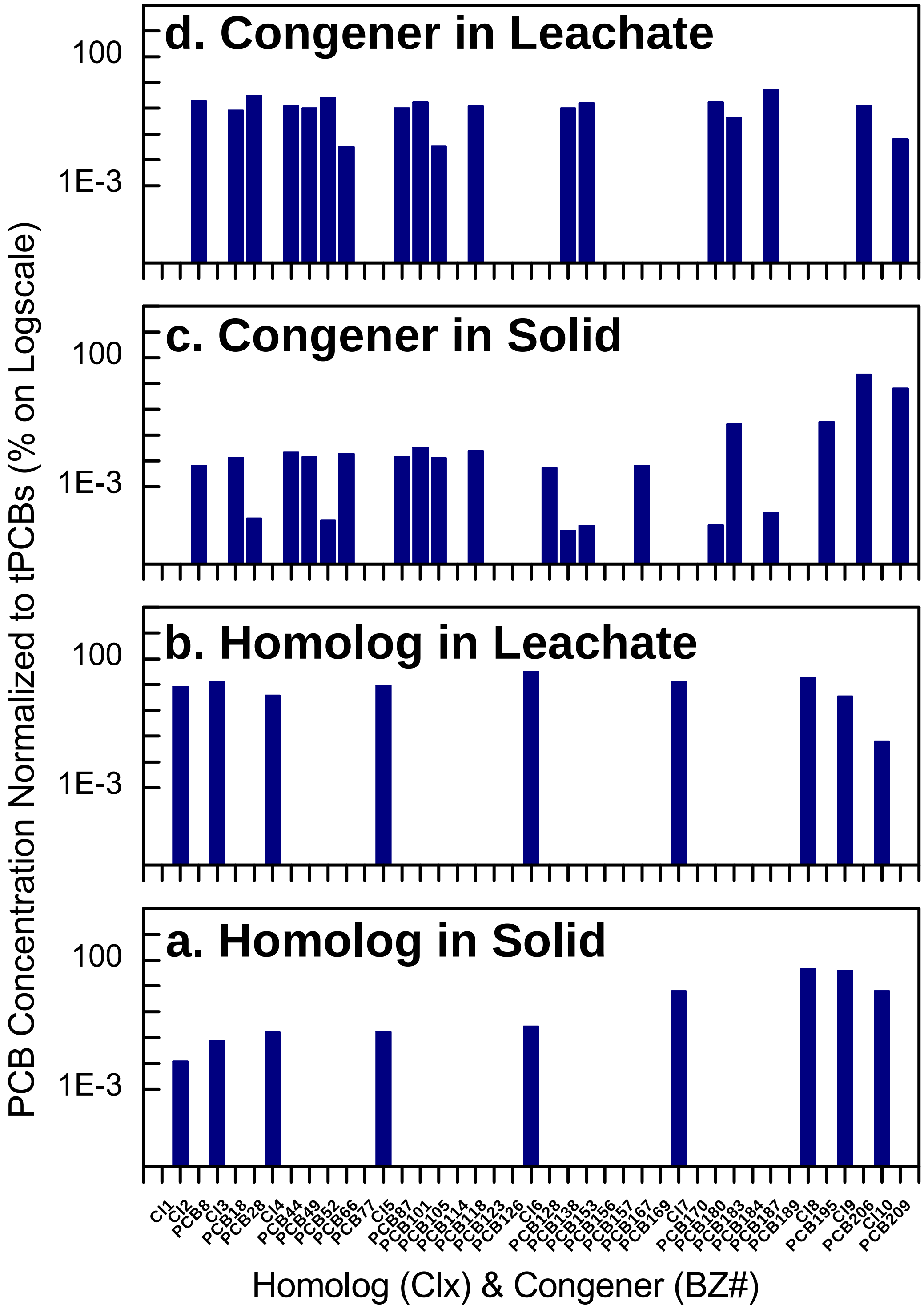


Figure 46 (a–d). Experimental homolog and congener PCB distributions at 4 °C and 300 bar for FGI solid (a and c) compared with total homolog and congener distributions of PCBs leached from FGI into seawater (b and d). Leachate distributions are derived from all PCBs released, which also corresponds to the cumulative leachate concentration endpoint for PCBs in Figure 45.

Figure 47 below follows the homolog and congener leachate distributions at various points in time over the course of the leaching experiment, corresponding to (a) the initial and maximum leach rate (iLR and mLR), (b) a post-maximum leach rate with narrow distribution (pmLR1), (c) a post-maximum leach rate with slightly broader distribution (pmLR2), and (d) the final leach rate (fLR) at the end of the experiment.

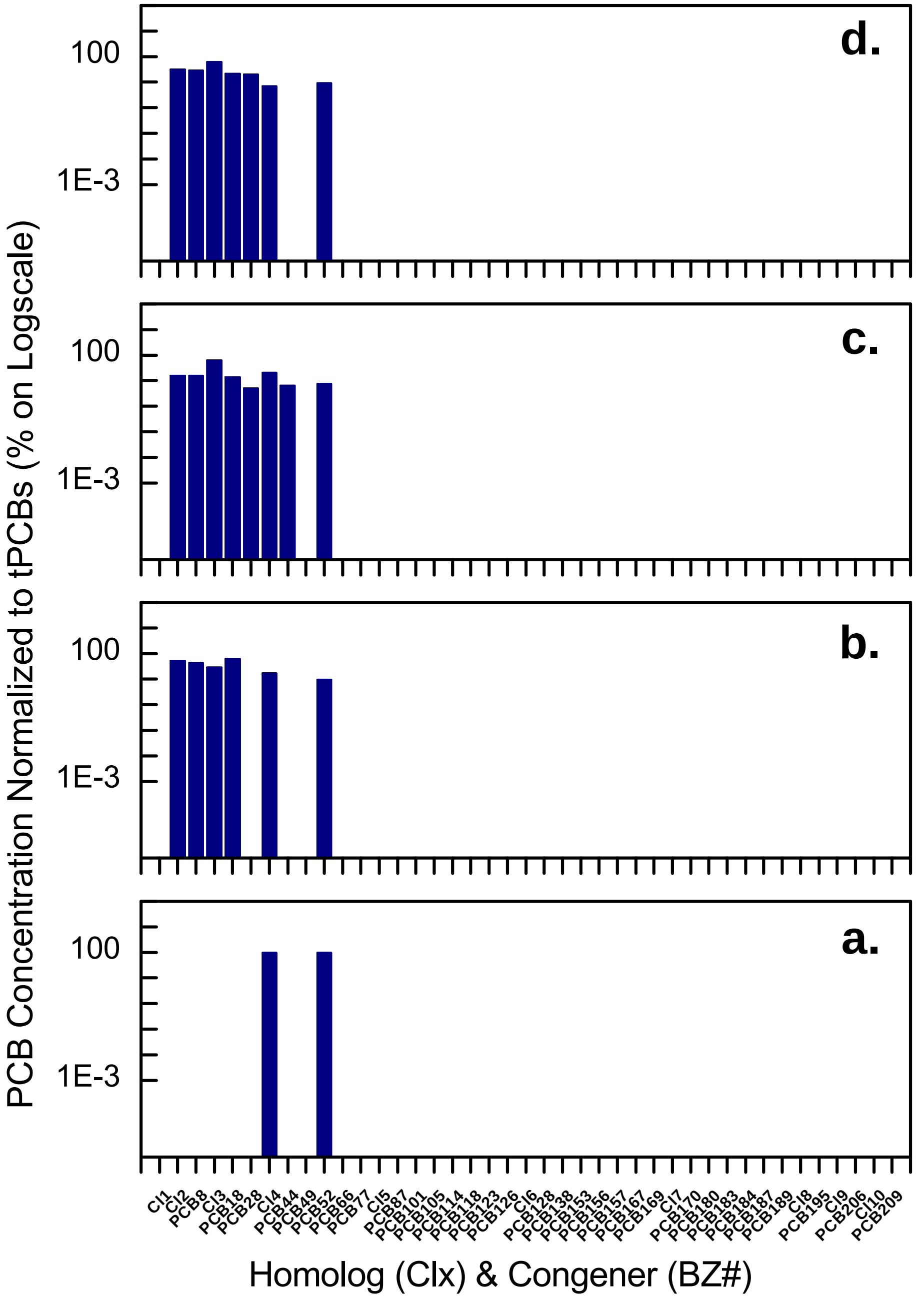
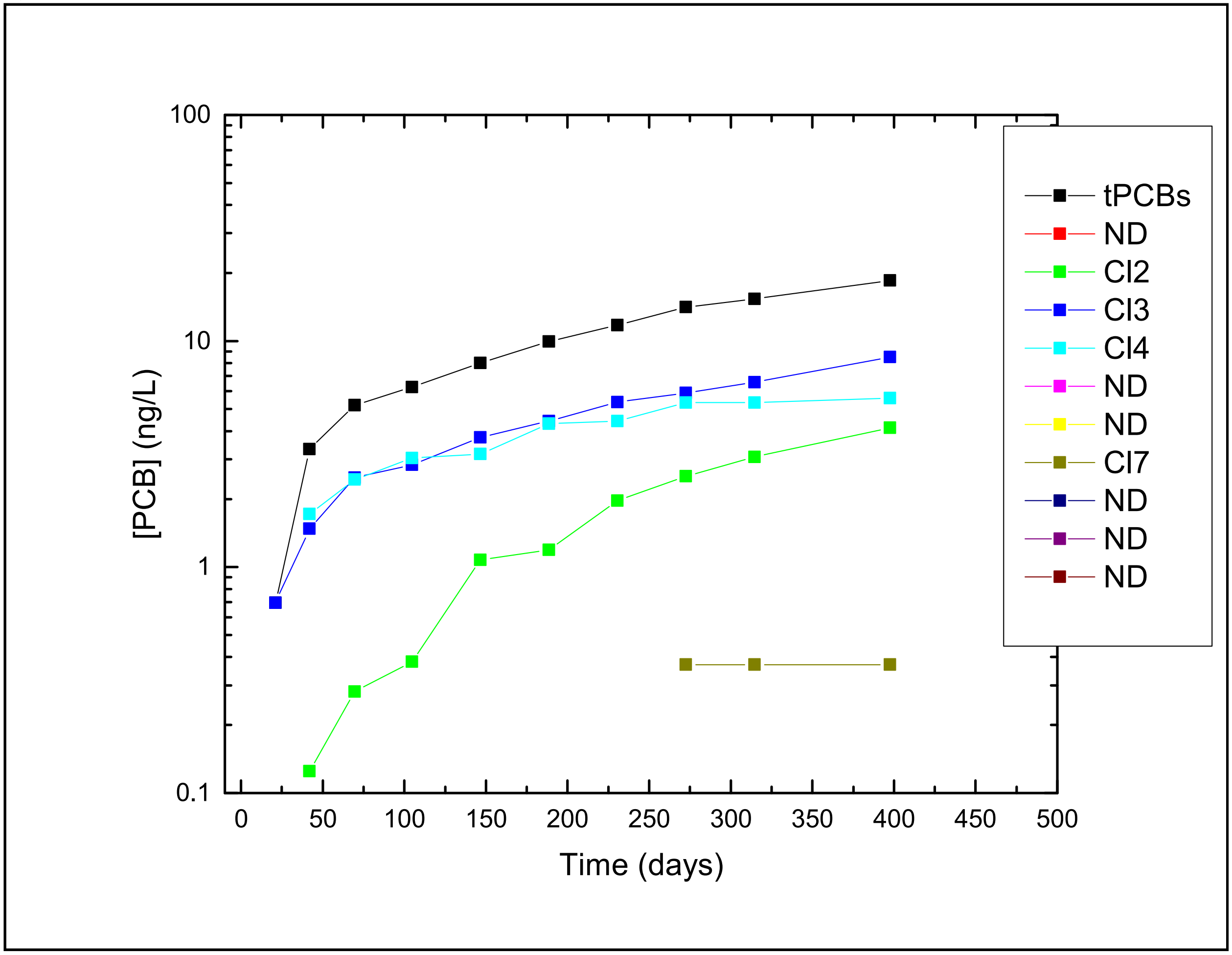


Figure 47 (a–d). Homolog and congener distributions during the 4 °C and 300 bar FGI leaching experiment, normalized as percent of total, corresponding to selected leaching intervals: (a) iLR and mLR – 0.07 d, (b) pmLR1 – 7 d, (c) pmLR2 – 49 d, and (d) fLR – 231 d.

3.4.8. Felt Gasket/Outer (FGO) Leaching Behavior

The leaching concentration behavior for FGO (0.619 g), containing 67.9 mg (11.0 wt%) tPCBs, leached at 4 °C/~1 bar for ~400 days, and exposed to 12.05 L total seawater volume is shown in Figure 48 (a) for tPCB and detected homologs Cl2 through Cl4 and Cl7, with abundances of Cl3 > Cl4 > Cl2 > Cl7 (only detected in 1 sample). The corresponding detected target congeners within each of these homolog group are also plotted in Figure 48 (b), with dominant congeners PCB18 ~ PCB28 > PCB8 > PCB52 > PCB44 > PCB49 ~ PCB187 > PCB66. This shipboard solid sample exhibited an Aroclor® 1268 distribution 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 appeared to contain a bit less Aroclor 1268 character. These were considered significant enough differences to expect a unique leaching behavior compared with FGI.

a)



b)

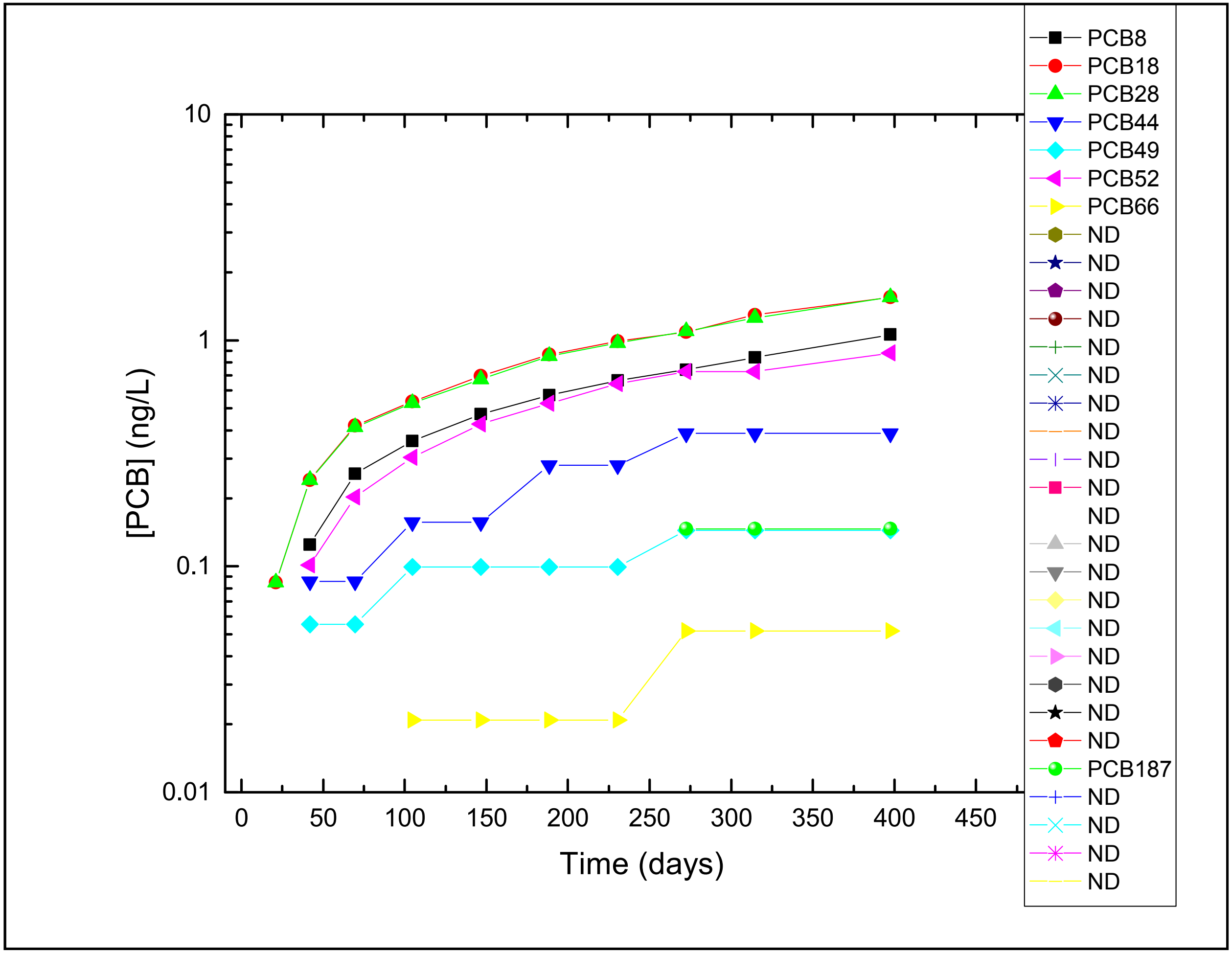


Figure 48 (a–b). Cumulative PCB concentration for tPCBs and homolgs (a) and congeners (b) versus leaching time at 4°C and 1 bar for FGO containing 67.9 mg (11.0 wt%) tPCBs exposed to a total volume of 12.05 L of seawater leachate over ~400 days. In plot (a) the sum of the homolog curves is equal to the upper tPCB curve.

Figure 49 shows total released homolog and congener distributions compared with the initial PCB distributions determined for FGO solid at 4 °C/1 bar. All detected homologs and congeners are normalized and plotted as percent of measured tPCBs in each matrix (leachate versus solid). Leachate distributions are derived from the cumulative leachate concentration endpoints plotted in Figure 48 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. 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 distributions. The highest levels of release from FGO were from homolog groups Cl2 through Cl4, which accounted for a much higher fraction in the leachate than in the solid. The heavier homologs (Cl9 and Cl10) and congeners 206 and 209 were not detected in the leachate even though they comprised some of the largest fractions in the solid. This is different from FGI leachate which had Cl9 and PCB206 detections in the leachate at 4°C/1 bar, and FGI at 4°C/300 bar which had detectable leachate levels of Cl9, PCB206, and Cl10 (PCB209).

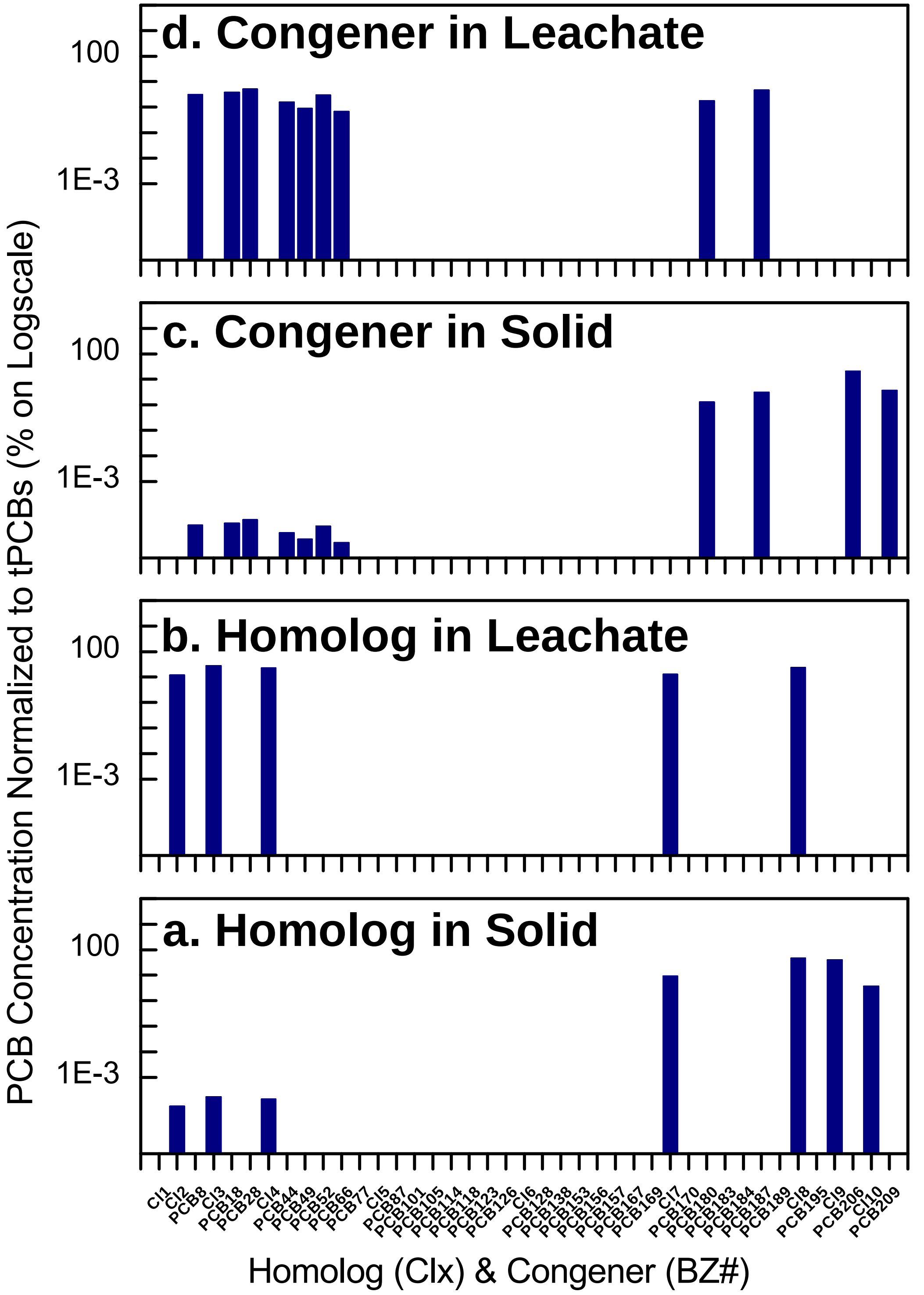


Figure 49 (a–d). Experimental homolog and congener PCB distributions for FGO solid (a and c) compared with total homolog and congener distributions of PCBs leached from FGO into seawater (b and d).

Specific leachate distributions are included below at key intervals across the entire FGO leaching experiment (exposure time). Figure 50 homolog group and congener distributions correspond to (a) the initial pre-maximum leach rate (iLR); (b) the maximum leach rate (mLR) and broadest distribution observed; (c) the post-maximum leach rate (pmLR), characterized by a decrease in tetraachlorbiphenyl congener contributions; and (d) the final empirical leach rate (fLR). The respective target congener distributions are shown in (b) illustrate the last detections for PCB 87 and PCB 118 over the leaching experiment.

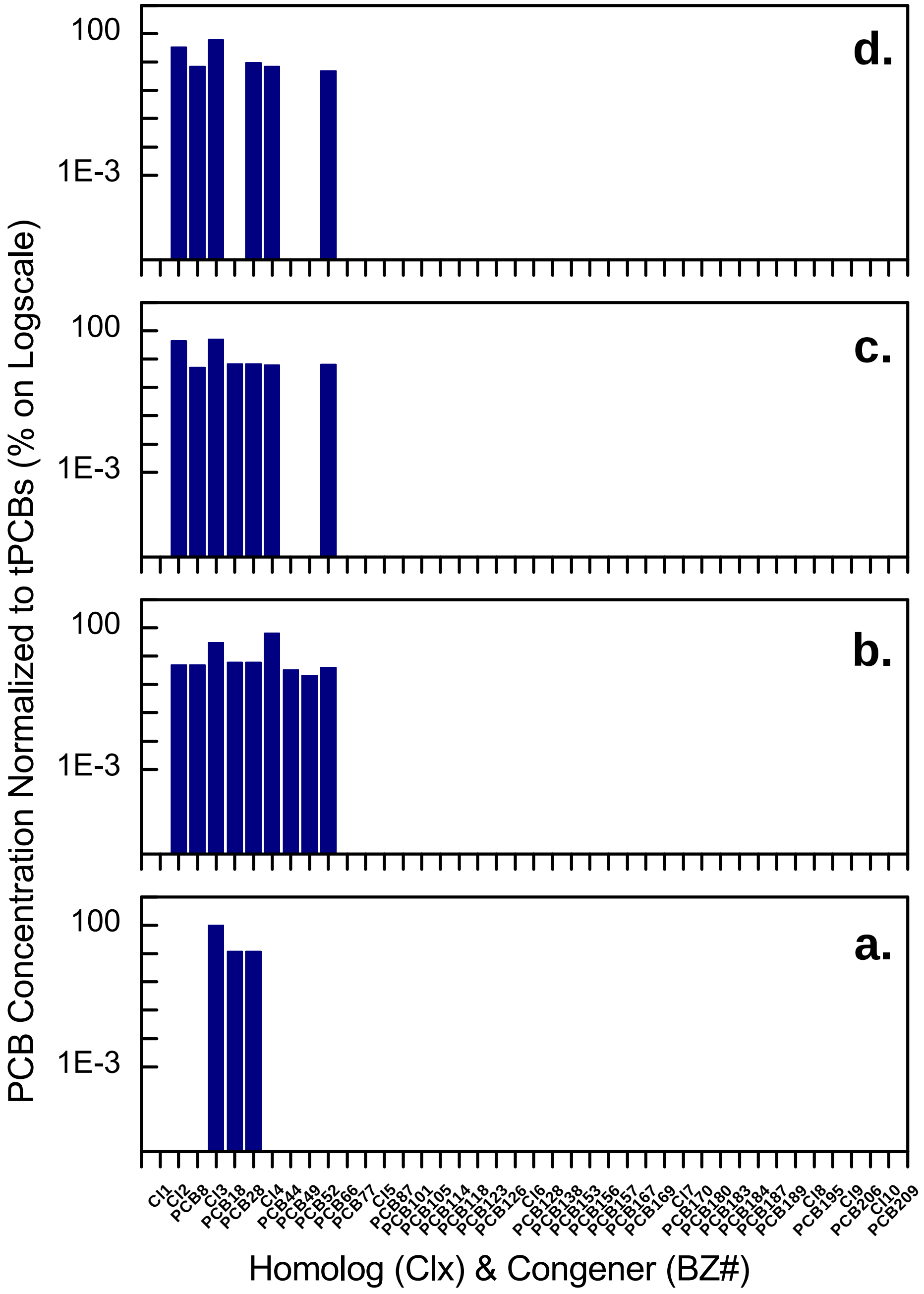
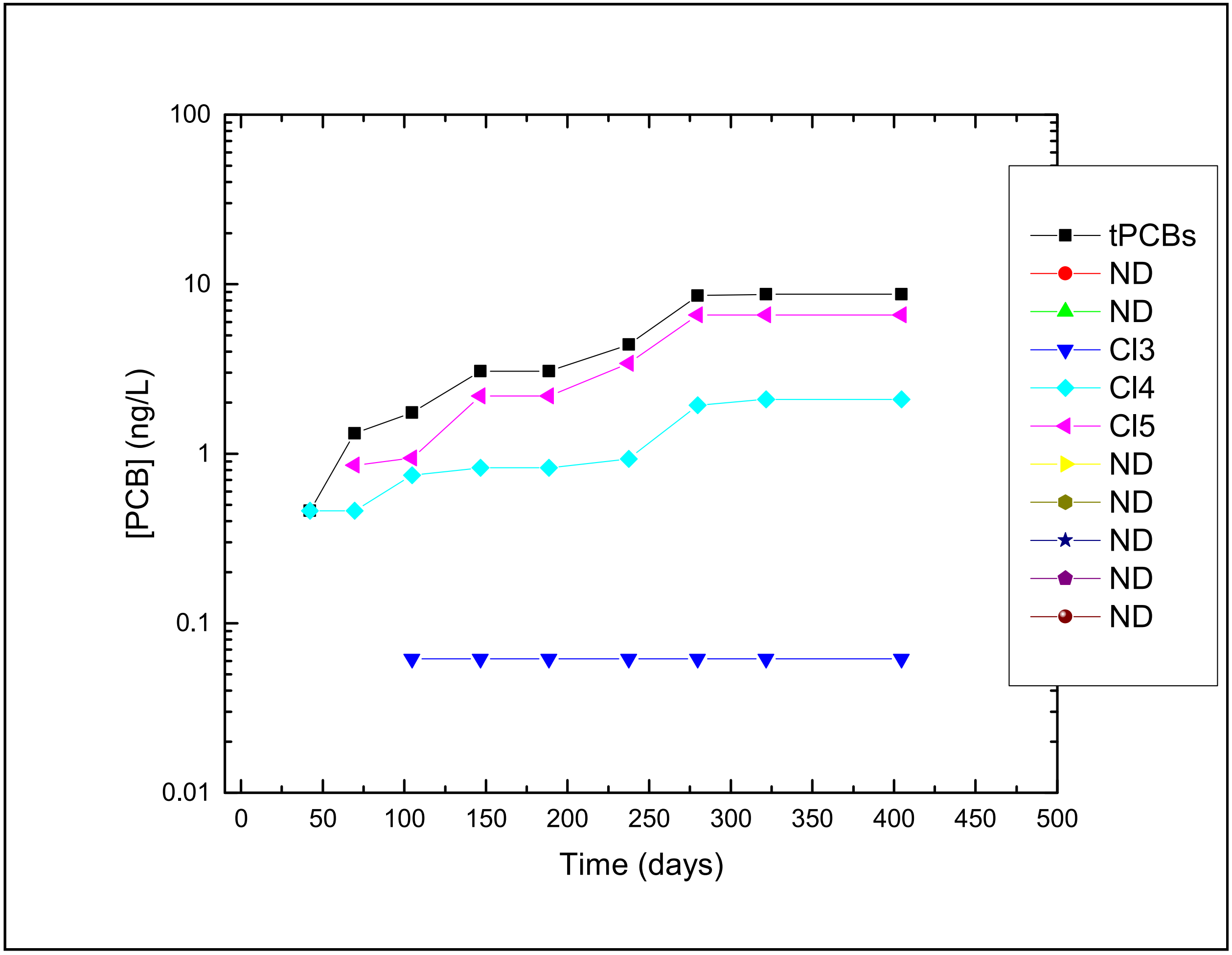


Figure 50 (a–d). Homolog distributions during the FGO leaching experiment, normalized as percent of total, corresponding to leaching intervals: (a) iLR – 21 d, (b) mLR – 42 d, (c) pmLR – 231 d, (d) fLR – 398 d.

3.4.9. Aluminized Paint (AP) Leaching Behavior

The leaching behavior for the AP subsample (1.20 g), containing 0.566 mg (0.0472 wt%) at 4 °C/~1 bar for 400 days and exposed to a total volume of 12.08 L of seawater leachate is shown in Figure 51 (a) for tPCBs concentration and contributing homolog group concentrations Cl3 through Cl5 versus leaching time, where the sum of the homolog curves is equal to the upper tPCB curve. The corresponding target congeners concentrations within homolog groups Cl3 through Cl5 are plotted versus leaching time in Figure 51 (b). This sample leached the least number of different homolog groups out of all leached solids, with Cl5 > Cl4 >> Cl3 and PCB52 ~ PCB101 >> PCB118 > PCB87. The diversity or number of PCBs do not necessarily translate into a lower leach rate overall, which is related only to the change in concentration over a change in time for any given analyte as described in Subsection 4.1.

a)



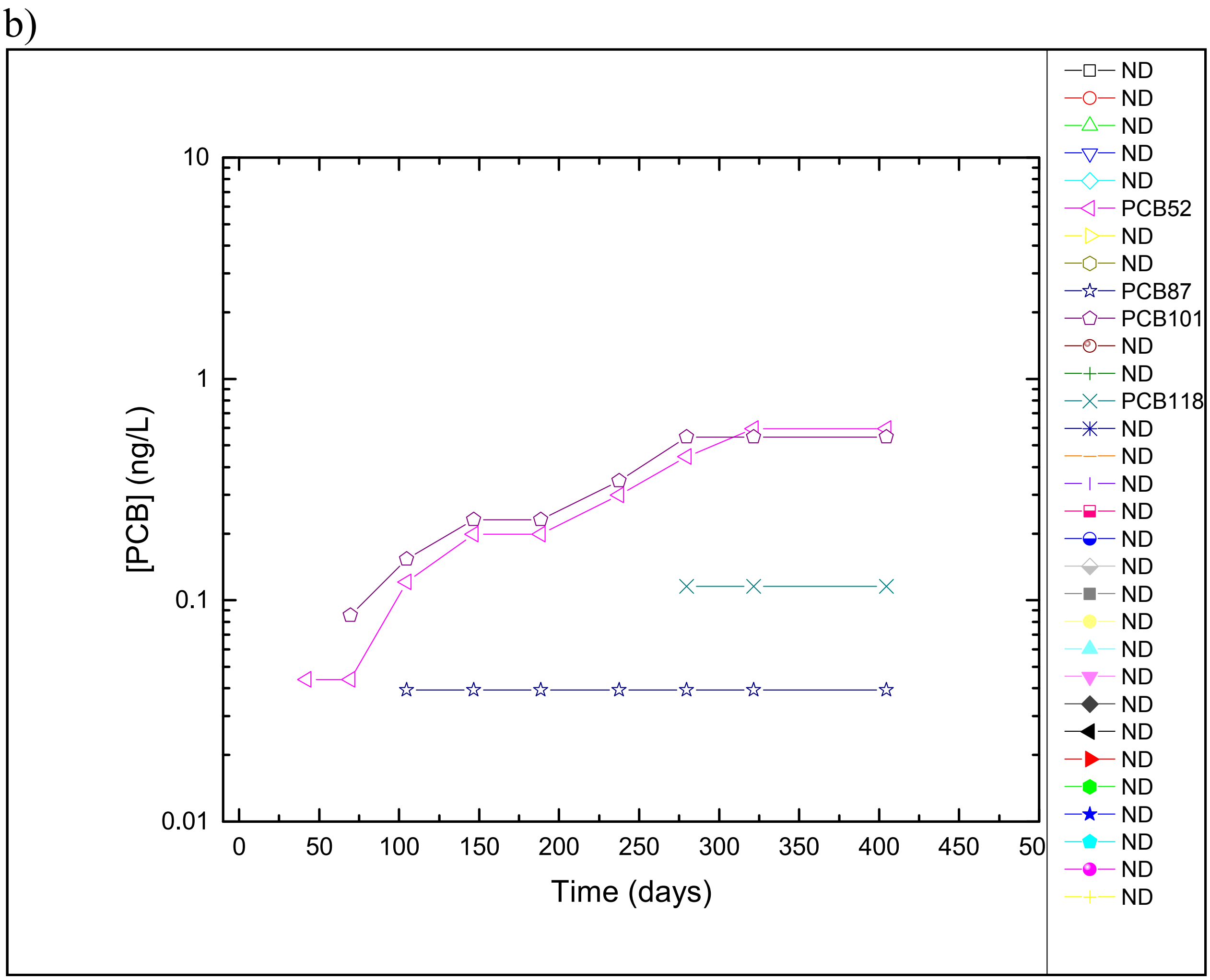


Figure 51 (a–b). Cumulative PCB concentration versus leaching time for AP containing 0.566 mg (0.0472 wt%) tPCBs exposed to a total volume of 12.08 L of ASW leachate at 4°C and 1 bar for 400 days.

Figure 52 shows total released homolog and congener distributions compared with the initial PCB distributions for AP solid. The detected homologs and congeners were normalized and plotted as percent of measured tPCBs in each matrix (leachate versus solid). 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 51. 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. 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 distributions. Despite the significant presence of homologs Cl3 – Cl10 and corresponding congeners in the AP solid, relatively few of the source PCBs were released during leaching. The highest levels of release from AP were from homolog groups Cl4, PCB52, Cl5, and PCB101, whereas Cl3 was observed as only a single detection at just over 100 days, but with no Cl3 target congeners detected. PCB87 and PCB118 (both Cl4) were each detected only once at just over 100 days and ~275 days, respectively.

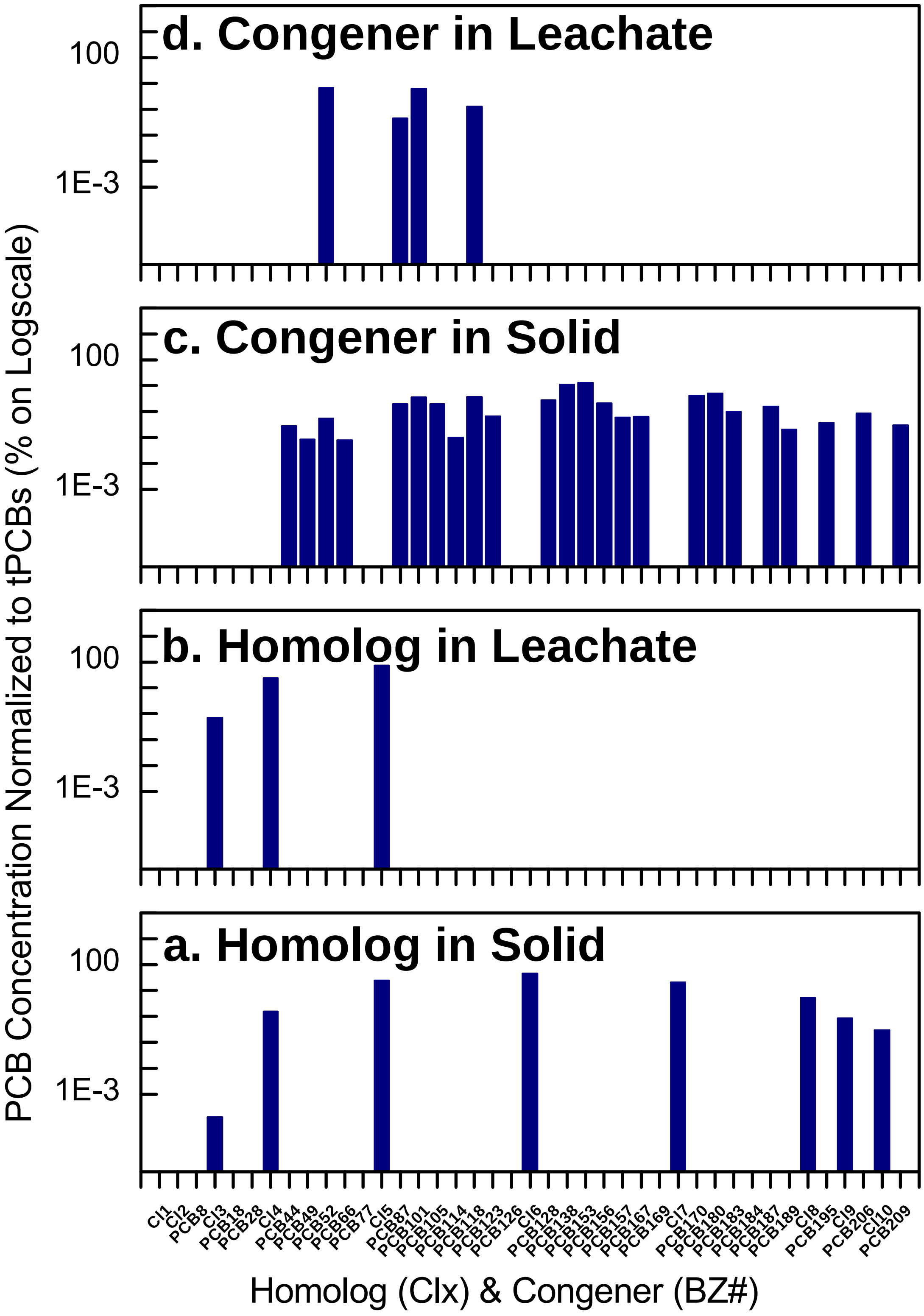


Figure 52 (a–d). Experimental homolog and congener PCB distributions at 4 °C and 1 bar for AP solid (a and c) compared with total homolog and congener distributions of PCBs leached from AP into seawater (b and d).

Normalized PCB distributions are shown for specific AP leachate samples at key intervals across the entire leaching experiment (exposure time). Figure 53 congener and homolog group distributions were observed to be extremely sporadic releases of PCBs in Cl3, Cl4, and Cl5, and correspond to (a) the initial leach rate (iLR, entirely Cl4 and PCB52), (b) the (post-initial) leach rate that immediately followed (piLR, entirely Cl4, Cl5, PCB52 and PCB101), (c) the maximum leach rate (mLR), and (d) the post-maximum final empirical leach rate (fLR, again entirely Cl4 and PCB52). Subsequent to this, at 405 days, no release was observed.

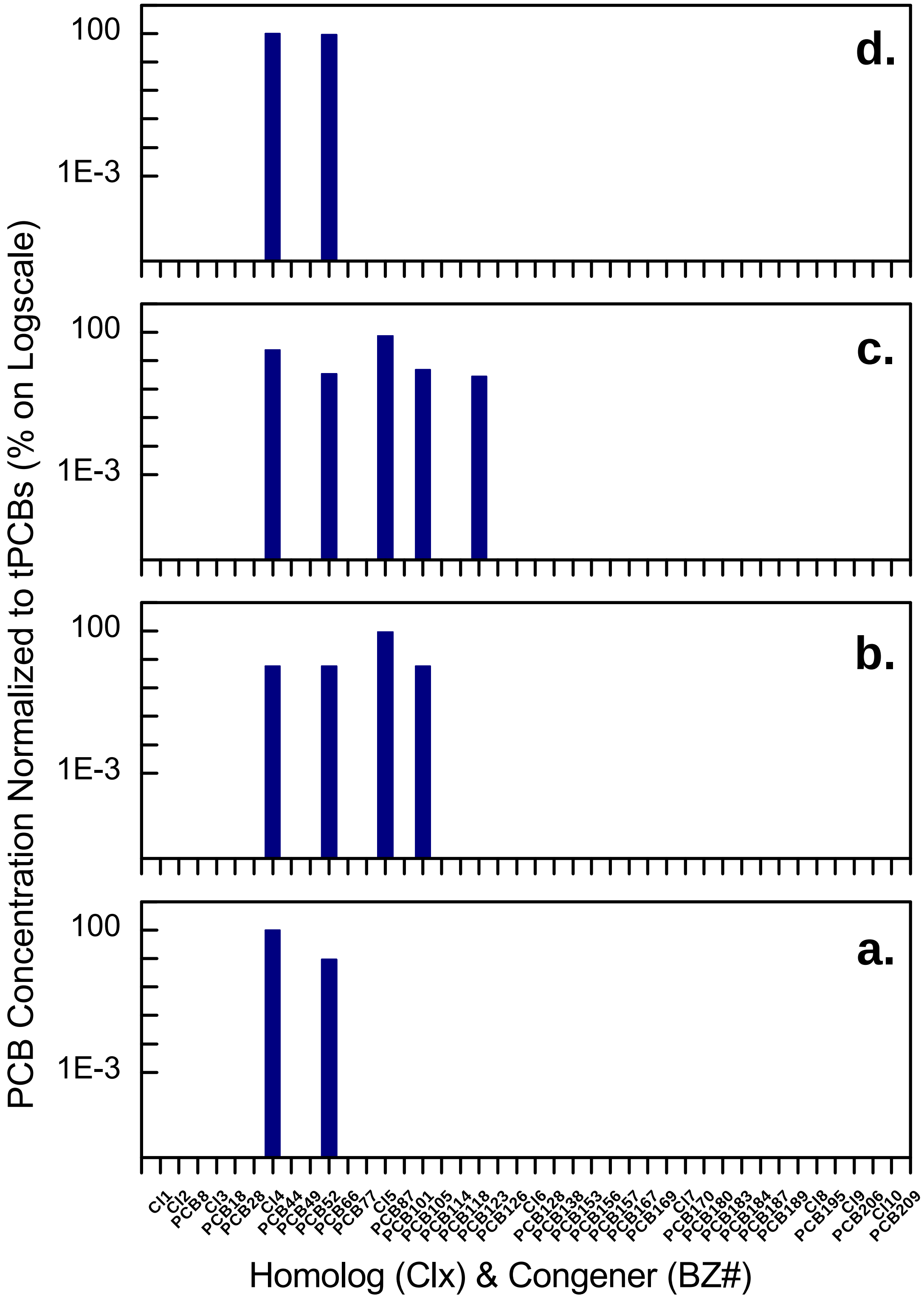


Figure 53 (a–d). Homolog and congener distributions during the 4 ^{o}C-1 bar AP leaching experiment, normalized as percent of total, for leaching intervals ending on days: (a),iLR – 21 d (b) pi LR – 28 d, (c) mLR – 280 d, and (d) fLR – 322 d (no subsequent release was observed at 405 d).

4. RESULTS AND SUMMARY

4.1. AVERAGE LEACH RATE CALCULATIONS

The average leach rate (AVgLR, Equation 5) for each analyte was calculated as described in Equation 5. These average leach rates were derived from the slopes between adjacent points on the respective cumulative concentration versus time curves (Section 3.4) for each sampling interval across the entire leaching experiment and then plotted as a function of leaching time to evaluate leach rate dynamics. In general, leach rates for all analytes from the leaching experiments were observed to first achieve some maximum value over days to months, and then slowly decreased over the remainder of the leaching time (experiment). In some instances, erratic leaching behavior was exhibited very early in the leaching process by extreme variations (increases and decreases up to ~ an order of magnitude) in leach rate. It is thought that this 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 interfacial processes that change the accessibility of seawater to the PCBs in the solid. Generally, a leach rate curve that first exhibited unstable behavior was followed by a leach rate curve that was considered steady state, indicative of a stabilized leaching condition. The AvgLR curves were qualitatively evaluated relative to our conceptual leaching model (Figure 13), for which the leach rate is expected to exhibit some variance upon initial seawater exposure and then achieve a stabilized release condition. This 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. Subsequently, a constant or decreasing rate with time should be observed as PCB congeners are slowly depleted at different rates from the seawater accessible surface area (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 (Figure 3).

The following plots present the average dissolution rate (for Aroclors®) and AvgLR (for shipboard solids) for tPCB, homologs, and congeners versus time for at 4 ^{o}C/1 bar or 4 ^{o}C/300 bar. The sum of the homolog average rate rates equals the average tPCBs release rate curve and lines connecting adjacent data points indicate detection in consecutive ASW samples (continued dissolution of that PCB congener or homolog group), while no line indicates a discontinuity in dissolution (analyte not detected in an adjacent ASW sample). Non-detected target congeners within are noted by ND on the figure legends (analyte list in Table 4). The leach rate data are tabulated in Appendix D along with the raw data-transformed into cumulative concentration data plotted in previous sections. Because this study was monitoring a process over time, it is not valid to make adjustment to very low or near-MDL analyte concentrations, such as might be done for discreet sample data as part of an uncertainty analysis and evaluation. Thus, leaching data were empirically derived without corrections or adjustments. If a homolog group or a target congener was not detected, a rate was not derived (represented as zero in Appendix D) for that leaching interval, and therefore is not plotted as part of the curve. These periods of time where no detectable release occurred are identified by discontinuities in the plotted leach rate curves. Summary statistics for the AvgLR data collected at 4 ^{o}C/1 bar and 4 ^{o}C/300 bar for the Aroclors® and shipbard solids are provided in Table 11.

4.1.1. Aroclor® 1254 (A1254) Analytical Control Dissolution Rates

The dissolution rate behaviors plotted below for the Aroclor® 1254 positive analytical control at 4 °C/1 bar and 4 °C/300 bar can be considered an upper limit of ASW PCB solvation capacity and a reference point for evaluating the leach rates of shipboard solids that contain A1254. 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 like a shipboard solid matrix, although the matrix is only 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 the shipboard solid matrix is expected to dominate during shipboard solid leaching if the PCBs are dispersed homogeneously throughout the solid. If PCBs are phase-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.

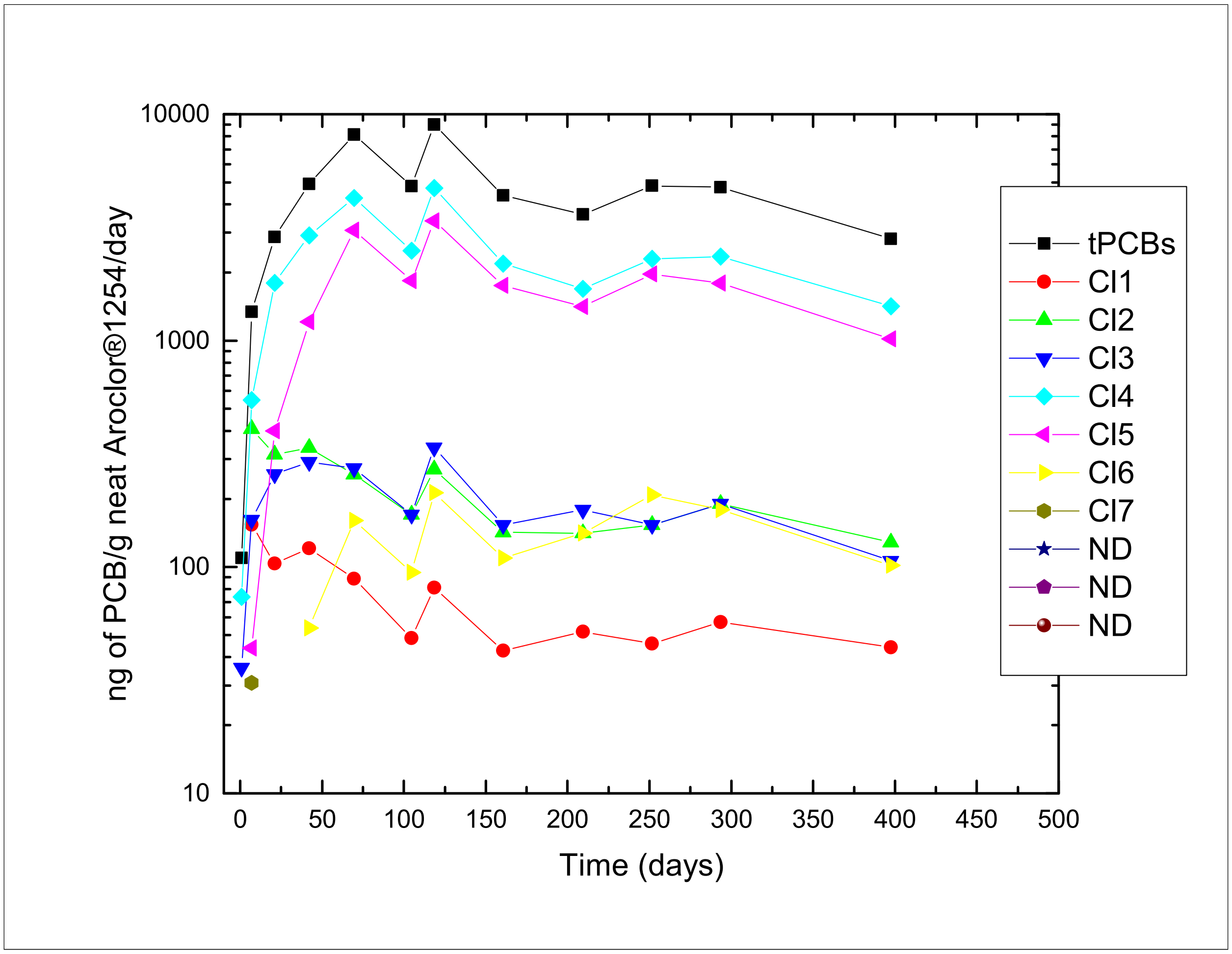
The PCBs could also be selectively phase-separated, that is, some regions of the shipboard solid could be rich in a particular PCB congener or congeners even though the bulk composition is closely matched with a particular Aroclor®. A very small congener-rich phase could affect the distribution of the congeners leached, particularly if the phase is present at the interface (SASA). Determining the interfacial compositions or relative magnitudes of PCB–PCB and various PCB-shipboard solid interactions at the molecular level is beyond the scope of this study. However, although the cohesive (PCB–PCB) interaction is probably stronger, the release is probably 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 a measure of A1254 solvation capacity in seawater under the leaching conditions of the study, a positive dissolution control rather than a true leaching surrogate, as it only represents the dissolution component of PCBs uninhibited by the solid matrix at active leaching surfaces of shipboard solids. Neat Aroclor® 1254 can, however, be considered a surrogate for the leaching behavior of highly mobile material matrices such as oils or greases that contain Aroclor® 1254.

Each average dissolution rate curve describes the release behavior in what would be the worst-case release scenario for a solid containing A1254, 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). Note that the process monitored 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.

The experimental design used in this study resulted in the neat Aroclor® solid matrix itself limiting the availability of PCBs at the ASW-shipboard solid interface (SASA), which dictates the dissolution behavior. For shipboard solids, the experimental design resulted in ASW exchanges at specific sample collection intervals to avoid saturation of the seawater as indicated by tPCB screening levels for A1254 congeners. For Aroclor® 1254 and 1268 dissolution experiments, saturation was considered a possibility during dissolution intervals (between seawater sampling/exchange points). The design, in effect, results in neat Aroclor® 1254 and 1268 dissolution control curves that represent the expected uninhibited A1254 PCB seawater dissolution behavior, under the same specific experimental conditions used in shipboard solid leaching measurements. Because of this similarity in leaching conditions, Aroclor® results are, at times, referred to as "leaching." 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. Similarly, the term "leachate" is used generically for the seawater surrounding a sample from which PCBs dissolve.

Aroclor 1254 dissolution rate results are shown below (Figure 54) for 4 °C/1 bar. The release (dissolution) rate is dominated by Cl4 > Cl5, which are much higher than Cl2 ~ Cl3 ~ Cl6 > Cl1, and Cl7 (the lowest rate observed) was only detected once early in the experiment.

a)



b)

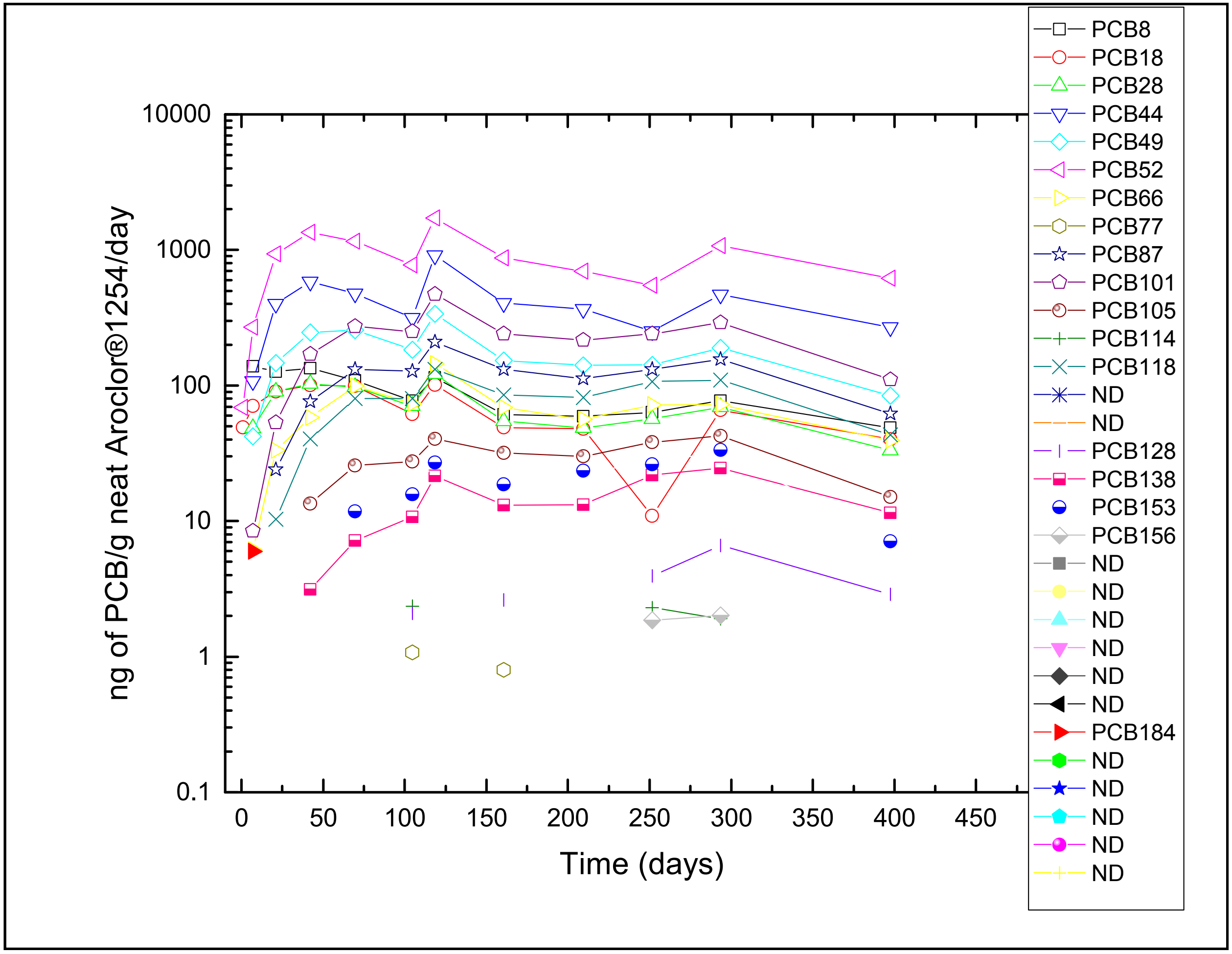


Figure 54(a–b). (a) tPCB and contributing homolog group average dissolution rates, and (b) target congener average dissolution rates within those detected homolog groups (Cl1–Cl7) for neat Aroclor® 1254 at 4 °C/1bar. Non-detected target congeners within detected homolog groups included PCB123 and PCB126 (Cl5); PCB157, PCB167, and PCB169 (Cl6); and PCB170, PCB180, PCB183, PCB187, and PCB189 (Cl7).

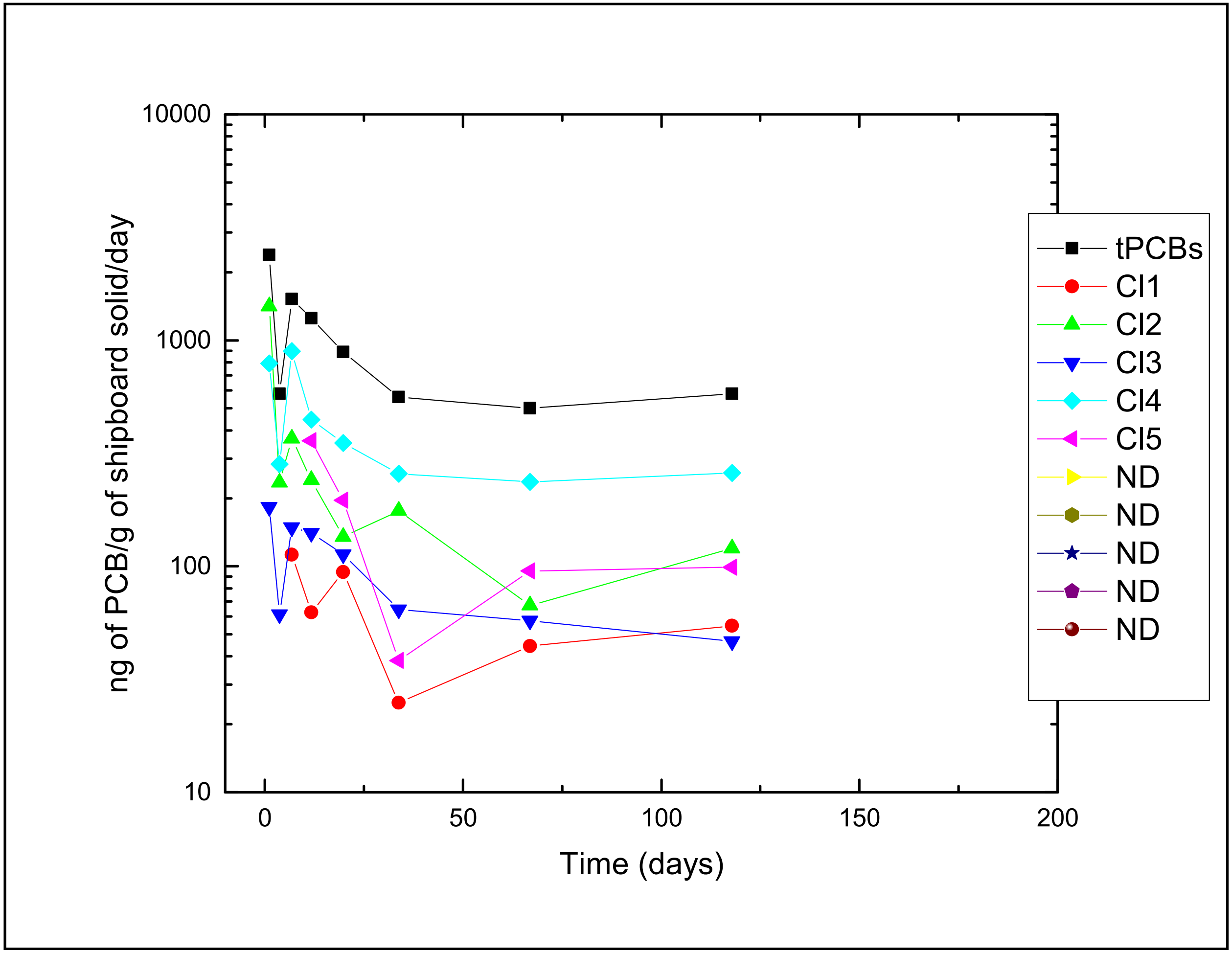
For A1254, average dissolution rate curves show rapid initial dissolution, observed as an increasing average rate observed prior to day 69, followed by a maximum rate (mLR) near day 120, a post maximum rate (pmLR) decrease beyond that, to reach a steady-state final rate (fLR) after day 300. Complete evaluation of this type of behavior cannot be addressed in this study because the leaching data collection interval was too long and dictated by sampling logistics (would require real-time data collection with acquisition time shorter than the kinetics associated with PCB dissolution). However, the tPCB average rates leading up to 69 days, which are derived from homolog data, correlate well with congener behaviors. The tPCB rates prior to day 69, calculated based on concentration data in Appendix C are 109 (= 0.17 pptr/1 day), 1,342 (=13.6 pptr/7 days), 2,875 (= 80.9 pptr/21 days), and 4,923 (= 252.4 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 increase, that is, it only took 7 days to change by 1,342 pptr, much faster than the following concentration change of 2,875 pptr, which took 21 days, nearly three times as long. Also, the subsequent concentration change (4,923 pptr) was larger by 3,581 pptr, but it took six times longer to reach this concentration, an indication of limiting behavior by the Aroclor® matrix, if indeed rapid PCB dissolution occurred initially. Although these observations may indicate that the magnitude might be an experimental artifact dictated somewhat by the time-interval that occurred before sampling, this is not the case. Rather this behavior is related to the availability of PCBs at the SASA interface and reflects the functional limiting complexities of PCB release by the solid matrix. Note that the calculated rates in this study were not instantaneous (distinct rates corresponding to a distinct point in leaching time), but lower resolution averages calculated over a leaching time-interval that cannot capture the real-time dynamics of the limiting behavior, only the overall effects of the limiting behavior.

The observed Aroclor® 1254 average dissolution rates are valid positive analytical controls for evaluating the PCB solvation capacity of the seawater under the empirical leaching conditions, for shipboard solids that contain Aroclor® 1254. To this end, each concentration leaching curve in Subsection 3.4 for shipboard solids that contained a significant amount of A1254 and/or 1260, but not A1268, were validated against the neat Aroclor® 1254 concentration versus time curves also in Subsection 3.4, i.e., black rubber pipe hanger liner (BRPHL), electrical cable (EC), and foam rubber/ Ensolite®(FRE). The results in Section 3 confirmed that shipboard solid leachate tPCB concentrations were all lower than tPCB concentrations for the Aroclor® analytical controls, consistent with PCB release suppressed only by the shipboard solid matrix (diffusion-limited). 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, where significant suppression of PCB concentrations by the shipboard solids was observed. The average release rates asubsequently calculated and plotted for these solids are thus below the effective saturation limit and considered valid measures of release. The neat A1254 results can also be used to estimate the worst-case leaching behavior for materials not tested in this work that might contain A1254, e.g., mobile A1254 or 1260-containing oils and greases.

Each analyte in the A1254 average leaching curves can be extrapolated beyond the experimental timeframe using standard data-treatment and curve-fitting methods described in Subsection 2.13. Extrapolated results can be especially useful for demonstrating that average leach rates are expected to continue decreasing beyond the average leach rates experimentally determined in this study.

For comparison, the average A1254 release rates at 4 °C and 300 bar (Figure 55) showed distinctly different release rate behavior compared to 4 °C/1 bar. The increased hydrostatic pressure resulted in an approximate four-fold decrease in A1254 homolog and target congener dissolution rates, with Cl6 and Cl7 homologs/congeners never detected (no release rate), PCB52 rates quantified only through ~75 days, and PCB118 rates only quantified from ~75 days on.

a)


10000
1000
100
10
ng of PCB/g of shipboard solid/day
0
50
100
150
200
Time (days)
tPCBs
Cl1
Cl2
Cl3
Cl4
Cl5
ND
ND
ND
ND
ND

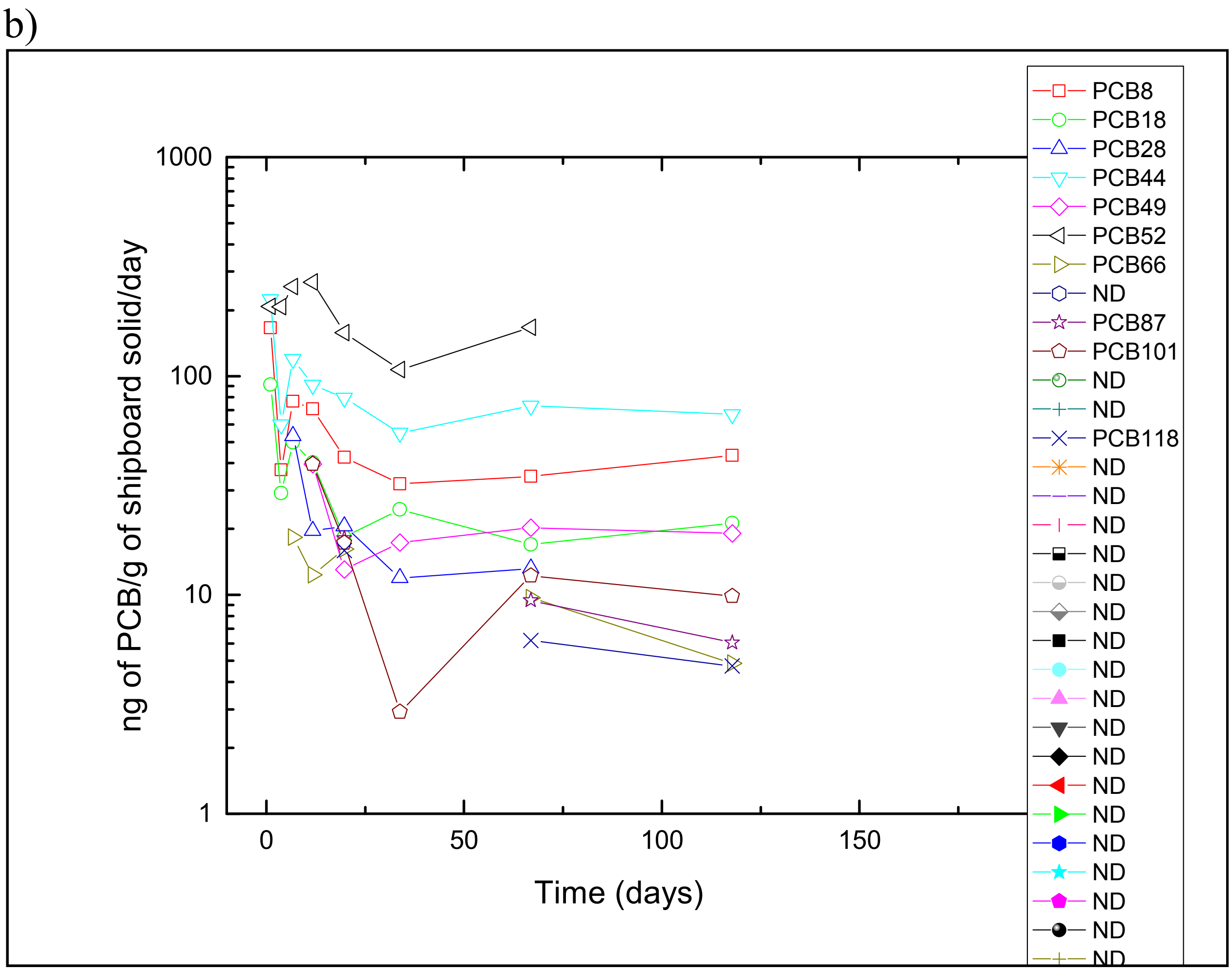
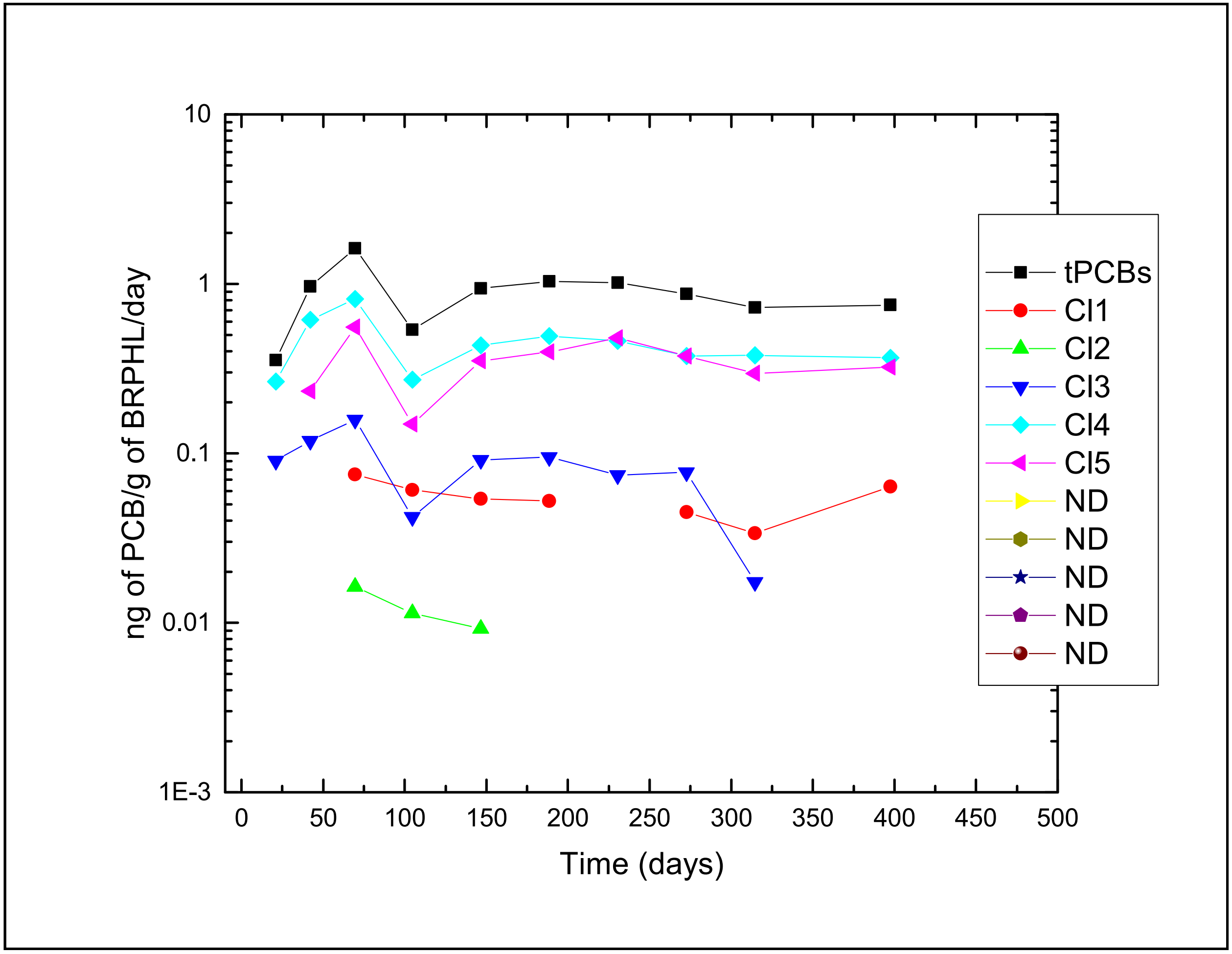


Figure 55(a–b). (a) tPCB and contributing homolog group average dissolution rates, and (b) target congener average dissolution rates within those detected homolog groups (Cl1–Cl5) for neat Aroclor® 1254 at 4 °C/300bar. Non-detected target congeners within detected homolog groups included PCB77 (Cl4); and PCB105, PCB114, PCB123 and PCB126 (Cl5).

4.1.2. Black Rubber Pipe Hanger Liner (BRPHL) Leach Rates

The BRPHL sample contained 0.19 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 9. The average leach rate curves for BRPHL for tPCBs, homologs, and target congeners is presented in Figure 56. The average leach rates for tPCBs were in the 1 ng/g shipboard solid-day range, significantly lower (by nearly 4 orders of magnitude) than the tPCBs average leach rate for A1254. This lower rate indicates significant suppression of PCB leaching by the BRPHL polymer matrix. Cl1 through Cl5 release rates were dominated by Cl4 ~ Cl5 > Cl1 ~ Cl3 > Cl2. Note that the Cl2 homolog and target congener PCB8 were only detected in the earliest stages of leaching, and the leaching had stopped for these analytes by the end of the first 5 months of leaching.

a)


ng of PCB/g of BRPHL/day
10
1
0.1
0.01
1E-3
0
50
100
150
200
250
300
350
400
450
500
Time (days)
tPCBs
Cl1
Cl2
Cl3
Cl4
Cl5
ND
ND
ND
ND
ND

b)

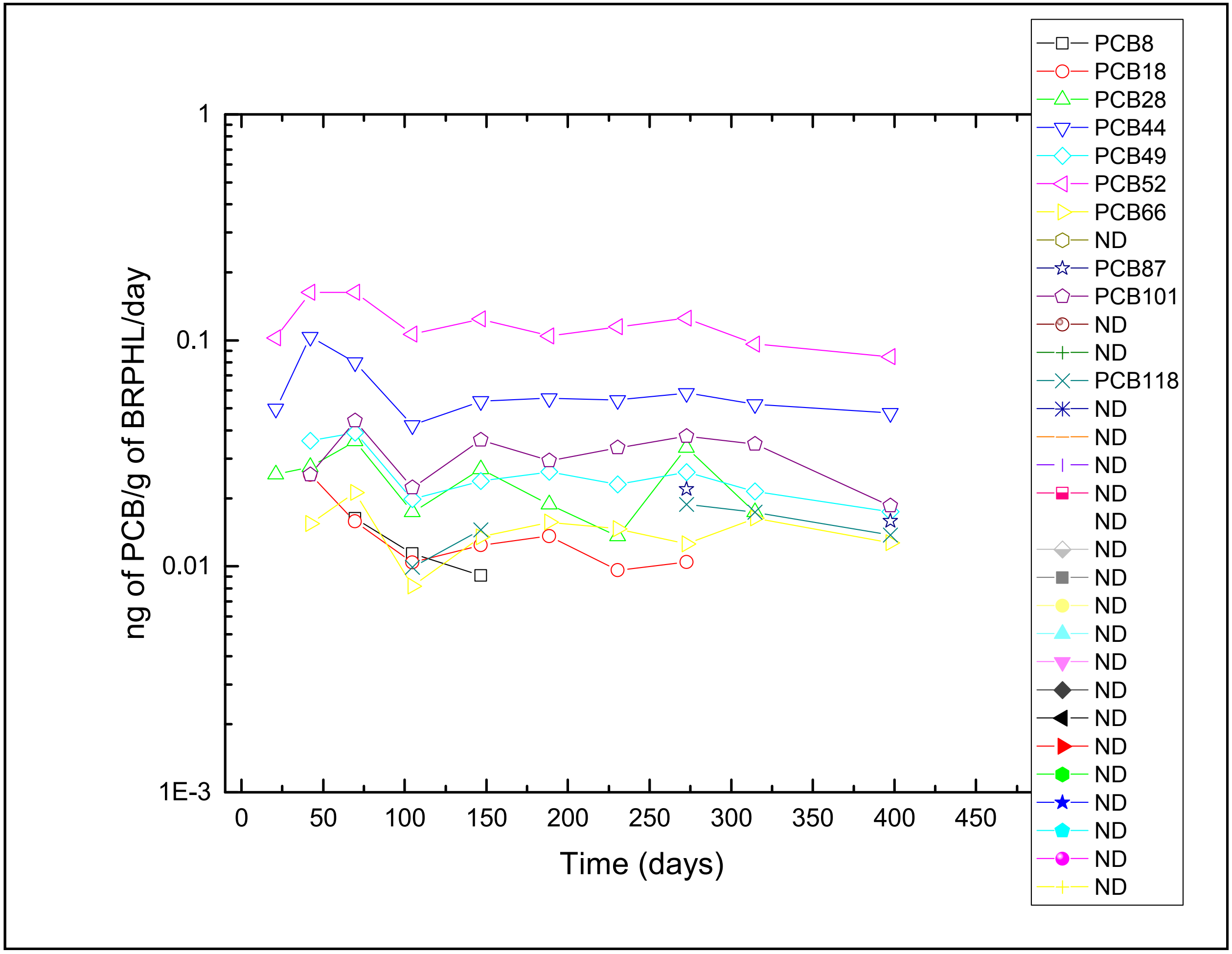
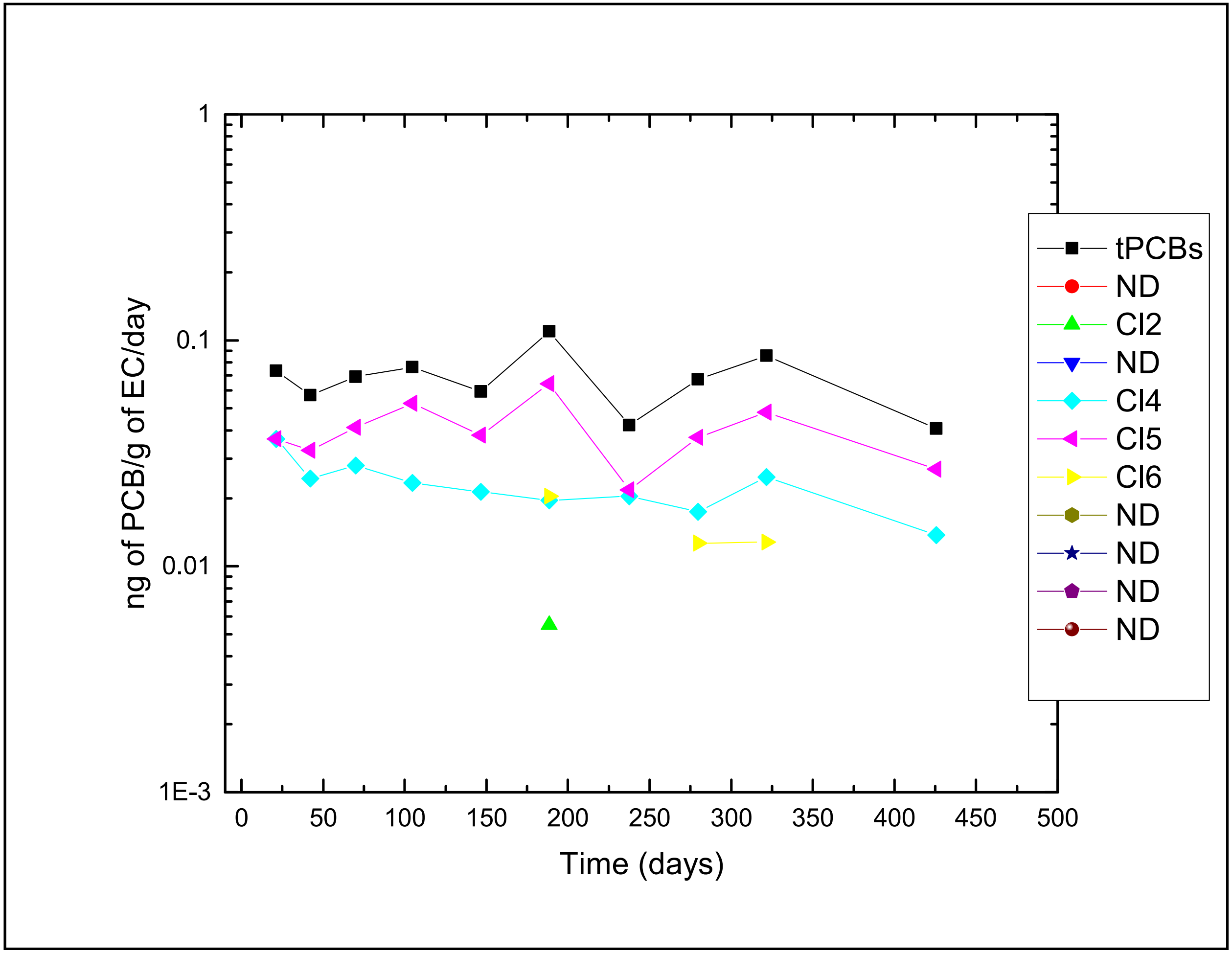


Figure 56(a–b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl1–Cl5) for BRPHL at 4 °C/1bar. Non-detected target congeners within detected homolog groups included PCB77 (Cl4); and PCB105, PCB114, PCB123, and PCB126 (Cl5).

4.1.3. Electrical Cable (EC) Leach Rates

The tPCB content for the intact EC shipboard solid sample was 0.11 wt%, with the likely primary component identified in Table 9 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 at 4 °C and 1 bar for tPCBs, homolog groups and target congeners is shown in Figure 57. The average leach rates for EC were generally less than 0.1 ng/g shipboard solid-day, 5 orders of magnitude below the A1254 average leach rates, signifying substantial leaching suppression by the EC solid matrix. Most leaching occurred in homolog groups Cl4 and Cl5 across the entire leaching timeframe, while the Cl2 and Cl6 homolog groups and corresponding target congeners were detected only sporadically.

a)


1
0.1
0.01
1E-3
ng of PCB/g of EC/day
0
50
100
150
200
250
300
350
400
450
500
Time (days)
tPCBs
ND
Cl2
ND
Cl4
Cl5
Cl6
ND
ND
ND
ND

b)

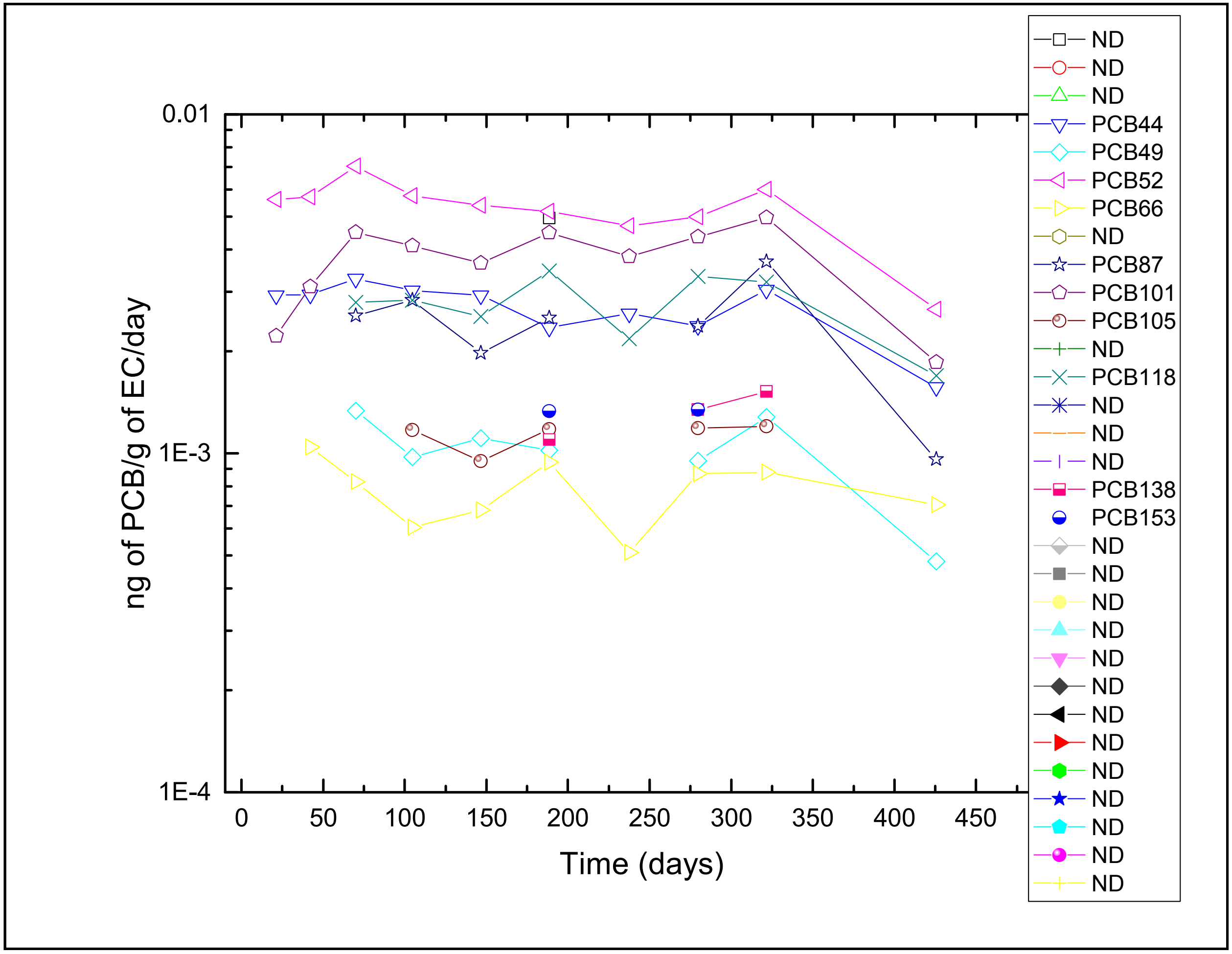
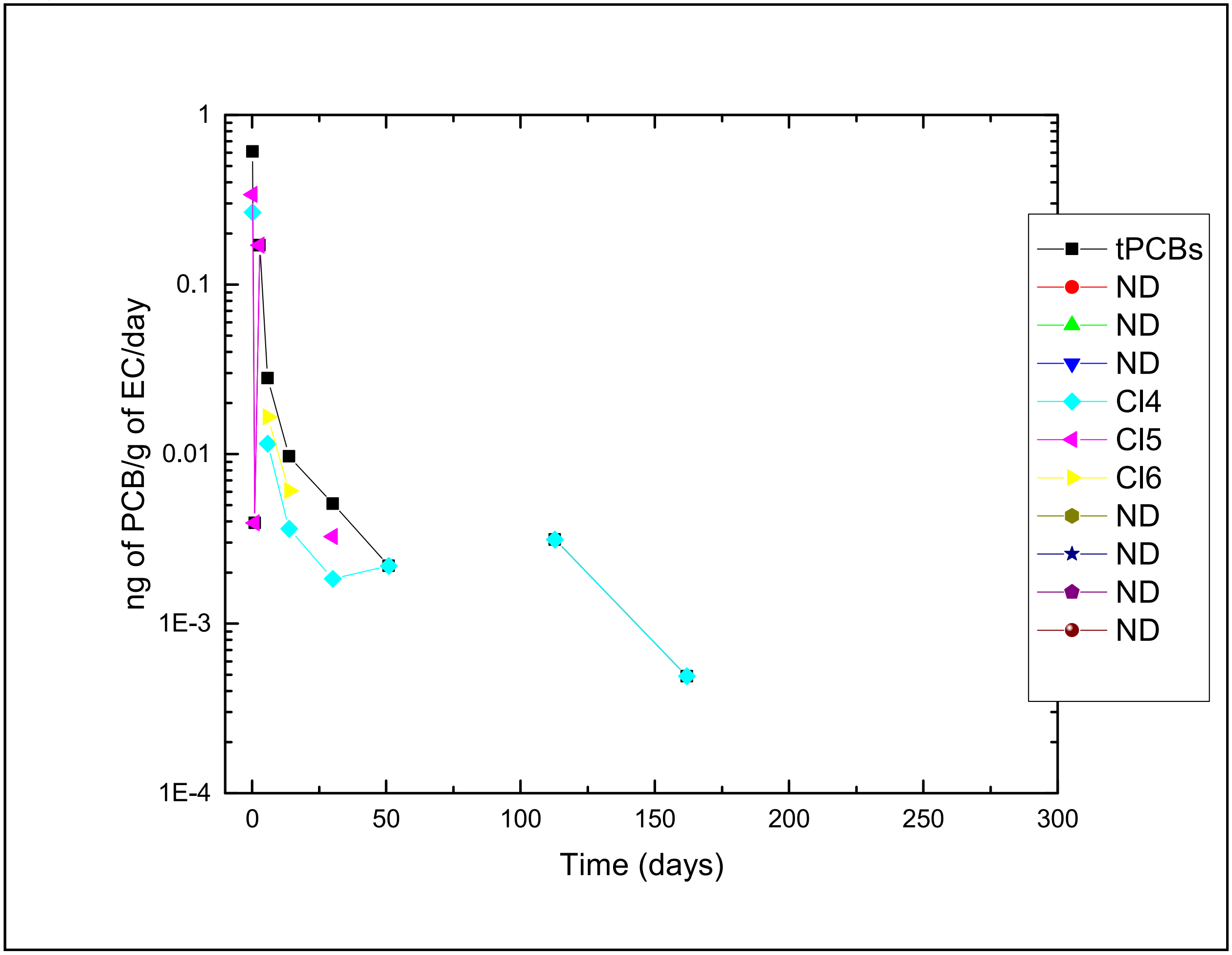


Figure 57(a–b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl2, Cl4–Cl6) for EC at 4 °C/1bar. Non-detected target congeners within detected homolog groups included PCB77 (Cl4), PCB114, PCB123, and PCB126 (Cl5); and PCB128, PCB156, PCB157, PCB167, and PCB169 (Cl6).

The average leach rate curves for EC (0.0865 wt%: nominally 91% Aroclor® 1254, 8% Aroclor® 1260 and 1% Aroclor® 1242) at 4 °C and 300 bar were below 0.01 ng/g shipboard solid-day (Figure 58), which is 4 orders of magnitude below the A1254 average leach rates at 4 °C and 300 bar, and an order of magnitude below the 4°C/1 bar EC leach rates above, illustrating significant pressure dependence. Release was dominated by homolog group Cl4 and corresponding target congener PCB52. Homologs and congeners in groups Cl5 and Cl6 contributed to high initial release rates, but were sporadic throughout the remainder of the leaching experiment.

a)


ng of PCB/g of EC/day
1
0.1
0.01
1E-3
1E-4
0
50
100
150
200
250
300
Time (days)
tPCBs
ND
ND
ND
Cl4
Cl5
Cl6
ND
ND
ND
ND

b)

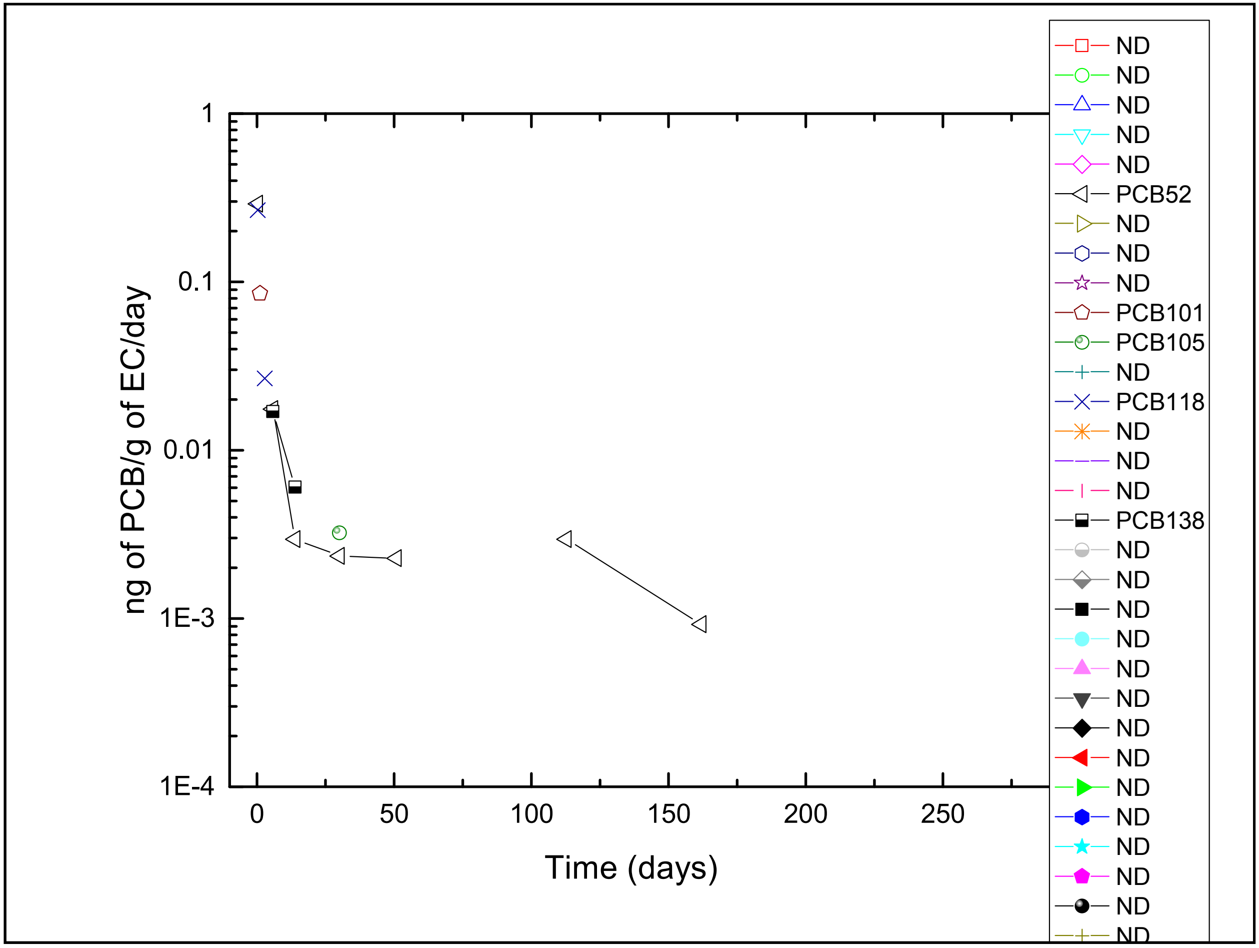
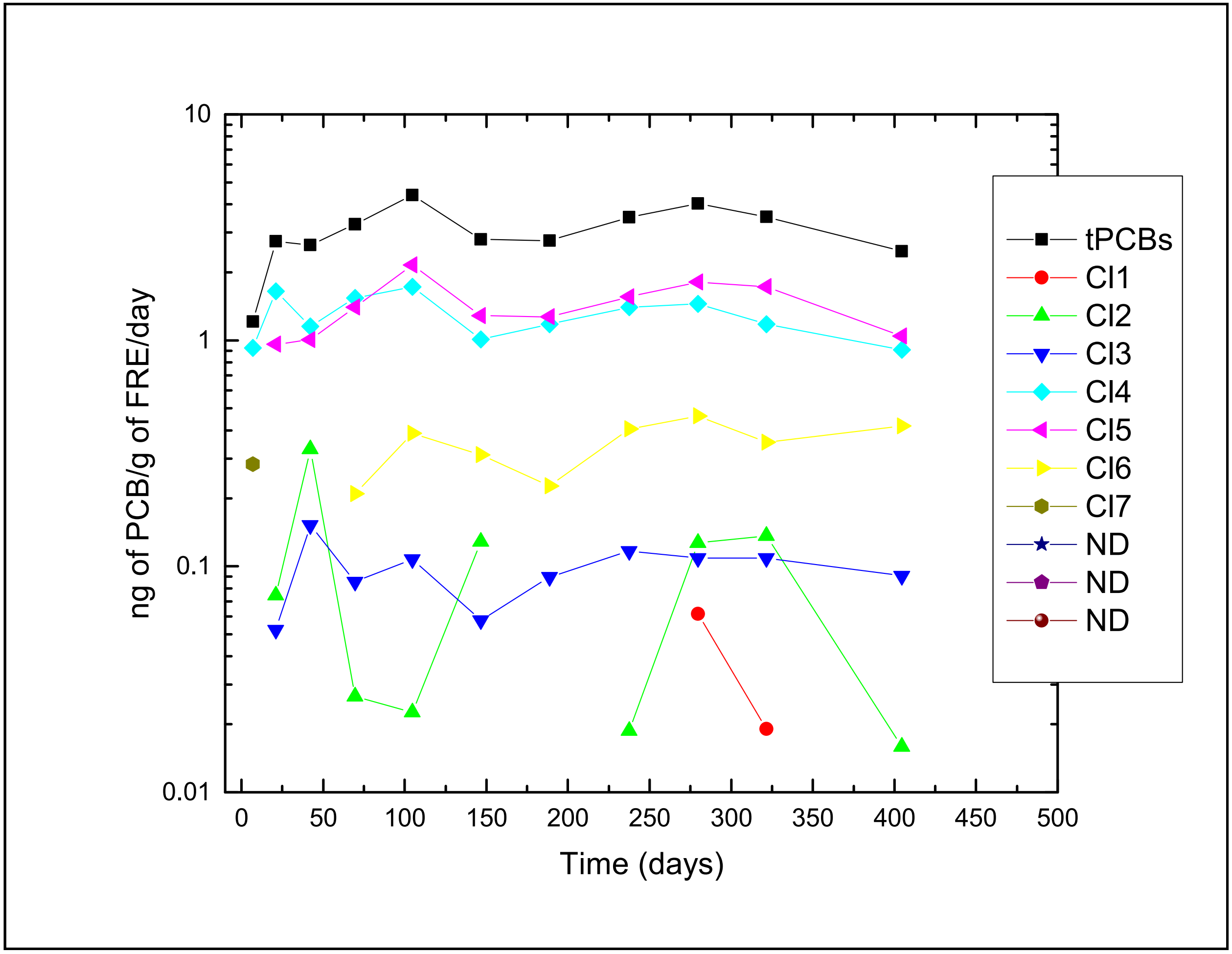


Figure 58(a-b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl4–Cl6) for EC at 4 °C/300bar. Non-detected target congeners within detected homolog groups included PCB44, PCB49, PCB66, PCB77 (Cl4), PCB87, PCB114, PCB123, and PCB126 (Cl5); and PCB128, PCB153, PCB156, PCB157, PCB167, and PCB169 (Cl6).

4.1.4. Foam Rubber/Ensolite® (FRE) Leach Rates

This shipboard solid sample contained 0.732 wt% tPCBs, composed primarily (Table 9) of Aroclor® 1254 (nominally 93%) and possibly Aroclor® 1260 (nominally 7%). The average leach rate curves for tPCBs, all detected homologs (Cl1 through Cl7), and corresponding target congeners, are shown in Figure 59. All homolog groups were present (leached) throughout the 438-day leaching period, with the exception of analytes Cl1 and Cl7 homolog group and congeners, which only appeared late and early during the leaching, respectively. Leaching of Cl7 stopped within the first month, and Cl1 was only observed later in the leaching experiment. Note that homolog group Cl7 and PCB184 appeared only once, at the onset of leaching. This solid was also one of several, including FGI and BRPHL, that exhibited Cl1 leaching, even though Cl1 was observed in A1254 and A1268 dissolution controls. The overall leaching curve behavior was qualitatively very similar to the leaching curves exhibited by BRPHL and EC, with a similar magnitude of release for BRPHL, but EC leach rate was 10 to 100 times lower.

a)


10
1
0.1
0.01
ng of PCB/g of FRE/day
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)

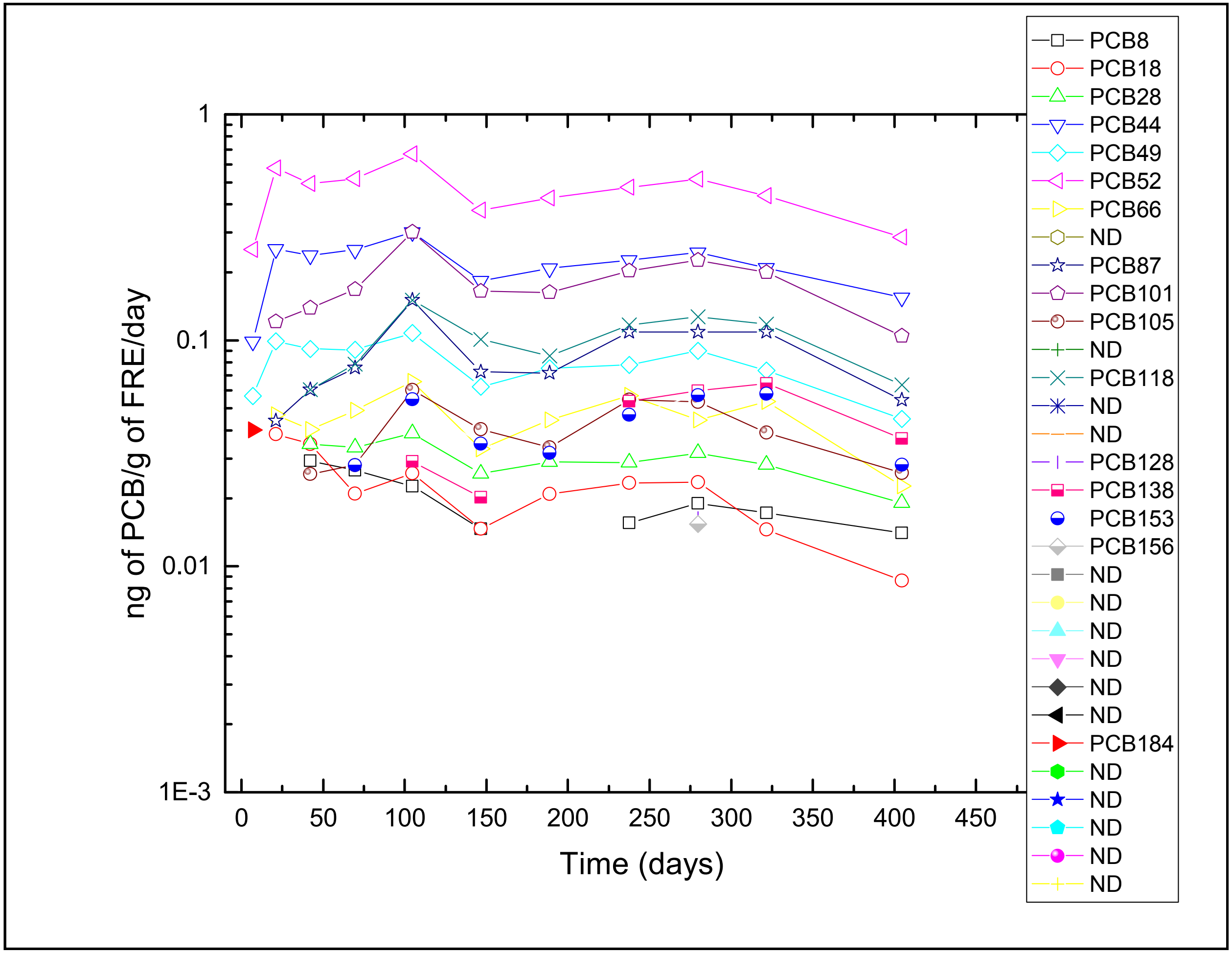


Figure 59(a–b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl1–Cl7) for FRE at 4 °C/1bar. Non-detected target congeners within detected homolog groups included congeners PCB77 (Cl4); PCB114, PCB123 and PCB126 (Cl5); PCB157, PCB167, PCB169 (Cl6); and PCB170, PCB180, PCB183, PCB187, and PCB189 (Cl7).

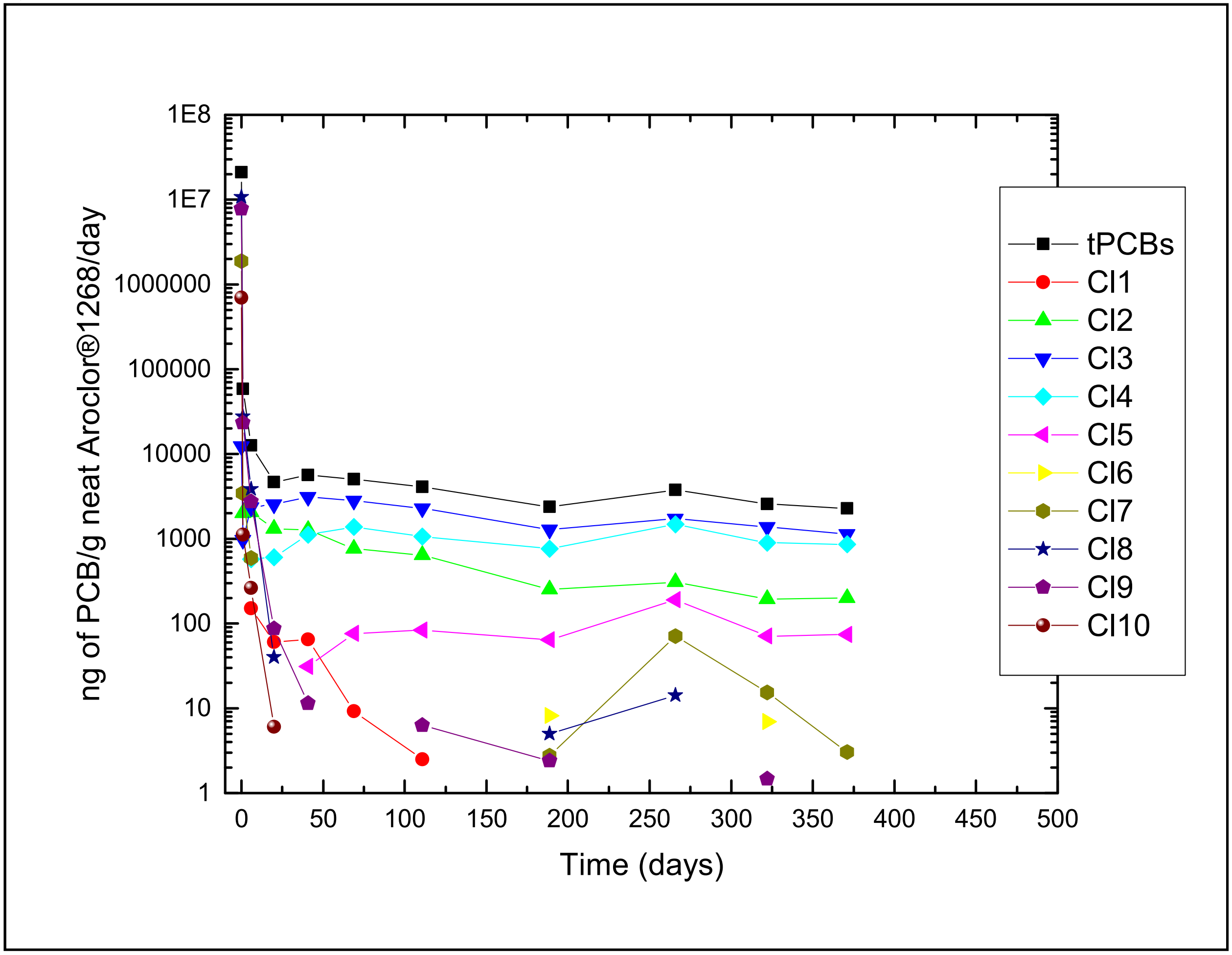
4.1.5. Aroclor® 1268 (A1268) Analytical Control Dissolution Rates

The release rate of neat A1268 at 4°C/1 bar (Figure 60) provides an upper limit for the dissolution rate component at 4 °C/1 bar for shipboard solids containing a significant amount of A1268. This Aroclor®exhibited PCB release from all homolog groups and in addition, an initial very high tPCB dissolution rate was observed, driven primarily by readily available congeners detected in homolog groups Cl7–Cl10 upon ASW contact. These homologs also decreased very rapidly and disappeared, at least temporarily, over the first ~3 weeks of the experiment, indicating a diminished availability of these species at the SASA interface once initial dissolution occured.

As observed for A1254, release of individual congeners comprised a fundamental dissolution behavior, and the mechanism for neat A1268 dissolution is effected similarly in that it is a PCB mixture without a shipboard solid matrix. Also, as with A1254, each PCB congener in A1268 exists in (and is released from) a matrix of a mixture of PCB congeners, resulting in only PCB–

PCB interactions (cohesion) in the solid contributing to the release mechanism. This contrasts 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, it is a much less significant contributor to the release behavior/mechanism. As mentioned previously, PCBs could also possibly 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 distribution for a particular Aroclor®. A very small congener-rich phase present at the SASA interface could significantly effect the observed leached congener distribution. For reasons similar to those discussed for Aroclor® 1254, the neat Aroclor® 1268 analytical control behavior can be considered a measure of A1268 PCB solvation capacity in seawater under the specified leaching conditions, and is representative of the dissolution component of those PCBs uninhibited by the solid matrix at active leaching surfaces of shipboard solids.

a)



b)

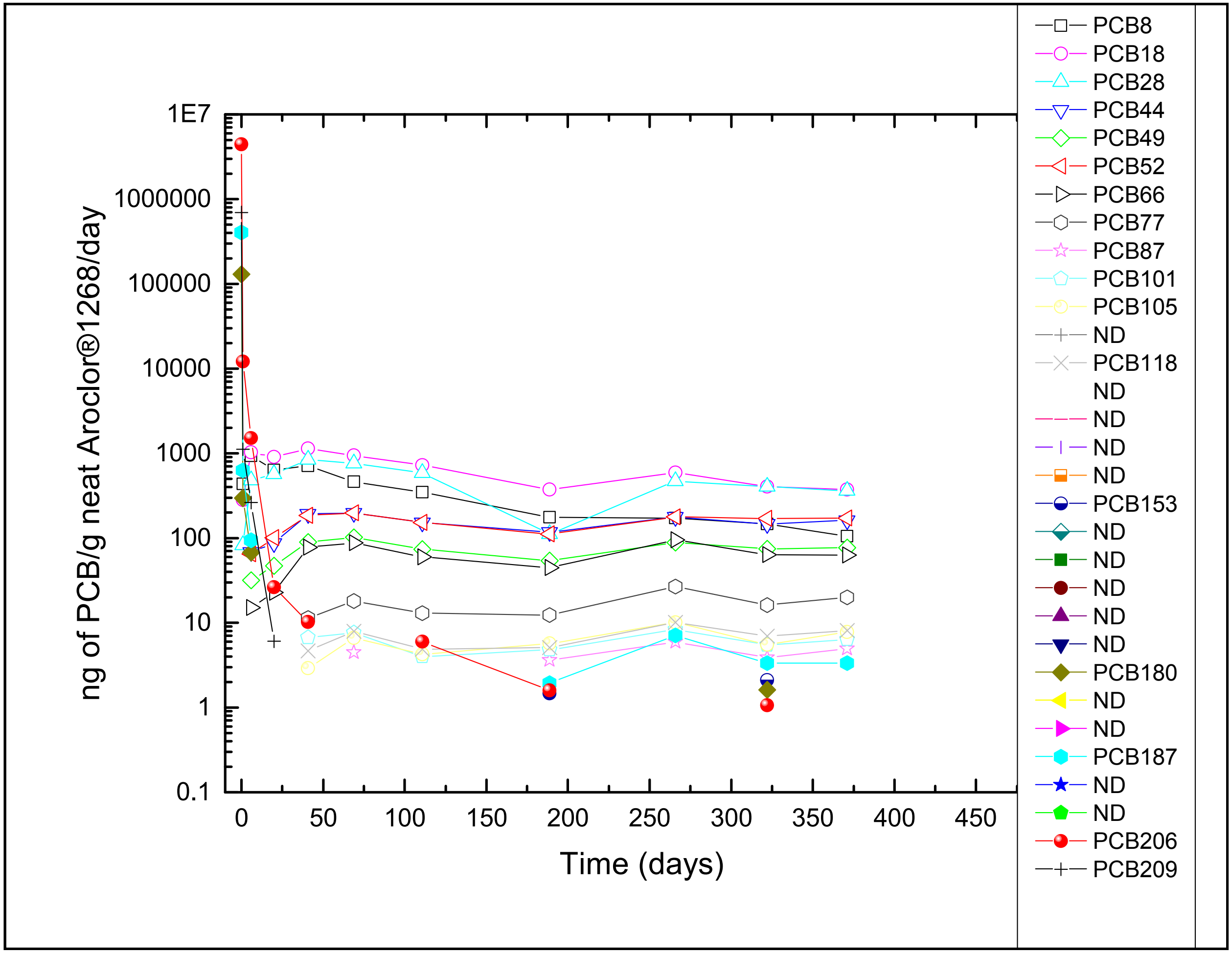


Figure 60(a–b). (a) tPCB and contributing homolog group average dissolution rates, and (b) target congener average dissolution rates within those detected homolog groups (Cl1–Cl10) for neat Aroclor® 1268 at 4 °C/1bar. Non-detected target congeners within detected homolog groups included PCBs 114, 123 and 126 (Cl5); PCBs 128, 138, 156,157, 167, and 169 (Cl6); PCBs 170, 183, 184, and 189 (Cl7); and PCB 195 (Cl8).

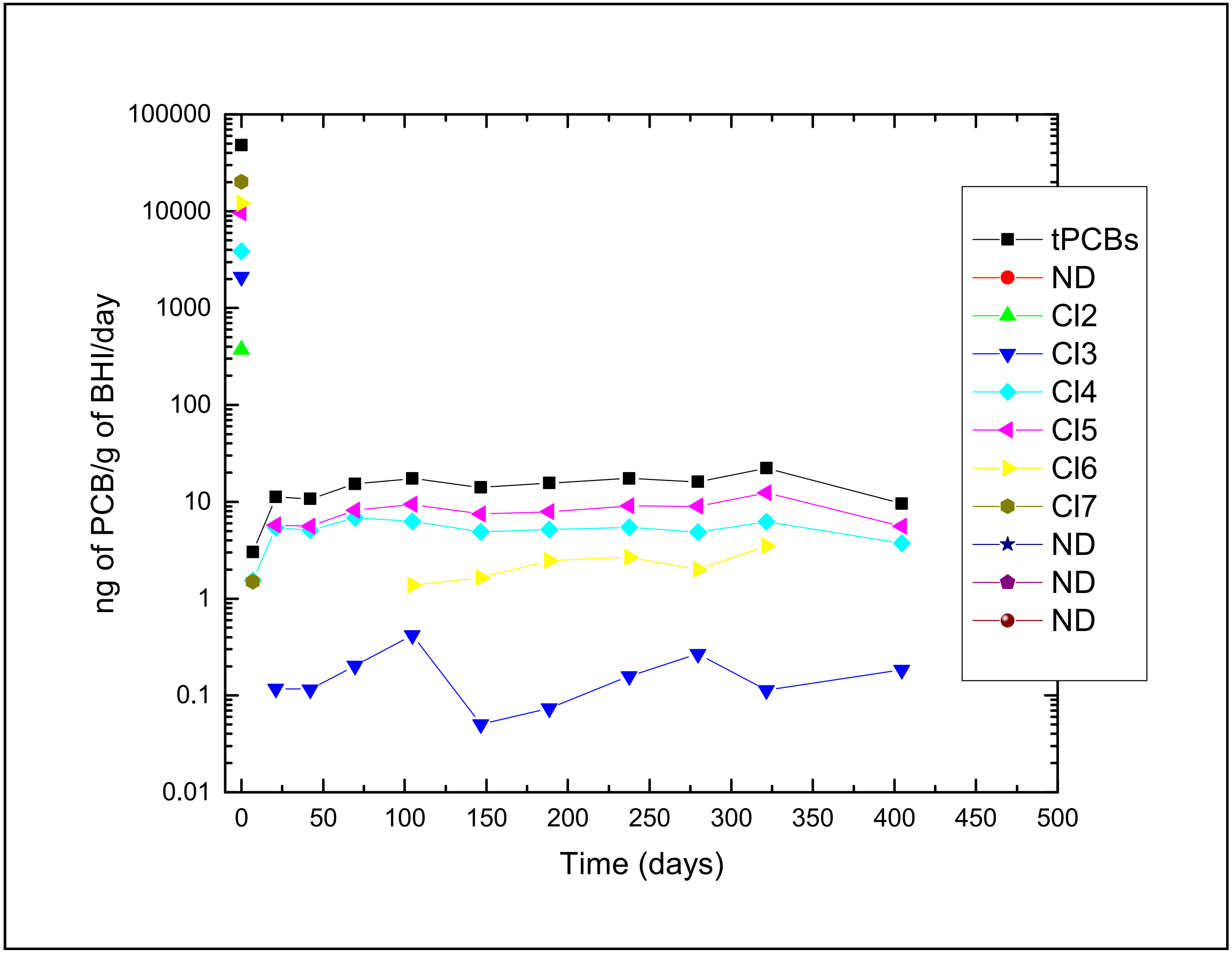
Each of the above 4 °C/1 bar A1268 average dissolution rate curves corresponds to a worst-case A1268 release scenario for a solid containing A1268 at the SASA interface. As indicated for the neat A1254 experiment, this type of experiment is a valid dissolution control, but it is not a valid "*leaching*" control/surrogate for shipboard solids. However, neat Aroclor® 1268 can be considered a surrogate for the leaching behavior of highly mobile material matrices such as Aroclor® 1268-containing oils or greases. Aroclor® 1268 results also do not represent a solubility experiment, where an excess of the neat 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 neat Aroclor® solid matrix itself limited the dissolution behavior, a feature of the experimental design; the seawater leachate was exchanged at sample collection intervals selected to avoid Aroclor® saturation in shipboard solid leaching experiments. However, this did not preclude the possibility of saturation between leachate exchange/sampling points. Effectively, a neat Aroclor® positive control curve represents the ASW PCB dissolution behavior under 4 °C/1 bar experimental leaching conditions identical to what was used in the shipboard solid leaching determinations. Due to this similarity, Aroclor® results are occasionally/inadvertently called "leaching," but PCB "release" is the correct term that includes PCB dissolution, but for shipboard solids also includes PCB transport (leaching) processes through the inert solid matrix.

Each *concentration versus time* leaching curve in Subsection 3.4 for shipboard solids contained A1268 only or A1268 with A1254 and/or A1260 (FGI, FGO, BHI, and AP), were evaluated against the neat Aroclor® 1268 *concentration versus time* curves, also in Subsection 3.4. BHI and AP results were also evaluated against A1254 because Aroclor® 1254 was possibly present in significant amounts in addition to A1268. The shipboard solid leachate PCB concentrations were *lower* than that for neat Aroclor®, consistent with the suppresion of PCB release by the shipboard solid matrix. The raw concentration data in Appendix C also showed similar significant suppression of PCB concentrations by the shipboard solids tested. As a result, the average leach rates subsequently calculated and plotted for the shipboard solids were considered valid leaching behaviors, which occurred well below the effective saturation limit.

4.1.6. Bulkhead Insulation (BHI) Leach Rates

This BHI sample contained 0.0410 wt% tPCBs, nominally 15.3% A1268, 31.3% A1260, and 54.3% A1254 (Table 9). The BHI sample exhibited the highest leach rates for all the shipboard solids tested; however, these leach rates were still ~3 orders of magnitude lower than those for either either Aroclor® 1254 or 1268. The average leach rates calculated for tPCBs, homolog groups (Cl2 through Cl7) and congeners (Figure 61) showed extremely high short-term initial release, followed by stable release rates dominated by Cl4–Cl6 homologs/congeners, and minor but persistent contributions from congeners in homolog group Cl3. Homolog groups Cl2 and Cl7, and corresponding target congeners, leached initially and then became undetectable just after initial exposure to seawater, whereas Cl6 continued and stopped after 321 days, and homolog groups Cl3-Cl5 continued leaching over the 404-day experiment.

a)



ng of PCB/g of BHI/day
100000
10000
1000
100
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Time (days)
tPCBs
ND
Cl2
Cl3
Cl4
Cl5
Cl6
Cl7
ND
ND
ND

b)

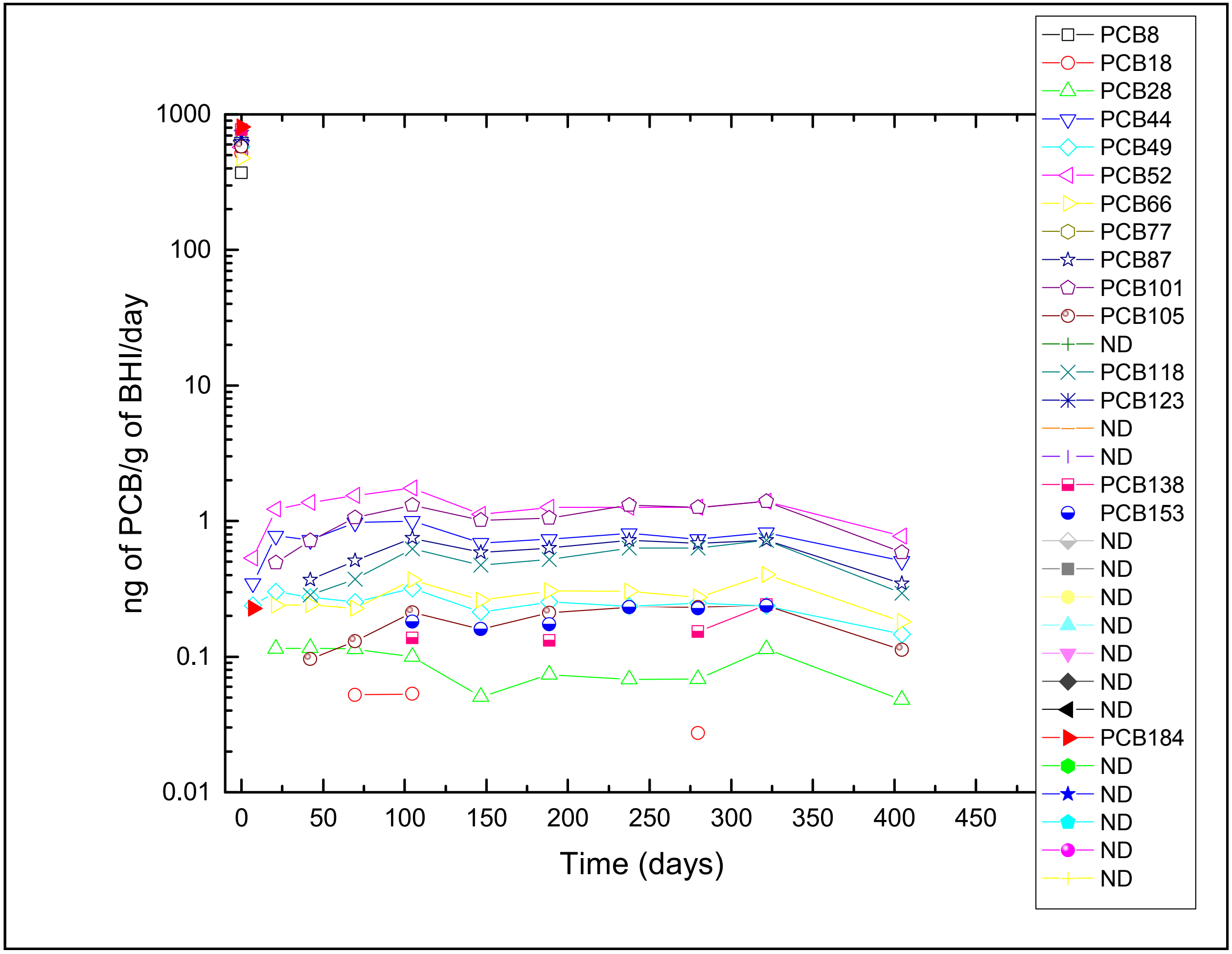
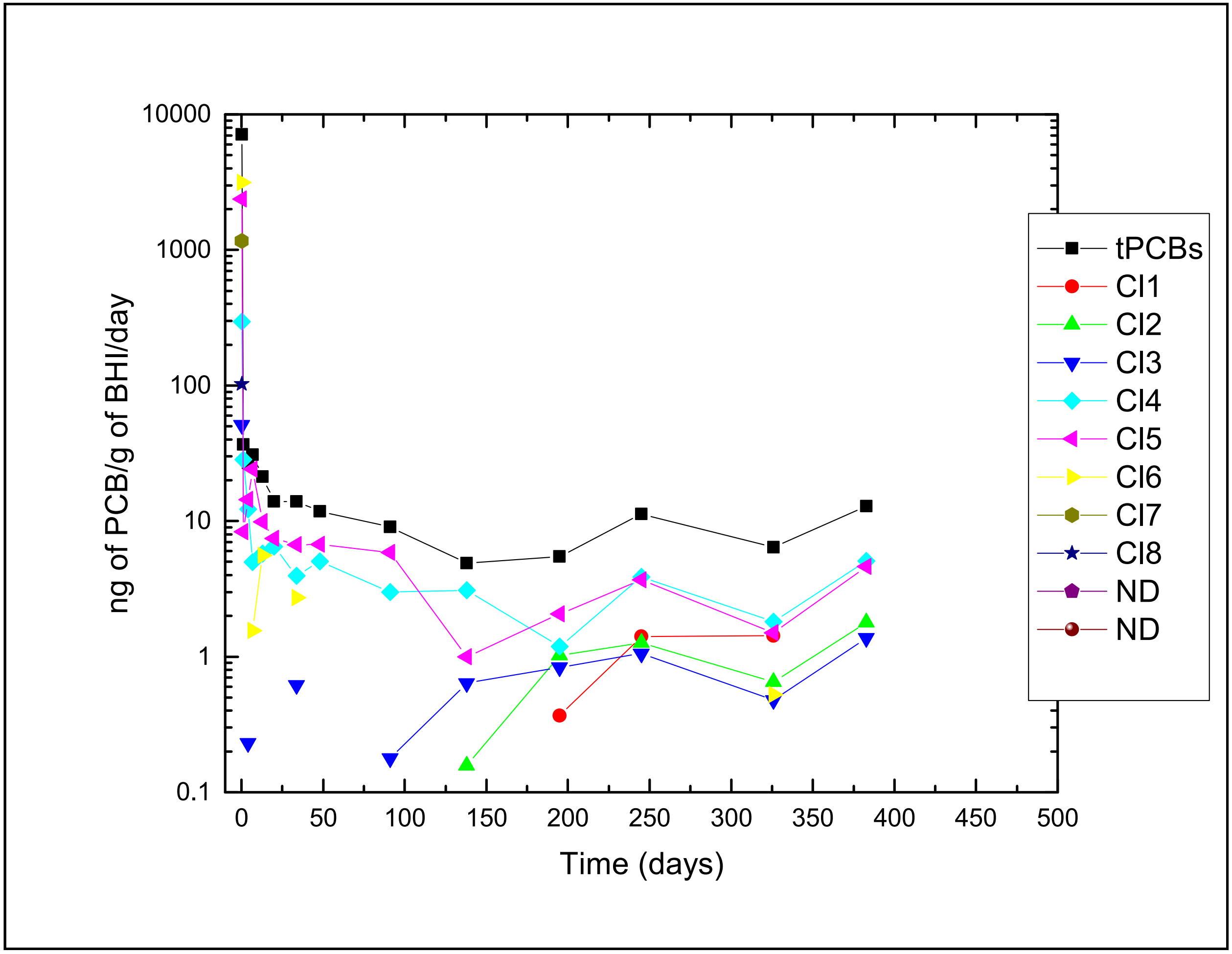


Figure 61(a–b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl2–Cl7) for BHI at 4 ^{o}C/1bar. Non-detected target congeners within detected homolog groups included PCB114 and PCB126 (Cl5); PCBs128, PCB156, PCB157, PCB167, PCB169 (Cl6); and PCB170, PCB180, PCB183, PCB187, PCB189 (Cl7).

The leaching results for BHI at 4 ^{o}C and 300 bar are shown in Figure 62. This subsample of BHI had a tPCB concentration of 0.106 wt%, over twice that of the BHI subsample tested above at 1 bar. This illustrates the sometimes extreme variation in PCB content found for shipboard solids, even within the same shipboard solid sample. As at 4 ^{o}C/1 bar, leach rates at 4 ^{o}C/300 bar were observed to initially spike, but achieved a maximum that was slightly less, followed by a rapid 3 order of magnitude decrease, stabilizing over a 2- to 3-week period, beyond which, leaching behavior was similar in magnitude to 4 ^{o}C/1 bar results (Figure 61). Unlike the results at 4^{o}C/1 bar, BHI leaching at 4 ^{o}C/300 bar show the appearance of homolog groups Cl1 and Cl8, and more Cl2 detections, perhaps attributable to higher shipboard solid concentrations of those homologs in the subsample leached at 4 ^{o}C/300 bar than the subsample leached at 4 ^{o}C/1 bar (see Figures 37a and 40a). However, the homolog and congener leaching behavior was more intermittent for Cl3 and Cl6, but similar for Cl5 across the experimental timeframe.

a)


10000
1000
100
10
1
0.1
ng of PCB/g of BHI/day
0
50
100
150
200
250
300
350
400
450
500
Time (days)
tPCBs
Cl1
Cl2
Cl3
Cl4
Cl5
Cl6
Cl7
Cl8
ND
ND

b)

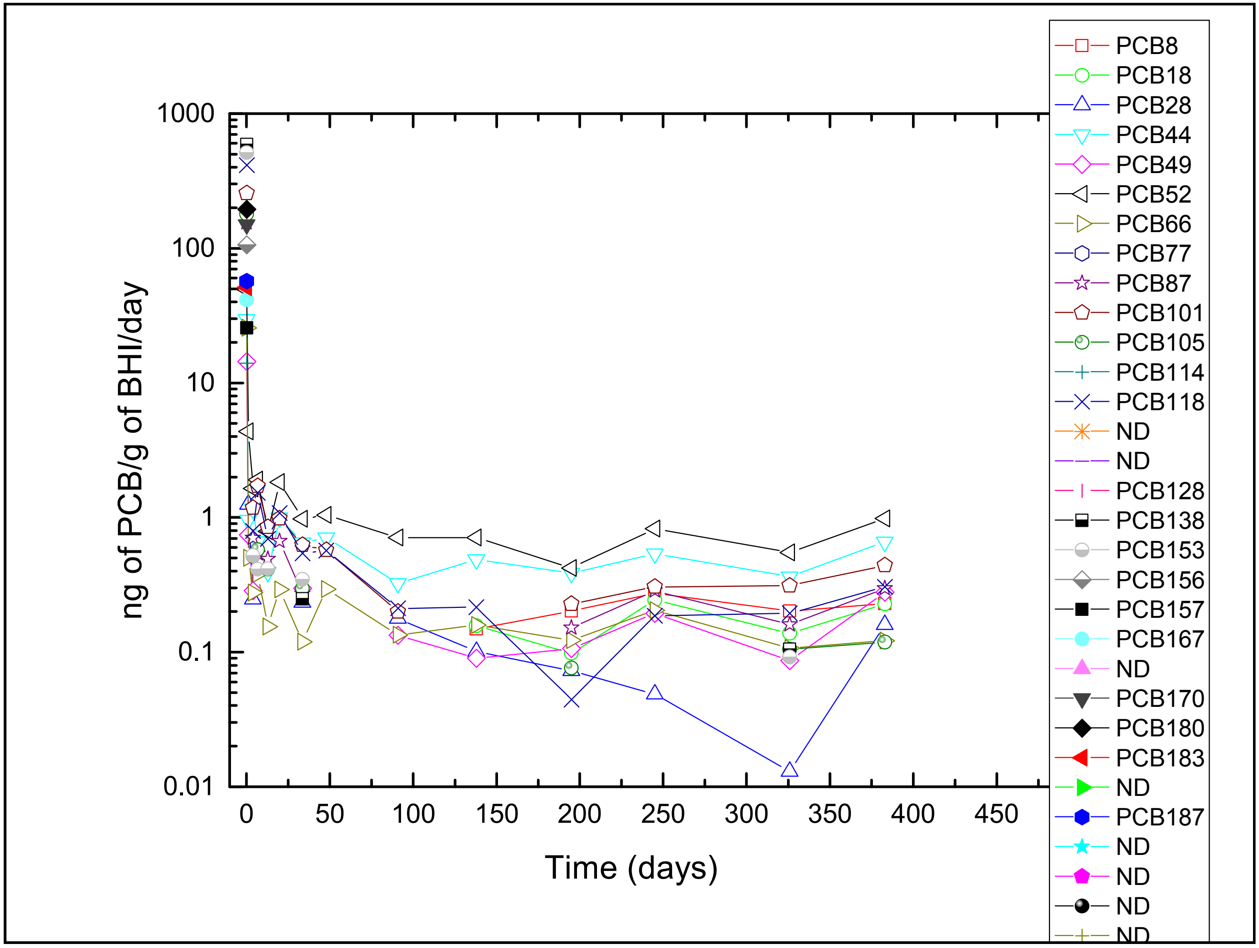
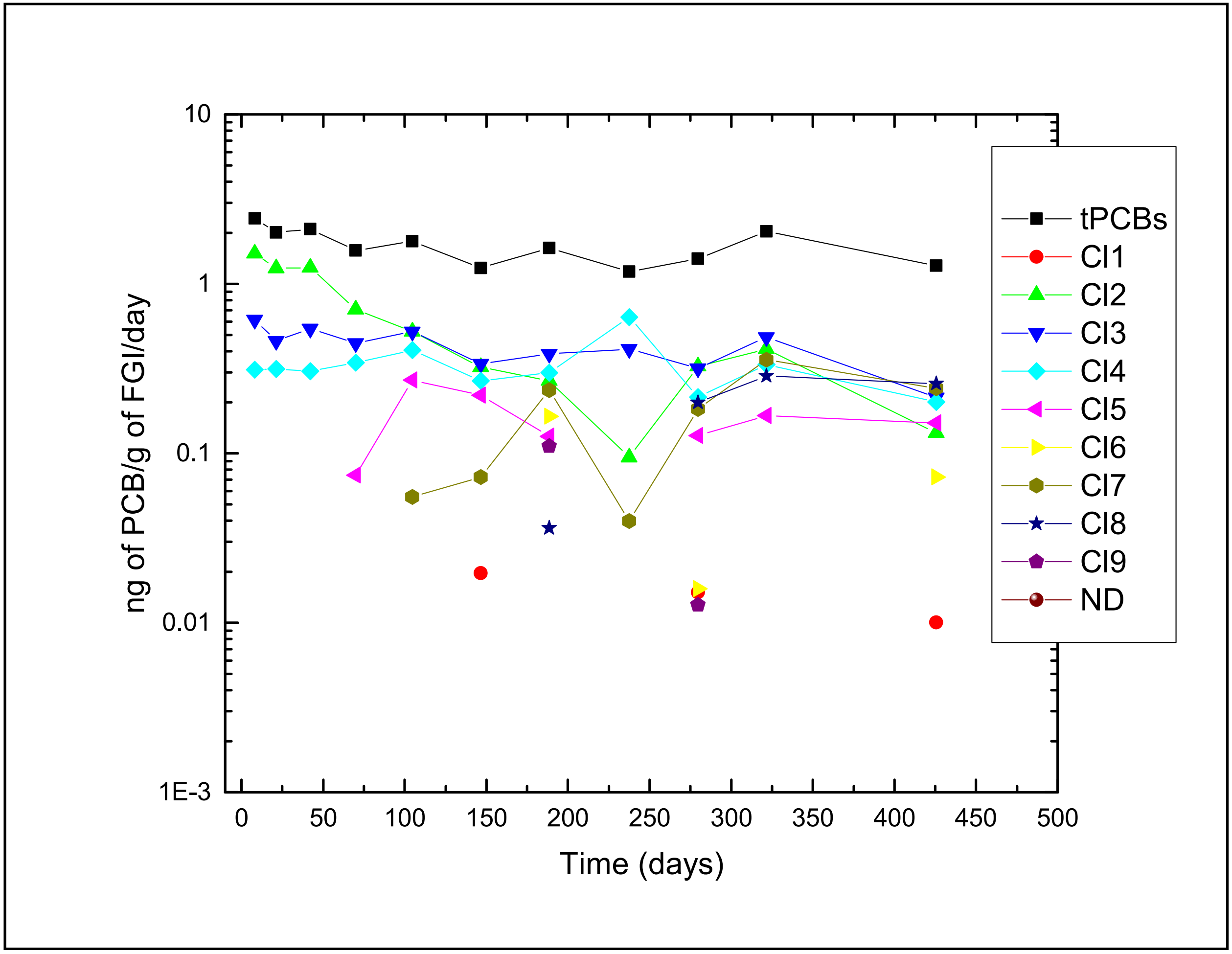


Figure 62(a-b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl1–Cl8) for BHI at 4 °C/300bar. Non-detected target congeners within detected homolog groups included PCB77 (Cl4); PCB123 and PCB126 (Cl5); PCB169 (Cl6); and PCB184 and PCB189 (Cl7); and PCB195 (Cl8).

4.1.7. Felt Gasket/Inner (FGI) Leach Rates

This shipboard FGI sample contained 17.0 wt% tPCBs, which was nominally A1268 only (Table 9). This shipboard solid had the highest tPCB concentration tested at 4 °C/1 bar, yet the average leach rates were quite low (Figure 63) for homolog groups observed (Cl1–Cl9). A surface-area-normalized leach rate would perhaps correlate with PCB content in the solid, but this was not within the scope of this experiment, considering that the ASW accessible surface area (SASA) interface is probably changing as a function of exposure time. As with other solids, FGI leach rates at 4 °C/1 bar were still lower (by ~4 orders of magnitude) than those for the neat Aroclor® 1268 dissolution rate control at 4 °C/1 bar. The homolog groups Cl1 and Cl5–Cl9 did not begin leaching immediately upon ASW exposure; with Cl1 starting at 105 days, Cl5 at 42 days, Cl6 and Cl8 at 147 days, and Cl7 at 70 days. The remaining homolog groups (Cl2, Cl3, Cl4) leached consistently throughout the entire leaching series.

a)


ng of PCB/g of FGI/day
10
1
0.1
0.01
1E-3
0
50
100
150
200
250
300
350
400
450
500
Time (days)
tPCBs
Cl1
Cl2
Cl3
Cl4
Cl5
Cl6
Cl7
Cl8
Cl9
ND

b)

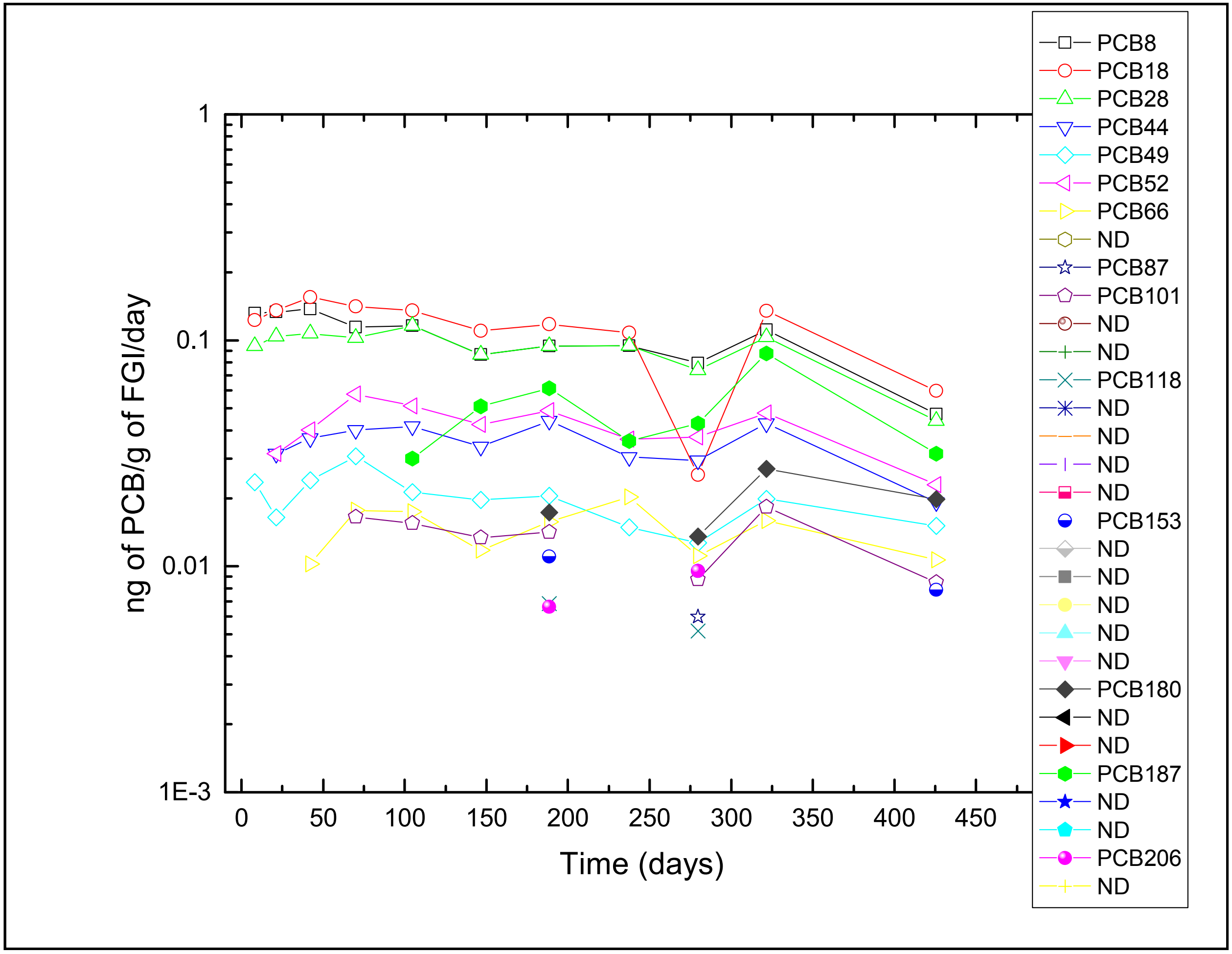
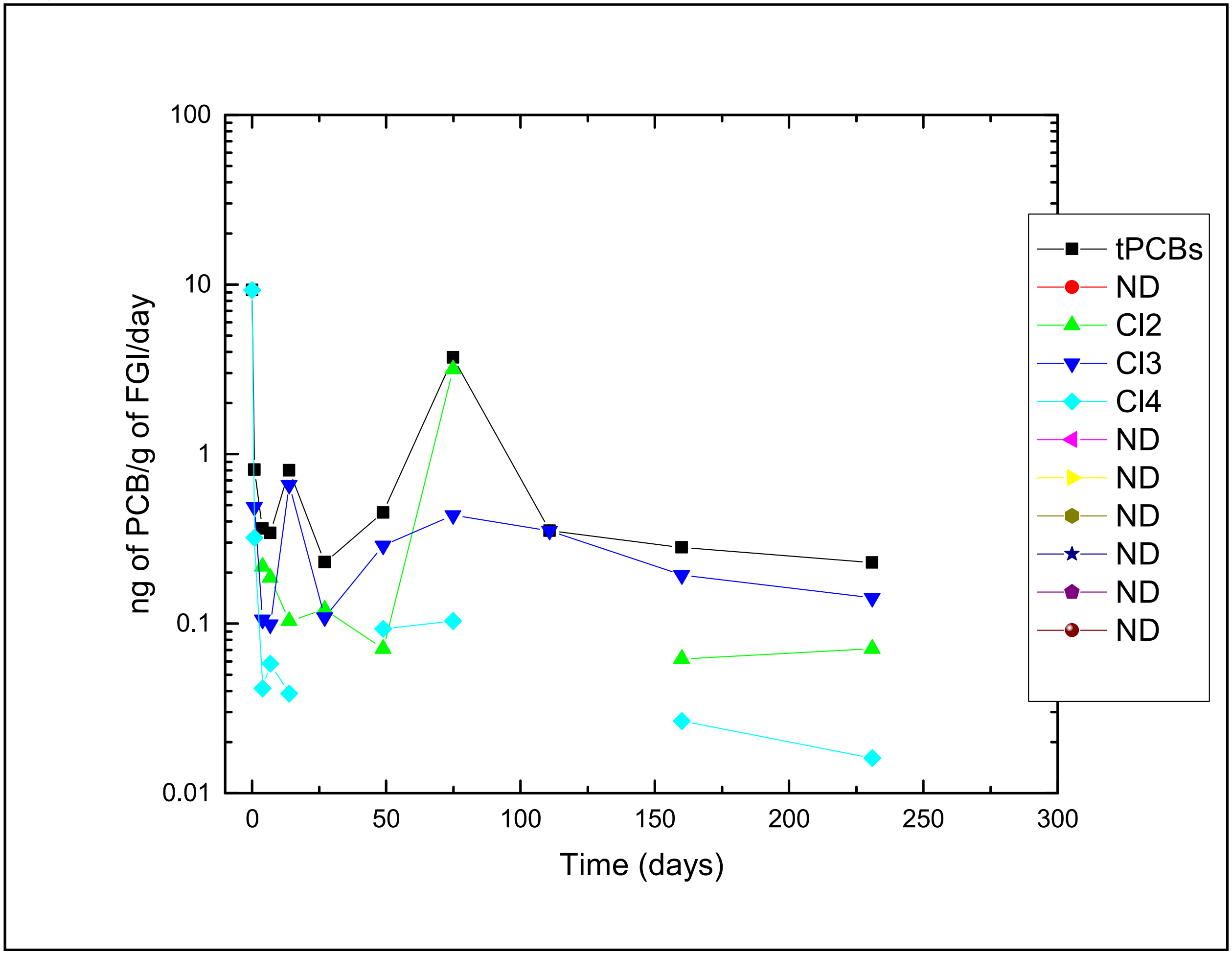


Figure 63(a–b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl1–Cl9) for FGI at 4 °C/1bar. Non-detected target congeners within detected homolog groups included PCB77 (Cl4); PCB105, PCB114, PCB123 and PCB126 (Cl5); PCB128, PCB138, PCB156, PCB157, PCB158, PCB167, and PCB169 (Cl6); PCB170, PCB183, PCB184, and PCB189 (Cl7); and PCB195 (Cl8).

A subsample of FGI was also tested at 4 °C/300 bar (Figure 64). This FGI subsample contained 12.6 wt% tPCBs. The leach rate magnitudes were slightly lower for homolog groups Cl2–Cl4 compared to results at 4 °C/1 bar, with homolog and congeners leaching behaviors more intermittent for Cl2 and Cl4. Unlike results at 4°C/1 bar, homolog groups Cl1 and Cl5-Cl9 were never detected at 4 °C/300 bar. This could be due to the lower tPCB concentration in this subsample, the increased pressure during the experiment, an unknown temporal and spatial history of PCBs in the sample (differing PCB transport pathways throughout the shipboard solid inside the HVAC duct flange onboard the vessel), or a combination of these factors.

a)


100
10
1
0.1
0.01
ng of PCB/g of FGI/day
0
50
100
150
200
250
300
Time (days)
tPCBs
ND
Cl2
Cl3
Cl4
ND
ND
ND
ND
ND
ND

b)

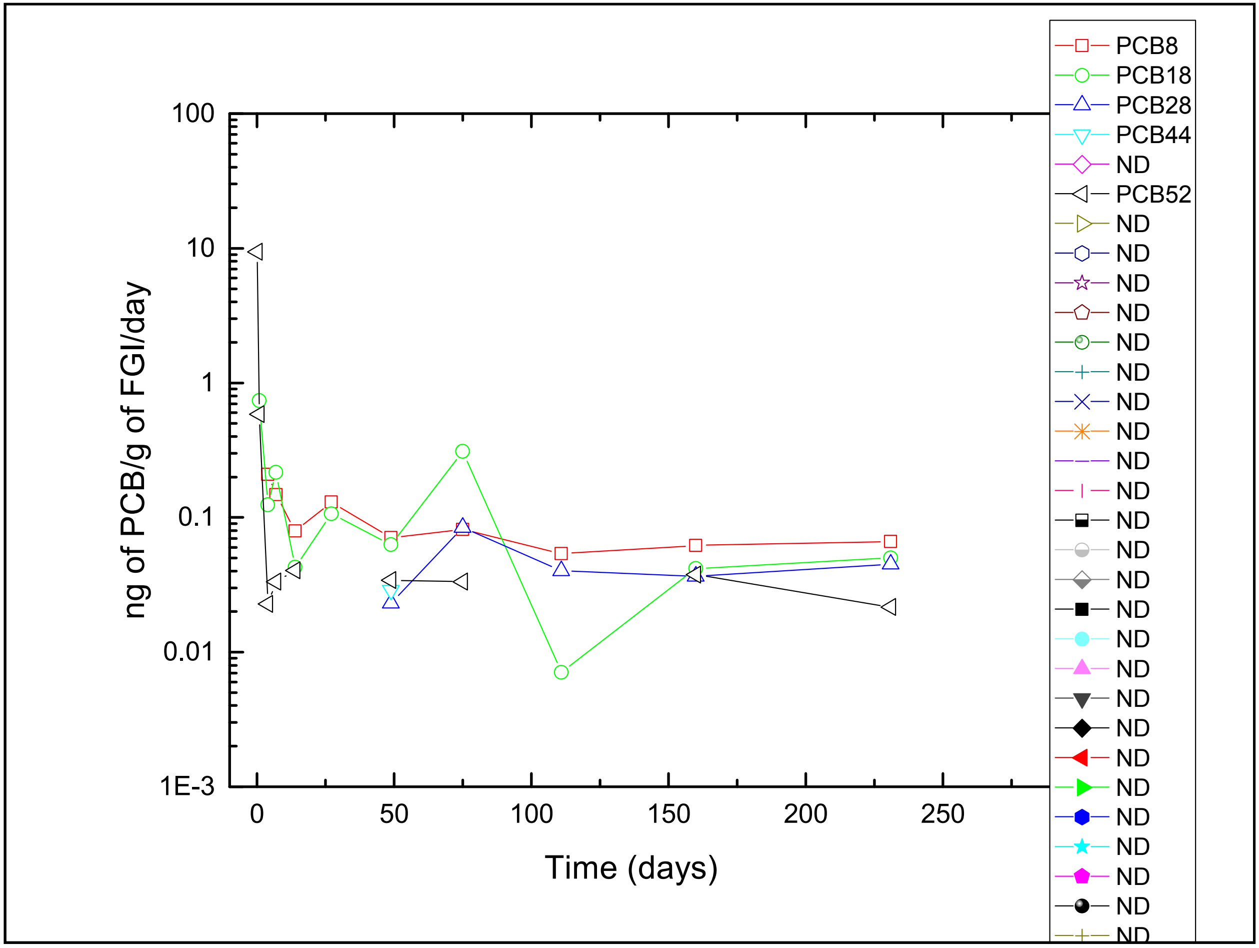
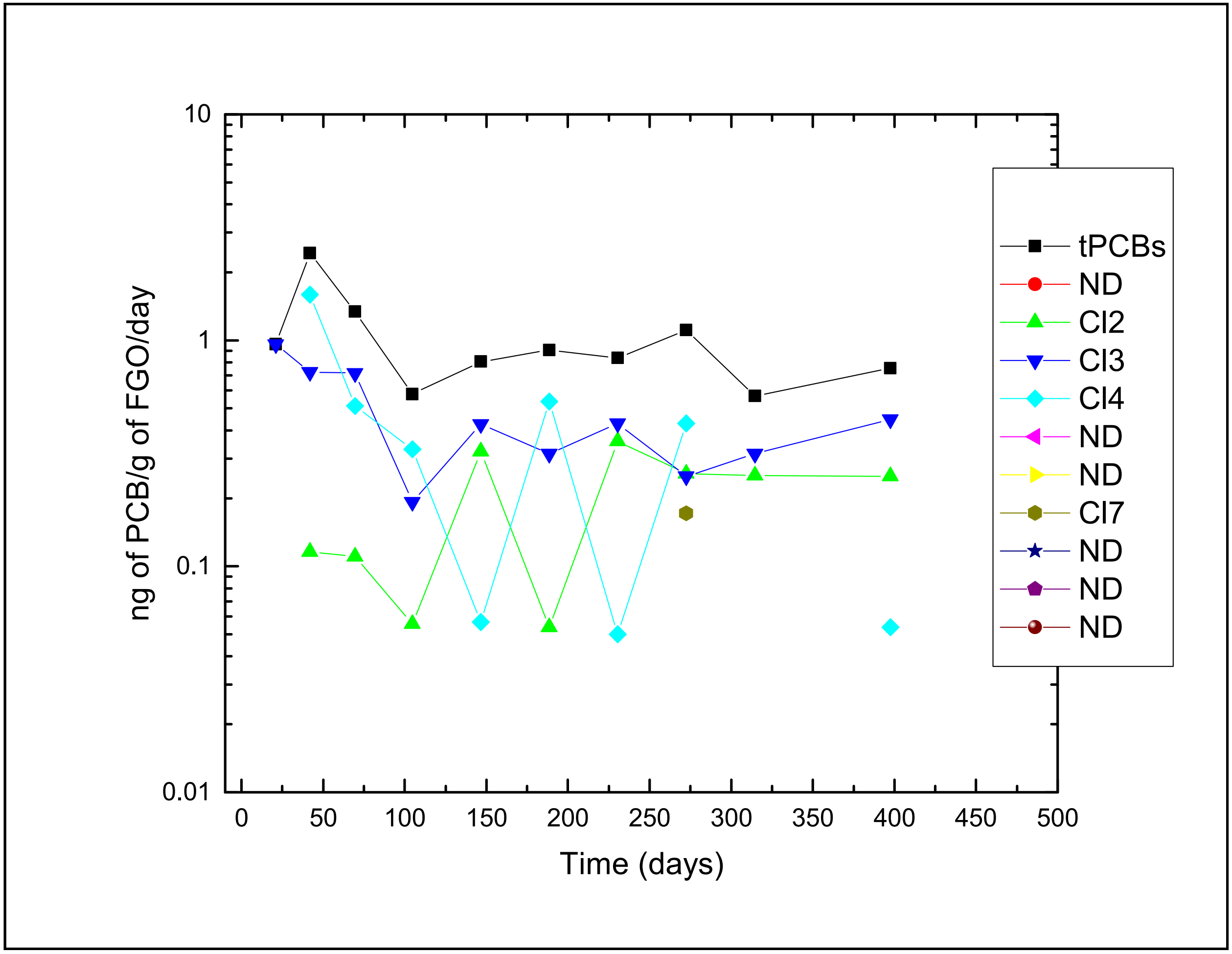


Figure 64(a-b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl2 – Cl4) for FGI at 4 °C/300bar. Non-detected target congeners within detected homolog groups included PCB49, PCB66, and PCB77 (Cl4).

4.1.8. Felt Gasket/Outer (FGO) Leach Rates

The FGO sample tested at 4 °C/1 bar contained 11.0 wt% tPCBs as Aroclor® 1268 (Table 9), similar to FGI tested at 4 °C/1 bar. However, FGO leaching behavior at 4 °C/1 bar was quite different (Figure 65). Homolog groups Cl2 through Cl4 represent the leaching behavior, with intermittent leaching of Cl4 beyond day 272. Homolog groups Cl5 and Cl6 were not observed, and only a single Cl7 (PCB187) detection was observed at 272 days of leaching. As with FGI, this solid contained a high level of PCBs (second highest concentration), but leached at ~4.5 orders of magnitude less than the A1268 dissolution control.

a)



ng of PCB/g of FGO/day
10
1
0.1
0.01
0
50
100
150
200
250
300
350
400
450
500
Time (days)
tPCBs
ND
Cl2
Cl3
Cl4
ND
ND
Cl7
ND
ND
ND

b)

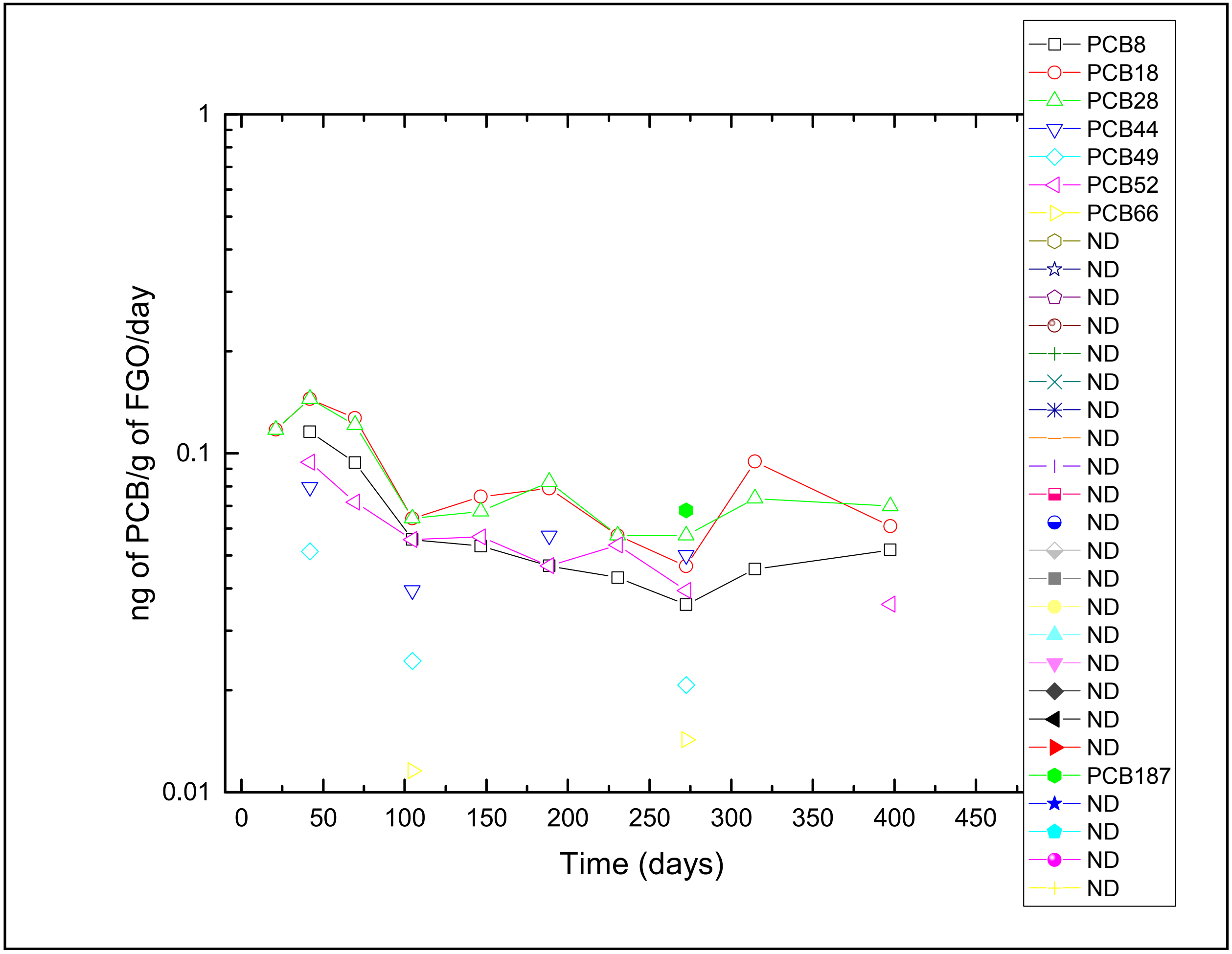
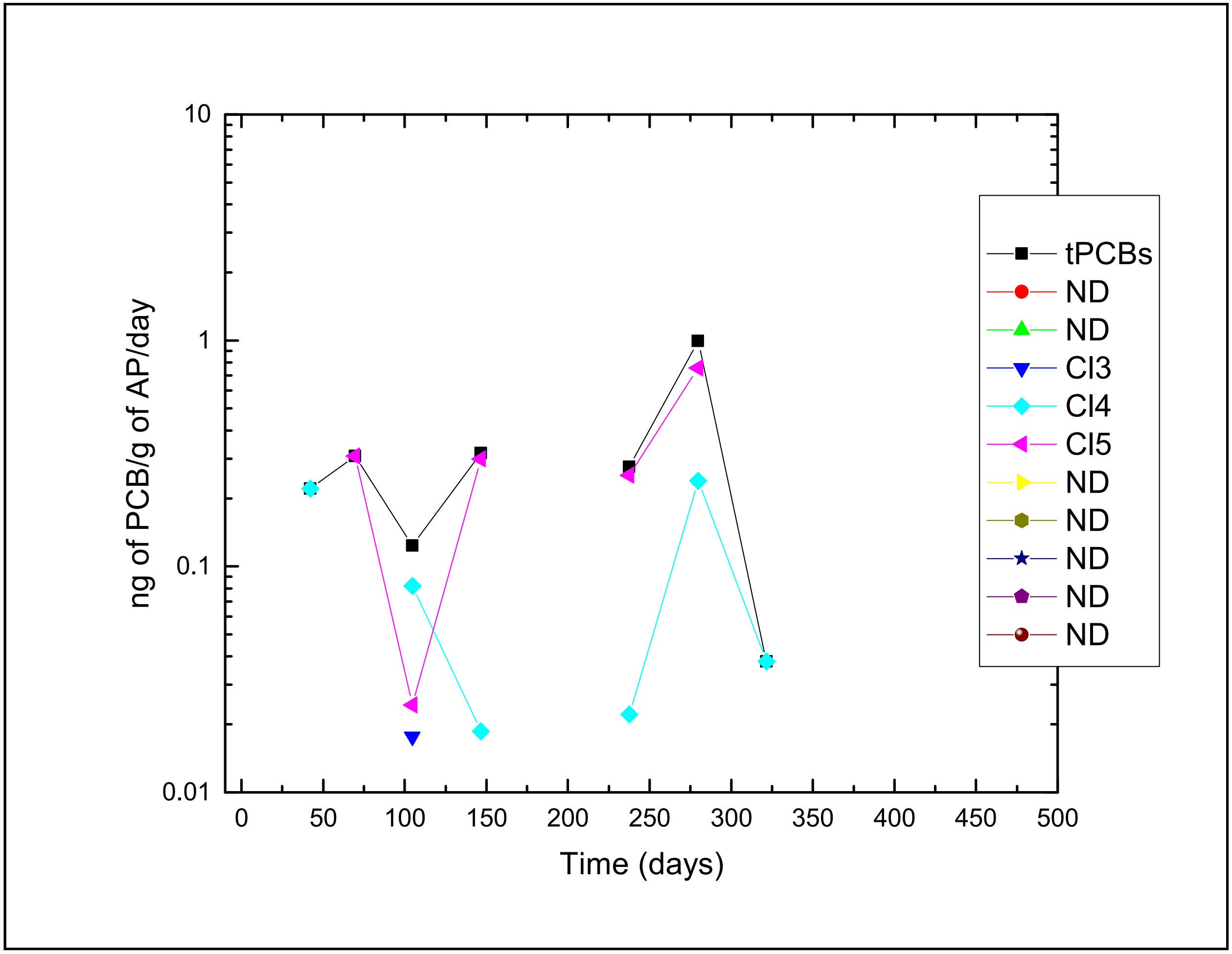


Figure 65(a–b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl2–Cl4, Cl7) for FGO at 4 °C/1bar. Non-detected target congeners within detected homolog groups included PCB77 (Cl4); and PCB170, PCB180, PCB183, PCB184, and PCB189 (Cl7).

4.1.9. Aluminized Paint (AP) Leach Rates

The AP sample tested at at 4 °C/1 bar contained 0.0472 wt%, nominally composed of 10.6% A1268, 47.8% A1260, and 41.6% A1254 (Table 9). The average leach rates (Figure 66) for this material were extremely intermittent and generally much lower than expected for this type of sample, considering the large sample surface area that resulted when the shipboard solid sample was collected as paint chips generated by use of a scraping tool. The mechanism for how PCBs might be more strongly bound in this solid matrix is not understood, but is likely related to encapsulation, and processes dictated by 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. Average leach rates for AP at 4 °C/1 bar were approximately 4 orders of magnitude below those observed for A1268 or A1254 controls at 4 °C/1 bar. Homolog groups Cl3 through Cl5 contributed to the PCB leaching; however, Cl3 was only detected once in the leaching series at day 105. The leaching for all homologs was also discontinuous, stopping midway through the leaching experiment timeframe.

a)



b)

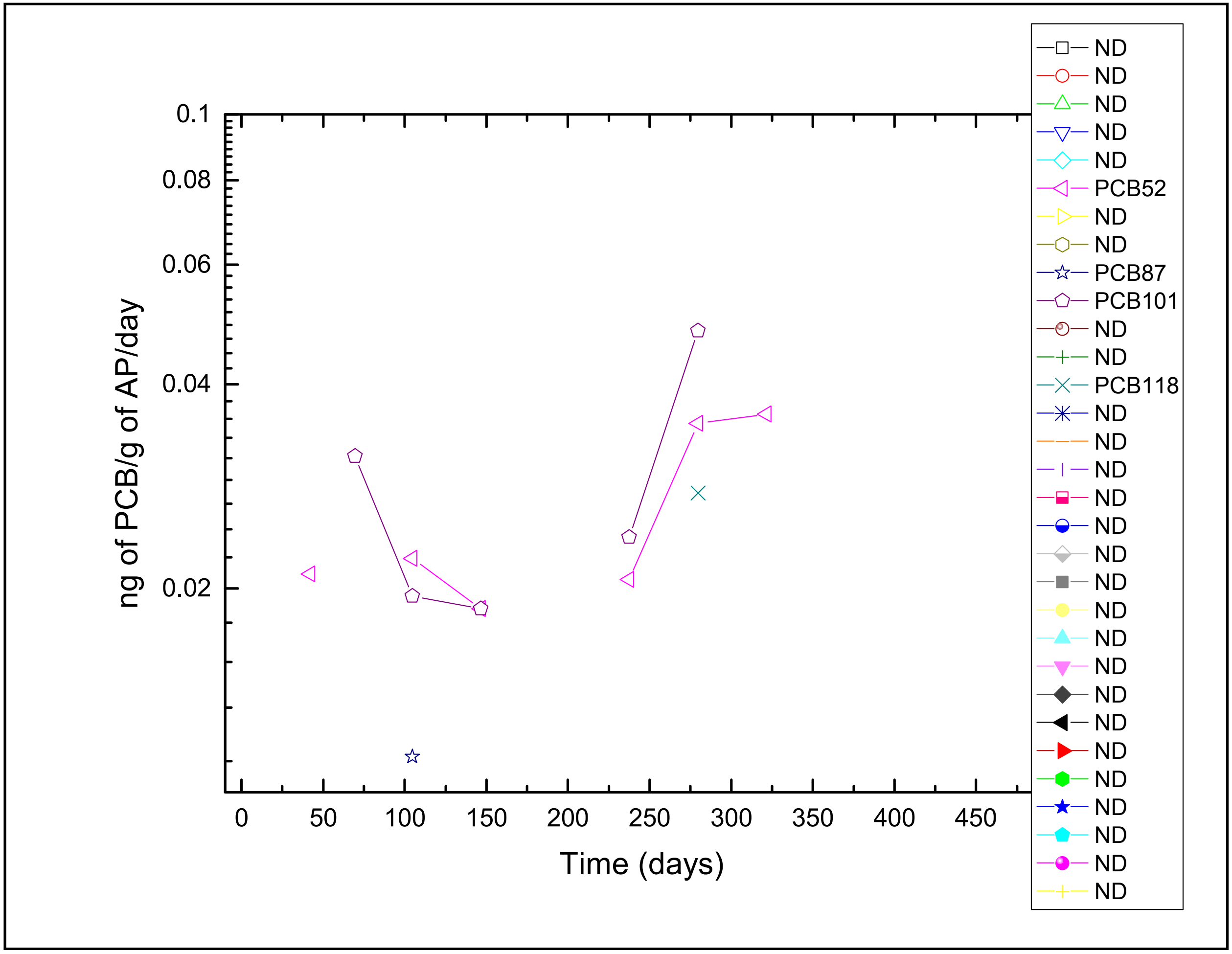


Figure 66 (a–b). (a) tPCB and contributing homolog group average leach rates, and (b) target congener average leach rates within those detected homolog groups (Cl3–Cl5) for AP at 4 °C/1bar. Non-detected target congeners within these detected homolog groups included PCB18 and PCB28 (Cl3); PCB44, PCB49, PCB66 and PCB77 (Cl4); and PCB87, PCB105, PCB114, PCB123 and PCB126 (Cl5).

4.2. SUMMARIZED LEACH RATE STUDY RESULTS.

Table 10 (a–m) summarizes leach rate study results to provide an at-a-glance synopsis of each deep-ocean shipboard solid leaching experiment and Aroclor® dissolution experiment, i.e., data collected at 4 °C/1 bar (a-i) and data collected at 4 °C/300bar (j-m). These summary includes the calculated minimum, maximum, mean, standard deviation, and median for release rates presented graphically above and tabulated in Appendix D; in addition to the final empirical leach rate for each analyte that can be used as a long-term, conservative leach rate. Alternatively, a regression analyses can be performed on the decreasing portion of each analyte curve, as was previously described in the SW-LRS report (George et al, 2006), with examples. For regression analysis, the final leach rate curve endpoints listed in these tables should be evaluated against results of regression analyses for those analytes with sufficient data from the observed maximum to endpoint (N_{m-e}) and predictive power (small p-value), using appropriate regression analysis confidence or prediction limits (e.g., at the 95th percentile).

Table 10 (a–m). Summary Statistics of data collected at 4 °C/1 bar are shown for Empirical Dissolution Rate Behaviors/Curves for A1254 and A1268 (a and e), and Empirical Leach Rate Behaviors/Curves for BRPHL, EC, FRE, BHI, FGI, FGO, and AP (b, c, d, f, g, h, i, respectively). Summary Statistics of data collected at 4 °C/300 bar are shown for A1254 Empirical Dissolution Rate Behaviors/Curves 4 (j), and Empirical Leach Rate Behaviors/Curves for EC, BHI, and FGI (k, l, m, respectively).

a.		**Dissolution Rate Results at 4 °C/1 bar (ng PCB/g neat A1254 day)**					
Aroclor® 1254 (A1254)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	11	4.74E+01	1.72E+02	6.33E+01	8.46E+01	4.13E+01	4.92E+01
Cl2	11	1.43E+02	4.54E+02	2.11E+02	2.53E+02	1.05E+02	1.43E+02
PCB8	11	5.41E+01	1.54E+02	8.60E+01	1.02E+02	3.71E+01	5.41E+01
Cl3	12	3.81E+01	3.75E+02	1.94E+02	2.13E+02	9.35E+01	1.18E+02
PCB18	12	1.22E+01	1.12E+02	7.09E+01	7.26E+01	3.13E+01	4.47E+01
PCB28	11	3.69E+01	1.35E+02	7.70E+01	8.01E+01	3.03E+01	3.69E+01
Cl4	12	7.83E+01	5.25E+03	2.49E+03	2.47E+03	1.47E+03	1.57E+03
PCB44	11	1.20E+02	1.01E+03	4.46E+02	4.60E+02	2.32E+02	3.00E+02
PCB49	11	4.72E+01	3.75E+02	1.70E+02	1.94E+02	9.10E+01	9.34E+01
PCB52	12	7.30E+01	1.91E+03	9.16E+02	9.32E+02	5.05E+02	6.88E+02
PCB66	11	6.86E+00	1.61E+02	7.66E+01	7.31E+01	3.99E+01	4.38E+01
PCB77	2	8.88E-01	1.20E+00	1.04E+00	1.04E+00	2.18E-01	8.88E-01
Cl5	11	4.89E+01	3.75E+03	1.95E+03	1.80E+03	1.10E+03	1.13E+03
PCB87	10	2.68E+01	2.32E+02	1.43E+02	1.29E+02	5.75E+01	6.88E+01
PCB101	11	9.43E+00	5.25E+02	2.67E+02	2.35E+02	1.40E+02	1.23E+02
PCB105	9	1.49E+01	4.72E+01	3.34E+01	3.26E+01	1.15E+01	1.67E+01
PCB114	3	2.11E+00	2.62E+00	2.55E+00	2.43E+00	2.78E-01	2.11E+00
PCB118	10	1.15E+01	1.46E+02	8.99E+01	8.54E+01	4.05E+01	4.82E+01
PCB123	0						
PCB126	0						
Cl6	9	5.97E+01	2.36E+02	1.57E+02	1.55E+02	6.04E+01	1.13E+02
PCB128	5	2.33E+00	7.33E+00	3.20E+00	4.03E+00	1.99E+00	3.20E+00
PCB138	9	3.48E+00	2.73E+01	1.46E+01	1.57E+01	8.02E+00	1.28E+01
PCB153	8	7.87E+00	3.73E+01	2.34E+01	2.27E+01	9.76E+00	7.87E+00
PCB156	2	2.07E+00	2.24E+00	2.15E+00	2.15E+00	1.19E-01	2.24E+00
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	1	3.43E+01	3.43E+01	3.43E+01	3.43E+01		3.43E+01
PCB170	0						
PCB180	0						
PCB183	0						
PCB184	1	6.69E+00	6.69E+00	6.69E+00	6.69E+00		6.69E+00

PCB187	0						
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	12	1.16E+02	1.00E+04	5.08E+03	4.76E+03	2.76E+03	3.13E+03

b.		Leach Rate Results at 4 °C/1 bar (ng PCB/g BRPHL-day)					
Black Rubber Pipe Hanger Liner (BRPHL)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	7	3.38E-02	7.37E-02	5.39E-02	5.47E-02	1.30E-02	6.35E-02
Cl2	3	9.22E-03	1.60E-02	1.14E-02	1.22E-02	3.48E-03	9.22E-03
PCB8	3	9.12E-03	1.60E-02	1.14E-02	1.22E-02	3.52E-03	9.12E-03
Cl3	9	1.74E-02	1.55E-01	9.06E-02	8.47E-02	4.01E-02	1.74E-02
PCB18	7	9.62E-03	2.54E-02	1.24E-02	1.39E-02	5.46E-03	1.04E-02
PCB28	9	1.36E-02	3.53E-02	2.56E-02	2.40E-02	7.60E-03	1.74E-02
Cl4	10	2.66E-01	8.01E-01	4.07E-01	4.46E-01	1.62E-01	3.65E-01
PCB44	10	4.21E-02	1.04E-01	5.41E-02	5.96E-02	1.82E-02	4.76E-02
PCB49	9	1.75E-02	3.85E-02	2.38E-02	2.58E-02	7.06E-03	1.75E-02
PCB52	10	8.47E-02	1.63E-01	1.11E-01	1.18E-01	2.59E-02	8.47E-02
PCB66	9	8.18E-03	2.08E-02	1.46E-02	1.44E-02	3.43E-03	1.27E-02
PCB77	0						
Cl5	9	1.49E-01	5.45E-01	3.52E-01	3.50E-01	1.20E-01	3.23E-01
PCB87	2	1.59E-02	2.19E-02	1.89E-02	1.89E-02	4.29E-03	1.59E-02
PCB101	9	1.85E-02	4.33E-02	3.35E-02	3.12E-02	7.97E-03	1.85E-02
PCB105	0						
PCB114	0						
PCB118	5	9.91E-03	1.88E-02	1.45E-02	1.49E-02	3.46E-03	1.38E-02
PCB123	0						
PCB126	0						
Cl6	0						
PCB128	0						
PCB138	0						
PCB153	0						
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	0						
PCB170	0						
PCB180	0						
PCB183	0						
PCB184	0						

PCB187	0						
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	10	3.56E-01	1.59E+00	9.08E-01	8.79E-01	3.32E-01	7.51E-01

c.		Leach Rate Results at 4 ^{o}C/1 bar (ng PCB/g EC-day)					
Electrical Cable (EC)	N	Leach Rate MIN Value	Leach Rate MAX Value	Median	Mean	Standard Deviation	Leach Rate Curve Endpoint
Cl1	0						
Cl2	1	5.49E-03	5.49E-03	5.49E-03	5.49E-03		5.49E-03
PCB8	1	4.94E-03	4.94E-03	4.94E-03	4.94E-03		4.94E-03
Cl3	0						
PCB18	0						
PCB28	0						
Cl4	10	1.38E-02	3.69E-02	2.22E-02	2.30E-02	6.32E-03	1.38E-02
PCB44	10	1.57E-03	3.28E-03	2.93E-03	2.70E-03	4.96E-04	1.57E-03
PCB49	7	4.80E-04	1.34E-03	1.02E-03	1.02E-03	2.81E-04	4.80E-04
PCB52	10	2.66E-03	7.04E-03	5.52E-03	5.30E-03	1.13E-03	2.66E-03
PCB66	9	5.10E-04	1.04E-03	8.25E-04	7.83E-04	1.72E-04	7.04E-04
PCB77	0						
Cl5	10	2.18E-02	6.43E-02	3.76E-02	3.99E-02	1.24E-02	2.69E-02
PCB87	7	9.61E-04	3.68E-03	2.51E-03	2.41E-03	8.24E-04	9.61E-04
PCB101	10	1.86E-03	4.96E-03	3.93E-03	3.70E-03	1.02E-03	1.86E-03
PCB105	5	9.50E-04	1.20E-03	1.18E-03	1.13E-03	1.04E-04	1.20E-03
PCB114	0						
PCB118	8	1.70E-03	3.45E-03	2.79E-03	2.75E-03	5.99E-04	1.70E-03
PCB123	0						
PCB126	0						
Cl6	3	1.27E-02	2.04E-02	1.28E-02	1.53E-02	4.42E-03	1.28E-02
PCB128	0						
PCB138	3	1.10E-03	1.52E-03	1.35E-03	1.32E-03	2.12E-04	1.52E-03
PCB153	2	1.33E-03	1.35E-03	1.34E-03	1.34E-03	9.10E-06	1.35E-03
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	0						
PCB170	0						
PCB180	0						

PCB183	0						
PCB184	0						
PCB187	0						
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	10	4.07E-02	1.10E-01	6.82E-02	6.80E-02	2.04E-02	4.07E-02

d.		**Leach Rate Results at 4 °C/1 bar (ng PCB/g FRE-day)**					
Foam Rubber/ Ensolite (FRE)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	2	1.91E-02	6.17E-02	4.04E-02	4.04E-02	3.01E-02	1.91E-02
Cl2	9	1.59E-02	3.30E-01	7.43E-02	9.77E-02	1.01E-01	1.59E-02
PCB8	8	1.41E-02	2.93E-02	1.81E-02	1.98E-02	5.64E-03	1.41E-02
Cl3	10	5.23E-02	1.52E-01	9.92E-02	9.69E-02	2.91E-02	9.09E-02
PCB18	10	8.63E-03	3.85E-02	2.21E-02	2.25E-02	9.10E-03	8.63E-03
PCB28	9	1.91E-02	3.88E-02	2.90E-02	2.99E-02	5.65E-03	1.91E-02
Cl4	11	9.09E-01	1.72E+00	1.18E+00	1.28E+00	2.83E-01	9.09E-01
PCB44	11	9.96E-02	3.01E-01	2.26E-01	2.15E-01	5.44E-02	1.54E-01
PCB49	11	4.50E-02	1.08E-01	7.79E-02	7.90E-02	1.89E-02	4.50E-02
PCB52	11	2.55E-01	6.67E-01	4.75E-01	4.56E-01	1.20E-01	2.86E-01
PCB66	10	2.27E-02	6.57E-02	4.56E-02	4.56E-02	1.21E-02	2.27E-02
PCB77	0						
Cl5	10	9.63E-01	2.15E+00	1.33E+00	1.42E+00	3.90E-01	1.04E+00
PCB87	10	4.40E-02	1.51E-01	7.34E-02	8.55E-02	3.28E-02	5.45E-02
PCB101	10	1.04E-01	3.01E-01	1.65E-01	1.79E-01	5.71E-02	1.04E-01
PCB105	9	2.57E-02	6.03E-02	3.90E-02	4.00E-02	1.33E-02	2.59E-02
PCB114	0						
PCB118	9	6.05E-02	1.51E-01	1.01E-01	1.00E-01	3.07E-02	6.36E-02
PCB123	0						
PCB126	0						
Cl6	8	2.07E-01	4.62E-01	3.71E-01	3.47E-01	9.17E-02	4.18E-01
PCB128	1	1.63E-02	1.63E-02	1.63E-02	1.63E-02		1.63E-02
PCB138	6	2.02E-02	6.44E-02	4.53E-02	4.40E-02	1.79E-02	3.68E-02
PCB153	8	2.75E-02	5.81E-02	4.08E-02	4.24E-02	1.33E-02	2.82E-02
PCB156	1	1.54E-02	1.54E-02	1.54E-02	1.54E-02		1.54E-02
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	1	2.86E-01	2.86E-01	2.86E-01	2.86E-01		2.86E-01
PCB170	0						
PCB180	0						
PCB183	0						
PCB184	1	4.05E-02	4.05E-02	4.05E-02	4.05E-02		4.05E-02
PCB187	0						
PCB189	0						

Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	11	1.22E+00	4.39E+00	2.79E+00	3.03E+00	8.53E-01	2.48E+00

e.		Dissolution Rate Results at 4 ^{o}C/1 bar (ng PCB/g neat A1268-day)					
Aroclor 1268 (A1268)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	5	2.50E+00	1.50E+02	6.03E+01	5.74E+01	5.92E+01	2.50E+00
Cl2	10	1.95E+02	2.07E+03	7.00E+02	8.99E+02	7.23E+02	2.00E+02
PCB8	10	1.05E+02	9.30E+02	3.90E+02	4.12E+02	2.78E+02	1.05E+02
Cl3	11	9.72E+02	1.24E+04	2.28E+03	2.91E+03	3.22E+03	1.14E+03
PCB18	10	2.82E+02	1.14E+03	6.60E+02	6.77E+02	3.13E+02	3.72E+02
PCB28	10	8.26E+01	8.47E+02	4.74E+02	4.67E+02	2.46E+02	3.62E+02
Cl4	9	5.73E+02	1.48E+03	8.94E+02	9.71E+02	3.20E+02	8.58E+02
PCB44	9	6.86E+01	1.98E+02	1.52E+02	1.45E+02	4.52E+01	1.62E+02
PCB49	9	3.19E+01	1.02E+02	7.48E+01	7.10E+01	2.26E+01	7.72E+01
PCB52	9	6.48E+01	1.98E+02	1.71E+02	1.48E+02	4.52E+01	1.72E+02
PCB66	9	1.50E+01	9.49E+01	6.29E+01	5.88E+01	2.73E+01	6.29E+01
PCB77	7	1.14E+01	2.67E+01	1.63E+01	1.68E+01	5.39E+00	2.00E+01
Cl5	7	3.12E+01	1.90E+02	7.43E+01	8.43E+01	4.95E+01	7.43E+01
PCB87	5	3.63E+00	5.93E+00	4.45E+00	4.58E+00	9.14E-01	4.96E+00
PCB101	7	4.02E+00	8.31E+00	6.38E+00	6.18E+00	1.52E+00	6.38E+00
PCB105	7	2.90E+00	1.01E+01	5.68E+00	6.12E+00	2.36E+00	7.81E+00
PCB114	0						
PCB118	7	4.68E+00	1.01E+01	6.99E+00	6.82E+00	2.03E+00	8.10E+00
PCB123	0						
PCB126	0						
Cl6	2	6.99E+00	8.20E+00	7.60E+00	7.60E+00	8.57E-01	6.99E+00
PCB128	0						
PCB138	0						
PCB153	2	1.47E+00	2.11E+00	1.79E+00	1.79E+00	4.59E-01	2.11E+00
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	7	2.75E+00	1.88E+06	7.12E+01	2.69E+05	7.11E+05	3.05E+00
PCB170	0						
PCB180	4	1.63E+00	1.30E+05	1.82E+02	3.27E+04	6.51E+04	1.63E+00
PCB183	0						
PCB184	0						
PCB187	7	1.93E+00	4.03E+05	7.12E+00	5.77E+04	1.52E+05	3.34E+00

PCB189	0						
Cl8	6	4.98E+00	1.08E+07	1.95E+03	1.80E+06	4.39E+06	1.42E+01
PCB195	0						
Cl9	8	1.46E+00	7.80E+06	4.93E+01	9.78E+05	2.76E+06	1.46E+00
PCB206	8	1.06E+00	4.44E+06	1.82E+01	5.56E+05	1.57E+06	1.06E+00
Cl10	4	6.03E+00	6.99E+05	6.90E+02	1.75E+05	3.49E+05	6.03E+00
PCB209	4	6.03E+00	6.99E+05	6.90E+02	1.75E+05	3.49E+05	6.03E+00
tPCBs	11	2.28E+03	2.11E+07	4.65E+03	1.93E+06	6.37E+06	2.28E+03

f.		Leach Rate Results at 4 ^{o}C/1 bar (ng PCB/g BHI-day)					
Bulkhead Insulation (BHI)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	1	1.14E-01	1.14E-01	1.14E-01	1.14E-01		1.14E-01
Cl2	1	3.71E+02	3.71E+02	3.71E+02	3.71E+02		3.71E+02
PCB8	1	3.71E+02	3.71E+02	3.71E+02	3.71E+02		3.71E+02
Cl3	11	5.06E-02	2.09E+03	1.84E-01	1.91E+02	6.32E+02	1.84E-01
PCB18	4	2.74E-02	5.16E+02	5.22E-02	1.29E+02	2.58E+02	2.74E-02
PCB28	11	4.80E-02	6.12E+02	1.00E-01	5.57E+01	1.85E+02	4.80E-02
Cl4	12	1.55E+00	3.87E+03	5.28E+00	3.27E+02	1.11E+03	3.74E+00
PCB44	12	3.53E-01	5.96E+02	7.57E-01	5.04E+01	1.72E+02	5.07E-01
PCB49	12	1.47E-01	5.80E+02	2.48E-01	4.86E+01	1.67E+02	1.47E-01
PCB52	12	5.40E-01	5.72E+02	1.27E+00	4.88E+01	1.65E+02	7.74E-01
PCB66	11	1.81E-01	4.75E+02	2.74E-01	4.35E+01	1.43E+02	1.81E-01
PCB77	1	6.37E+02	6.37E+02	6.37E+02	6.37E+02		6.37E+02
Cl5	11	5.58E+00	9.67E+03	8.00E+00	8.86E+02	2.91E+03	5.60E+00
PCB87	10	3.47E-01	6.28E+02	6.59E-01	6.34E+01	1.99E+02	3.47E-01
PCB101	11	4.91E-01	5.80E+02	1.05E+00	5.37E+01	1.75E+02	5.87E-01
PCB105	10	9.59E-02	5.80E+02	2.12E-01	5.82E+01	1.83E+02	1.12E-01
PCB114	0						
PCB118	10	2.84E-01	1.13E+03	5.73E-01	1.13E+02	3.57E+02	2.93E-01
PCB123	1	6.77E+02	6.77E+02	6.77E+02	6.77E+02		6.77E+02
PCB126	0						
Cl6	7	1.38E+00	1.21E+04	2.48E+00	1.73E+03	4.57E+03	3.51E+00
PCB128	0						
PCB138	5	1.32E-01	7.73E+02	1.53E-01	1.55E+02	3.46E+02	2.42E-01
PCB153	6	1.60E-01	2.37E-01	2.04E-01	2.02E-01	3.37E-02	2.37E-01
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	2	1.51E+00	2.01E+04	1.01E+04	1.01E+04	1.42E+04	1.51E+00
PCB170	0						
PCB180	0						
PCB183	0						
PCB184	2	2.31E-01	8.06E+02	4.03E+02	4.03E+02	5.70E+02	2.31E-01

PCB187	0						
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	12	3.06E+00	4.82E+04	1.53E+01	4.03E+03	1.39E+04	9.52E+00

g.		**Leach Rate Results at 4 °C/1 bar (ng PCB/g FGI-day)**					
Felt Gasket - Inner (FGI)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	2	1.51E-02	1.97E-02	1.74E-02	1.74E-02	3.21E-03	1.51E-02
Cl2	11	9.46E-02	1.52E+00	4.13E-01	6.17E-01	4.96E-01	1.32E-01
PCB8	11	4.72E-02	1.37E-01	1.11E-01	1.04E-01	2.73E-02	4.72E-02
Cl3	11	2.14E-01	6.17E-01	4.48E-01	4.31E-01	1.14E-01	2.14E-01
PCB18	11	2.54E-02	1.55E-01	1.23E-01	1.13E-01	3.84E-02	5.98E-02
PCB28	11	4.40E-02	1.15E-01	9.49E-02	9.28E-02	1.95E-02	4.40E-02
Cl4	11	2.01E-01	6.35E-01	3.13E-01	3.30E-01	1.16E-01	2.01E-01
PCB44	10	1.92E-02	4.41E-02	3.53E-02	3.50E-02	7.64E-03	1.92E-02
PCB49	11	1.27E-02	3.07E-02	1.99E-02	1.99E-02	5.10E-03	1.51E-02
PCB52	10	2.30E-02	5.78E-02	4.12E-02	4.16E-02	1.01E-02	2.30E-02
PCB66	9	1.02E-02	2.03E-02	1.57E-02	1.45E-02	3.64E-03	1.07E-02
PCB77	0						
Cl5	7	7.43E-02	2.67E-01	1.51E-01	1.62E-01	6.43E-02	1.51E-01
PCB87	1	5.96E-03	5.96E-03	5.96E-03	5.96E-03		5.96E-03
PCB101	7	8.49E-03	1.83E-02	1.42E-02	1.36E-02	3.73E-03	8.49E-03
PCB105	0						
PCB114	0						
PCB118	2	5.17E-03	6.85E-03	6.01E-03	6.01E-03	1.19E-03	5.17E-03
PCB123	0						
PCB126	0						
Cl6	3	1.59E-02	1.65E-01	7.23E-02	8.45E-02	7.55E-02	7.23E-02
PCB128	0						
PCB138	0						
PCB153	3	7.86E-03	1.10E-02	9.54E-03	9.48E-03	1.58E-03	7.86E-03
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	7	3.99E-02	3.58E-01	1.83E-01	1.69E-01	1.19E-01	2.42E-01
PCB170	0						
PCB180	4	1.35E-02	2.70E-02	1.86E-02	1.94E-02	5.69E-03	1.98E-02
PCB183	0						
PCB184	0						
PCB187	7	2.96E-02	8.74E-02	4.29E-02	4.85E-02	2.05E-02	3.15E-02

PCB189	0						
Cl8	4	3.62E-02	2.86E-01	2.28E-01	1.95E-01	1.12E-01	2.58E-01
PCB195	0						
Cl9	2	1.27E-02	1.10E-01	6.15E-02	6.15E-02	6.90E-02	1.27E-02
PCB206	2	6.61E-03	9.54E-03	8.08E-03	8.08E-03	2.07E-03	9.54E-03
Cl10	0						
PCB209	0						
tPCBs	11	1.18E+00	2.45E+00	1.63E+00	1.70E+00	4.14E-01	1.27E+00

h.		Leach Rate Results at 4 ^{o}C/1 bar (ng PCB/g FGO-day)					
Felt Gasket - Outer (FGO)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	0						
Cl2	9	5.37E-02	3.58E-01	2.51E-01	1.97E-01	1.15E-01	2.51E-01
PCB8	9	3.57E-02	1.16E-01	5.19E-02	5.99E-02	2.63E-02	5.19E-02
Cl3	10	1.93E-01	9.63E-01	4.27E-01	4.77E-01	2.45E-01	4.48E-01
PCB18	10	4.65E-02	1.45E-01	7.66E-02	8.64E-02	3.28E-02	6.09E-02
PCB28	10	5.72E-02	1.45E-01	7.17E-02	8.54E-02	3.07E-02	6.98E-02
Cl4	8	5.01E-02	1.59E+00	3.79E-01	4.44E-01	5.07E-01	5.37E-02
PCB44	4	3.94E-02	7.96E-02	5.37E-02	5.66E-02	1.70E-02	5.00E-02
PCB49	3	2.07E-02	5.14E-02	2.44E-02	3.22E-02	1.67E-02	2.07E-02
PCB52	8	3.58E-02	9.41E-02	5.47E-02	5.65E-02	1.87E-02	3.58E-02
PCB66	2	1.16E-02	1.43E-02	1.29E-02	1.29E-02	1.93E-03	1.43E-02
PCB77	0						
Cl5	0						
PCB87	0						
PCB101	0						
PCB105	0						
PCB114	0						
PCB118	0						
PCB123	0						
PCB126	0						
Cl6	0						
PCB128	0						
PCB138	0						
PCB153	0						
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	1	1.72E-01	1.72E-01	1.72E-01	1.72E-01		1.72E-01
PCB170	0						

PCB180	0						
PCB183	0						
PCB184	0						
PCB187	1	6.79E-02	6.79E-02	6.79E-02	6.79E-02		6.79E-02
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	10	5.67E-01	2.43E+00	8.71E-01	1.03E+00	5.43E-01	7.52E-01

i.		Leach Rate Results at 4 ^{o}C/1 bar (ng PCB/g AP-day)					
Aluminized Paint (AP)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	0						
Cl2	0						
PCB8	0						
Cl3	1	1.77E-02	1.77E-02	1.77E-02	1.77E-02		1.77E-02
PCB18	0						
PCB28	0						
Cl4	6	1.87E-02	2.40E-01	5.99E-02	1.04E-01	1.01E-01	3.79E-02
PCB44	0						
PCB49	0						
PCB52	6	1.87E-02	3.61E-02	2.16E-02	2.56E-02	7.82E-03	3.61E-02
PCB66	0						
PCB77	0						
Cl5	5	2.43E-02	7.56E-01	2.98E-01	3.28E-01	2.66E-01	7.56E-01
PCB87	1	1.13E-02	1.13E-02	1.13E-02	1.13E-02		1.13E-02
PCB101	5	1.87E-02	4.79E-02	2.38E-02	2.81E-02	1.21E-02	4.79E-02
PCB105	0						
PCB114	0						
PCB118	1	2.77E-02	2.77E-02	2.77E-02	2.77E-02		2.77E-02
PCB123	0						
PCB126	0						
Cl6	0						
PCB128	0						
PCB138	0						
PCB153	0						
PCB156	0						
PCB157	0						
PCB167	0						

PCB169	0						
Cl7	0						
PCB170	0						
PCB180	0						
PCB183	0						
PCB184	0						
PCB187	0						
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	7	3.79E-02	9.96E-01	2.76E-01	3.26E-01	3.13E-01	3.79E-02

j.		Dissolution Rate Results at 4 ^{o}C/300 bar (ng PCB/g neat A1254-day)					
Aroclor® 1254 (A1254)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	6	2.49E+01	1.12E+02	5.85E+01	6.55E+01	3.24E+01	5.45E+01
Cl2	8	6.71E+01	1.41E+03	2.06E+02	3.44E+02	4.42E+02	1.20E+02
PCB8	8	3.21E+01	1.66E+02	4.30E+01	6.30E+01	4.49E+01	4.34E+01
Cl3	8	4.66E+01	1.83E+02	8.86E+01	1.02E+02	5.13E+01	4.66E+01
PCB18	8	1.70E+01	9.14E+01	2.69E+01	3.65E+01	2.49E+01	2.13E+01
PCB28	5	1.19E+01	5.32E+01	1.96E+01	2.37E+01	1.69E+01	1.32E+01
Cl4	8	2.36E+02	8.95E+02	3.17E+02	4.40E+02	2.59E+02	2.59E+02
PCB44	8	5.50E+01	2.24E+02	7.64E+01	9.62E+01	5.57E+01	6.68E+01
PCB49	5	1.30E+01	3.96E+01	1.91E+01	2.19E+01	1.03E+01	1.91E+01
PCB52	7	1.07E+02	2.69E+02	2.07E+02	1.96E+02	5.69E+01	1.67E+02
PCB66	5	4.86E+00	1.83E+01	1.24E+01	1.23E+01	5.33E+00	4.86E+00
PCB77	0						
Cl5	5	3.82E+01	3.60E+02	9.91E+01	1.58E+02	1.26E+02	9.91E+01
PCB87	3	6.04E+00	1.81E+01	9.42E+00	1.12E+01	6.21E+00	6.04E+00
PCB101	5	2.91E+00	3.96E+01	1.22E+01	1.64E+01	1.40E+01	9.85E+00
PCB105	0						
PCB114	0						
PCB118	3	4.73E+00	1.60E+01	6.19E+00	8.96E+00	6.10E+00	4.73E+00
PCB123	0						
PCB126	0						
Cl6	0						
PCB128	0						
PCB138	0						
PCB153	0						
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	0						
PCB170	0						
PCB180	0						

PCB183	0						
PCB184	0						
PCB187	0						
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	8	5.01E+02	2.39E+03	7.35E+02	1.03E+03	6.61E+02	5.80E+02

k.		Leach Rate Results at 4 °C/300 bar (ng PCB/g EC-day)					
Electrical Cable (EC)	N	Leach Rate MIN Value	Leach Rate MAX Value	Median	Mean	Standard Deviation	Leach Rate Curve Endpoint
Cl1	0						
Cl2	0						
PCB8	0						
Cl3	0						
PCB18	0						
PCB28	0						
Cl4	7	4.89E-04	2.67E-01	3.13E-03	4.14E-02	9.95E-02	4.89E-04
PCB44	0						
PCB49	0						
PCB52	7	9.22E-04	2.91E-01	2.96E-03	4.57E-02	1.08E-01	9.22E-04
PCB66	0						
PCB77	0						
Cl5	4	3.26E-03	3.40E-01	8.72E-02	1.29E-01	1.61E-01	3.26E-03
PCB87	0						
PCB101	1	8.51E-02	8.51E-02	8.51E-02	8.51E-02		8.51E-02
PCB105	1	3.23E-03	3.23E-03	3.23E-03	3.23E-03		3.23E-03
PCB114	0						
PCB118	2	2.68E-02	2.67E-01	1.47E-01	1.47E-01	1.70E-01	2.68E-02
PCB123	0						
PCB126	0						
Cl6	2	6.07E-03	1.66E-02	1.13E-02	1.13E-02	7.42E-03	6.07E-03
PCB128	0						
PCB138	2	6.01E-03	1.70E-02	1.15E-02	1.15E-02	7.74E-03	6.01E-03
PCB153	0						
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						

Cl7	0						
PCB170	0						
PCB180	0						
PCB183	0						
PCB184	0						
PCB187	0						
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	9	4.89E-04	6.07E-01	5.10E-03	9.22E-02	2.00E-01	4.89E-04

I.		Leach Rate Results at 4 ^{o}C/300 bar (ng PCB/g BHI-day)					
Bulkhead Insulation (BHI)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	3	3.67E-01	1.43E+00	1.41E+00	1.07E+00	6.06E-01	1.43E+00
Cl2	5	1.57E-01	1.79E+00	1.02E+00	9.78E-01	6.18E-01	1.79E+00
PCB8	5	1.49E-01	2.74E-01	2.02E-01	2.11E-01	4.55E-02	2.29E-01
Cl3	9	1.78E-01	5.12E+01	6.38E-01	6.29E+00	1.69E+01	1.38E+00
PCB18	5	9.82E-02	2.43E-01	1.57E-01	1.73E-01	6.13E-02	2.28E-01
PCB28	9	1.30E-02	1.25E+00	1.60E-01	2.55E-01	3.80E-01	1.60E-01
Cl4	14	1.19E+00	2.96E+02	5.02E+00	2.72E+01	7.75E+01	5.07E+00
PCB44	14	3.24E-01	2.96E+01	6.54E-01	2.70E+00	7.73E+00	6.57E-01
PCB49	10	8.67E-02	1.44E+01	2.36E-01	1.66E+00	4.48E+00	2.77E-01
PCB52	14	4.20E-01	4.93E+01	9.81E-01	4.72E+00	1.29E+01	9.86E-01
PCB66	14	1.07E-01	2.56E+01	1.82E-01	2.03E+00	6.79E+00	1.21E-01
PCB77	0						
Cl5	14	1.00E+00	2.36E+03	6.70E+00	1.76E+02	6.30E+02	4.63E+00
PCB87	10	1.52E-01	1.56E+02	3.94E-01	1.59E+01	4.91E+01	2.98E-01
PCB101	12	1.99E-01	2.56E+02	5.98E-01	2.20E+01	7.38E+01	4.41E-01
PCB105	8	7.59E-02	1.79E+02	3.56E-01	2.27E+01	6.33E+01	1.18E-01
PCB114	1	1.40E+01	1.40E+01	1.40E+01	1.40E+01		1.40E+01
PCB118	13	4.45E-02	4.14E+02	5.42E-01	3.23E+01	1.15E+02	3.04E-01
PCB123	0						
PCB126	0						
Cl6	5	5.26E-01	3.15E+03	2.73E+00	6.33E+02	1.41E+03	5.26E-01
PCB128	1	1.52E+02	1.52E+02	1.52E+02	1.52E+02		1.52E+02
PCB138	3	1.05E-01	5.91E+02	2.48E-01	1.97E+02	3.41E+02	1.05E-01
PCB153	6	9.20E-02	5.12E+02	4.13E-01	8.57E+01	2.09E+02	9.20E-02
PCB156	1	1.06E+02	1.06E+02	1.06E+02	1.06E+02		1.06E+02
PCB157	1	2.56E+01	2.56E+01	2.56E+01	2.56E+01		2.56E+01
PCB167	1	4.14E+01	4.14E+01	4.14E+01	4.14E+01		4.14E+01
PCB169	0						
Cl7	1	1.16E+03	1.16E+03	1.16E+03	1.16E+03		1.16E+03
PCB170	1	1.50E+02	1.50E+02	1.50E+02	1.50E+02		1.50E+02
PCB180	1	1.95E+02	1.95E+02	1.95E+02	1.95E+02		1.95E+02
PCB183	1	5.12E+01	5.12E+01	5.12E+01	5.12E+01		5.12E+01

PCB184	0						
PCB187	1	5.71E+01	5.71E+01	5.71E+01	5.71E+01		5.71E+01
PCB189	0						
Cl8	1	1.02E+02	1.02E+02	1.02E+02	1.02E+02		1.02E+02
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	14	4.89E+00	7.13E+03	1.34E+01	5.24E+02	1.90E+03	1.29E+01

m.		Leach Rate Results at 4°C/300 bar (ng PCB/g FGI-day)					
Felt Gasket - Inner (FGI)	**N**	**Leach Rate MIN Value**	**Leach Rate MAX Value**	**Median**	**Mean**	**Standard Deviation**	**Leach Rate Curve Endpoint**
Cl1	0						
Cl2	8	6.20E-02	3.17E+00	1.12E-01	5.00E-01	1.08E+00	7.09E-02
PCB8	9	5.37E-02	2.09E-01	7.95E-02	1.00E-01	5.18E-02	6.64E-02
Cl3	10	9.89E-02	6.59E-01	2.41E-01	2.87E-01	1.93E-01	1.42E-01
PCB18	10	7.07E-03	7.37E-01	8.47E-02	1.70E-01	2.20E-01	5.02E-02
PCB28	5	2.31E-02	8.45E-02	4.02E-02	4.59E-02	2.31E-02	4.49E-02
Cl4	9	1.61E-02	9.28E+00	5.80E-02	1.11E+00	3.07E+00	1.61E-02
PCB44	1	2.89E-02	2.89E-02	2.89E-02	2.89E-02		2.89E-02
PCB49	0						
PCB52	9	2.15E-02	9.39E+00	3.41E-02	1.13E+00	3.10E+00	2.15E-02
PCB66	0						
PCB77	0						
Cl5	0						
PCB87	0						
PCB101	0						
PCB105	0						
PCB114	0						
PCB118	0						
PCB123	0						
PCB126	0						
Cl6	0						
PCB128	0						
PCB138	0						
PCB153	0						
PCB156	0						
PCB157	0						
PCB167	0						
PCB169	0						
Cl7	0						

PCB170	0						
PCB180	0						
PCB183	0						
PCB184	0						
PCB187	0						
PCB189	0						
Cl8	0						
PCB195	0						
Cl9	0						
PCB206	0						
Cl10	0						
PCB209	0						
tPCBs	11	2.29E-01	9.28E+00	3.64E-01	1.53E+00	2.76E+00	2.29E-01

5. DISCUSSION AND RECOMMENDATIONS

5.1. LEACHING RESULTS

In this study, leaching data were collected for representative solid materials containing PCBs (PCBs-ISM) that were commonly found in shipboard components on board older, out-of-service surface U.S. Navy vessels and submarines, under laboratory conditions simulated to reflect typical deep ocean environments. The test conditions used organic-free artificial seawater under gentle mixing to simulate dynamic flow, at a representative pH of 8.1, a salinity of 35 psu, low temperature (4 °C) at ambient hydrostatic pressure (~1 bar), and low temperature (4 °C) at high hydrostatic pressure (~300 bar) to approximate conditions at depths greater than 3000 meters. Leaching experiments were designed to avoid any effects caused by unintentional PCB saturation in seawater, organic particulate sorptive processes, or biological processes (uptake/metabolism/ bioaccumulation of PCBs). Previously, George et al (2006) reported the leaching results for the same set of solids under the same labotory conditions but with ambient temperature (25 °C) and hydrostatic pressure (~1 bar) to simulate shallow water environments.

The shipboard solids tested at 4 ^{o}C and 1 bar included neat Aroclor® 1254 (A1254), Aroclor® 1268 (A1268), and shipboard solids containing A1254: black rubber pipe hanger liner (BRPHL), electrical cable (EC), foam rubber/Ensolite® (FRE), in addition to shipboard solids that contained A1268 alone, or A1268 in addition to A1254: bulkhead insulation (BHI), felt gasket/inner (FGI), felt gasket/outer (FGO), and aluminized paint (AP). A subset of these shipboard solids was also tested at 4 ^{o}C and 300 bar, including A1254, EC, BHI, and FGI (see general descriptions in Table 3). All solids except for AP were tested intact to simulate what would occur in a compartment onboard a sunken vessel. Shipboard solid samples with high total Aroclor shipboard solid concentrations were deliberately chosen to ensure detectable leaching concentrations. Such solids with high PCB concentrations represent an upper limit rather than an average or mean concentration for PCBs-ISM on board decommissioned vessels and would typically account for only a very small fraction of the PCBs-ISM onboard a vessel (JJMA, 1999).

The reasons for testing the neat Aroclors® A1254 and A1268 were threefold: (1) A1254 and A1268 are the most common types of Aroclors® found on vessels as PCBs-ISM, (2) A1254 and A1268 were the two primary Aroclors® identified in the specific shipboard solids tested, and (3) the neat A1254 and A1268 represent the worst case for a release scenario—PCB dissolution uninhibited by a shipboard solid matrix. The results from A1254 and A1268 dissolution release experiments served as positive analytical controls for the shipboard solid leachate in experiments (maximum PCB concentrations observable in ASW from A1254 or A1268 sources).

For all experiments, PCBs were measured in the ASW 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 from an ecological and human health perspective. In addition, a true measure of total PCBs (tPCBs) was preferred over the conventional estimated (calculated) tPCBs based on Aroclor® or derived from congener patterns. To accomplish this goal, each level of PCB chlorination (homolog group) was quantified and then summed to provide an empirical tPCB value ($tPCBs = \sum homolog_i$, where $i = 1 - 10$ for each level of chlorination).

All PCB analytes measured during leaching (31 congeners, 10 homologs, and sum of homologs for tPCBs) included congeners commonly evaluated in other studies of PCB fate and effects and included the same congeners evaluated for decommissioned Navy vessels for artificial reefs[2, 3] and SINKEX studies (26 congeners, 10 homologs for tPCBs).[6] The leaching data presented in this report are focused on the deep ocean scenario (low temperature and high hydrostatic pressure). Some of the leach rate data from the shallow water scenario reported in George et al., (2006) have been incorporated in the discussion below to compare with data from this study to show temperature dependence on leaching and demonstrate the applicability of the data as an experimental replicate (Appendix E).

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 (batch 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 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 leaching curves exhibited a period characterized by sometimes erratic initial release behaviors before reaching a maximum rate. All of the leach rate curves did exhibit an increase up to some maximum rate, followed by a slow, generally monotonic decreasing release rate with time. This latter decreasing portion of the release curves is suitable for curve-fitting and for extrapolation out to very long leaching times to determine if the leaching behavior continues to decrease under the conditions tested. Arguably, some portion of PCBs in shipboard solids should be strongly and irreversibly bound, particularly if the solids are organic or polymeric[11] (Cseh et al., 1989). However, as a conservative approximation, it was assumed that all PCBs in the solid are available for leaching.

5.1.1. Leach Rate Temperature Dependence Summary

As indicated previously, a concurrent effort was conducted to evaluate the leaching behavior of the shipboard solids at ambient pressure (~1 bar) and temperature (25 °C) to simulate a shallow/reef scenario (George et al., 2006). Leach rate results were determined for all analytes in Table 4 and Table 5 (congeners, homologs, homolog-derived tPCBs) as a function of time. These ambient-temperature leach rate data are applicable to this study for purposes of demonstrating the behavior of leach rates as a function of temperature in a deep-ocean leaching scenario. Ambient-pressure (~1 bar) leach rates are summarized below for comparing homolog-derived tPCB leaching behavior in response to the two temperatures studied, 25 °C and 4 °C, as a function of leaching time. In general, leach rates were lower at reduced temperature, as one would expect from thermodynamic (solubility) considerations. Initial kinetics at lower temperature also appear somewhat suppressed for many 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 were generally slower relative to what

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[11] Wool felt, for example is a natural fiber similar to silk. It is a polypeptide composed of a polyamide backbone containing sidechains of amino acid residues. PCBs in wool felt and other polymeric materials are likely contained within the polymer molecular matrix as a result of being incorporated during formulation or by transport caused by PCB migration (absorption). Conversely, a material such as bulkhead insulation is composed of inorganic glass fibers and PCBs associated with this material and are expected to be present at the surface of the fibers rather than within the glass-fiber molecular matrix itself.

was observed at 25 °C, exhibiting flatter, more gradual monotonically decreasing leach rates as a function of time. This slow decrease is probably related to less PCB depletion with time at the seawater–solid interface as leaching into the seawater progressed. Temperature appears to affect leach rates for shipboard solids to a greater extent than for the neat solid Aroclors®.

In addition to tPCB comparisons for each shipboard solid and Aroclor dissolution control tested at constant ambient pressure (~1 bar), homologs and congeners tested at constant ambient pressure at each temperature, 25 °C and 4 °C, were also compared and reported herein.

The average leach rates measured for tPCB at 1 bar for 25 °C (Figure 67a) and 4 °C (Figure 67b) showed much higher release rates at 25 °C than 4 °C for all materials tested except for A1268. As discussed in the previous section, there was a very high initial tPCB dissolution rate for A1268, driven by homolog groups Cl7–Cl10 that occurred upon initial contact with ASW (Figure 60), which decreased very rapidly and disappeared within the first ~3 weeks of the experiment, indicating these species were available and readily released from the SASA interface once initial dissolution occured. In general, the median release rate was 1.65–4.64 times higher for releases at 25 °C than at 4 °C, however the mean release rate for tPCB was highly variable, with much higher release rates measured for A1268 and BHI at the low temperature, while much lower release rates were measured for A1254, BRPHL, FGI, FGO, and AP at low temperature. The endpoint of the leach rate curves were fairly similar for each of the materials except for BHI which had a much higher endpoint release rate at 25 °C than at 4 °C.

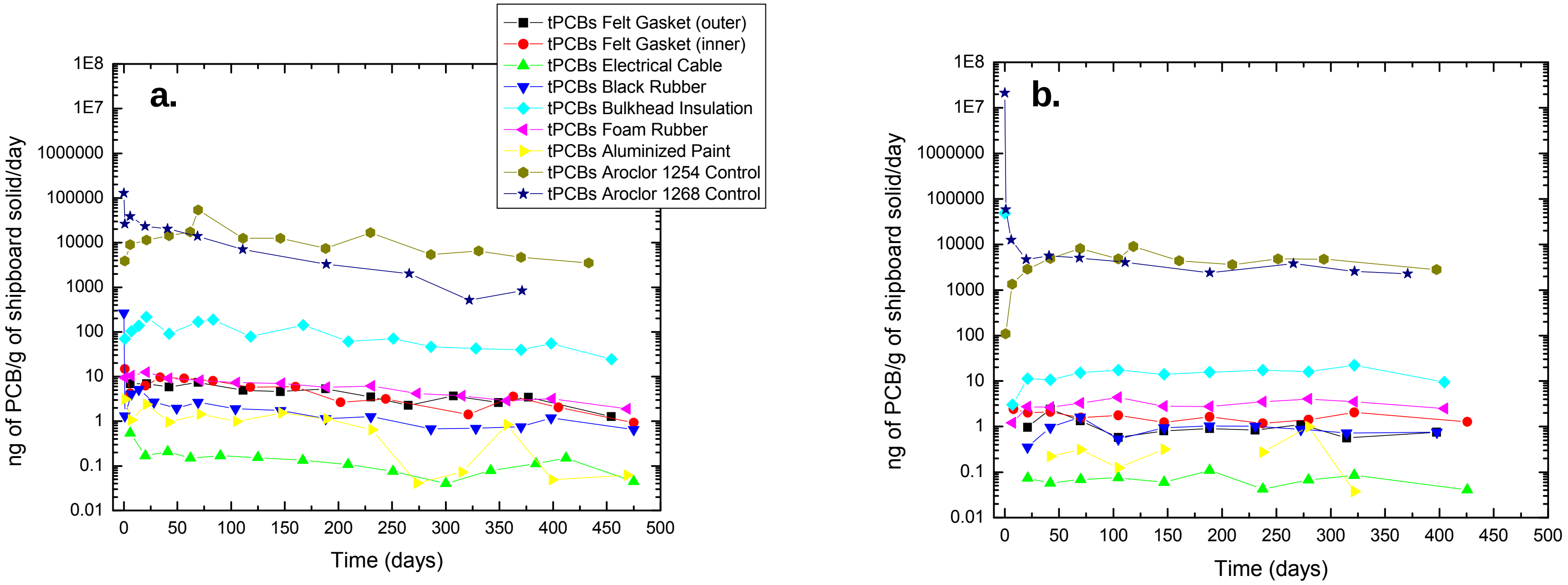

Figure 67(a-b). Overview of tPCB average leach rates at constant ambient pressure (~1 bar) and (a) 25 °C, compared to (b) 4 °C for the suite of shipboard solid tested.

Table 11. Release rate (ng PCB/g shipboard solid- day) of tPCBs for solids tested at 4 °C 1-bar and 25 °C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 67.

		4 °C 1-bar			25 °C 1-bar			(R) 25 °C/4C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
A1254	tPCBs	5080	4760	3130	9000	12000	3500	1.77	2.52	1.12
BRPHL	tPCBs	0.908	0.879	0.751	1.5	18	0.66	1.65	20.48	0.88
EC	tPCBs	0.0682	0.068	0.0407	0.12	0.13	0.044	1.76	1.91	1.08
FRE	tPCBs	2.79	3.03	2.48	6.1	6.1	1.9	2.19	2.01	0.77
A1268	tPCBs	4650	1930000	2280	14000	24000	840	3.01	0.01	0.37
BHI	tPCBs	15.3	4030	9.52	71	91	24	4.64	0.02	2.52
FGI	tPCBs	1.63	1.7	1.27	4.2	5.1	0.93	2.58	3.00	0.73
FGO	tPCBs	0.871	1.03	0.752	3.7	3.9	1.3	4.25	3.79	1.73
AP	tPCBs	0.276	0.326	0.0379	0.95	0.95	0.062	3.44	2.91	1.64

5.1.2. A1254 Temperature Dependence

The release rates of homologs and congeners from A1254 measured under ambient pressure at 25 °C and 4 °C (Figure 68) resulted in slightly higher release rates at the higher temperature which ranged from about 1.5–4 times higher than the mean release rates measured at 4 °C. The maximum release rate at 25 °C occurred after about 75 days and tended to decrease thereafter, while the release rate measured at 4 °C appeared to plateau at 75 to 125 days and then gradually declined. The release rates were dominated by the Cl4 and Cl5 homologs at both temperatures, while the heavier homologs (Cl8–Cl10) were not detected in either experiment. The long-term leach rate endpoints for both temperatures were within a factor two with higher release rates observed for 25 °C except for Cl1 which was about two times higher at 4 °C than 25 °C.

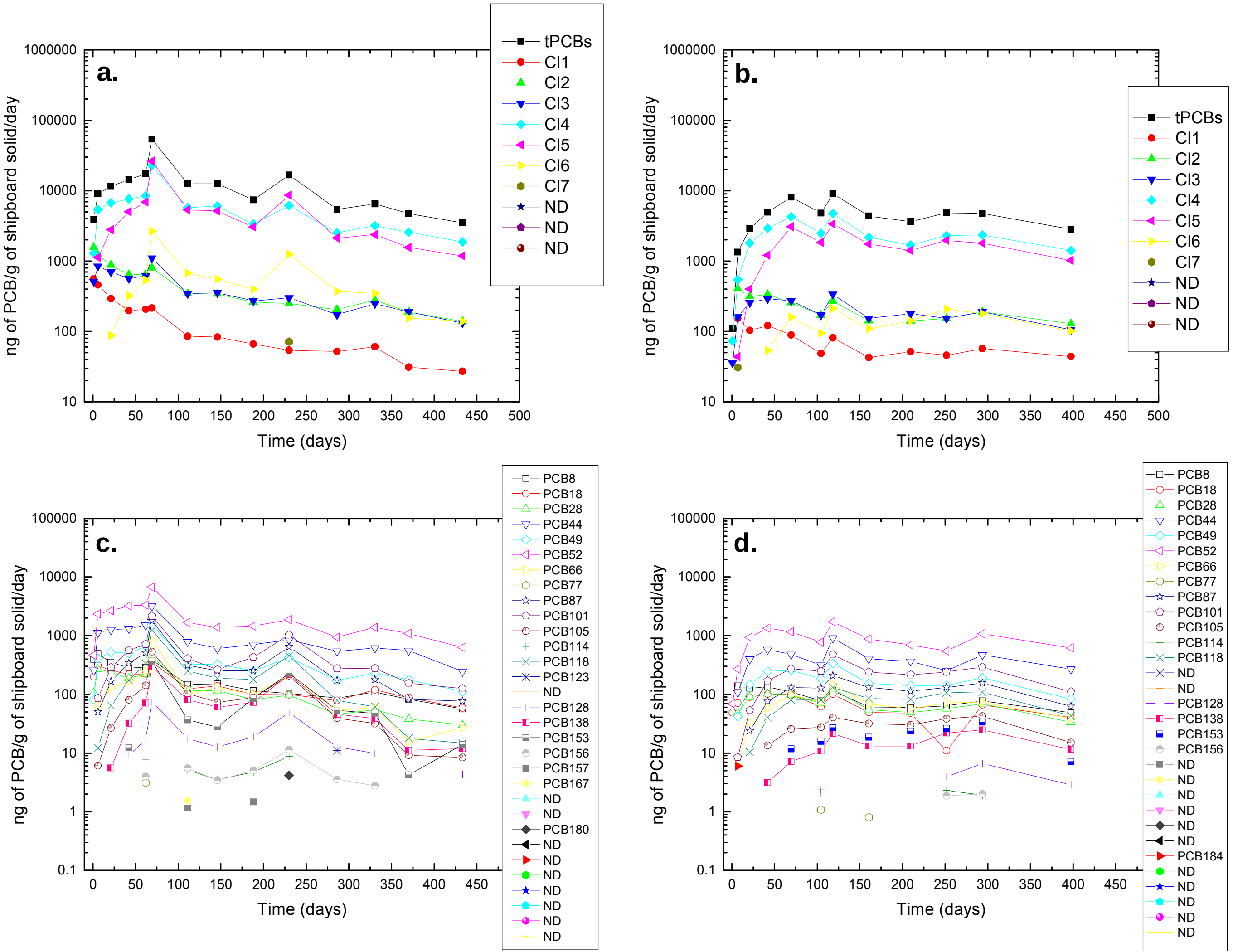

Figure 68. Comparison of A1254 average dissolution rates at constant ambient pressure (~1 bar) and 25 °C (a, c), to 4 °C (b, d) for homologs and congeners.

Table 12. Release rates (ng PCB/g neat A1254-day) for neat A1254 tested at 4 °C 1-bar and 25 °C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the dissolution rate curves shown in Figure 68.

		4 °C 1-bar			25 °C 1-bar			(R) 25 °C/4 °C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
A1254	Cl1	63.3	84.6	49.2	75	150	27	1.18	1.77	0.55
A1254	Cl2	211	253	143	310	520	140	1.47	2.06	0.98
A1254	Cl3	194	213	118	260	320	130	1.34	1.50	1.10
A1254	Cl4	2490	2470	1570	3300	5100	1900	1.33	2.06	1.21
A1254	Cl5	1950	1800	1130	1600	3900	1200	0.82	2.17	1.06
A1254	Cl6	157	155	113	380	620	140	2.42	4.00	1.24
A1254	Cl7	34.3	34.3	34.3	72	72	72	2.10	2.10	2.10
A1254	Cl8									
A1254	Cl9									
A1254	Cl10									
A1254	tPCBs	5080	4760	3130	9000	12000	3500	1.77	2.52	1.12

5.1.3. BRPHL Temperature Dependence

The release rates of homologs and congeners from BRPHL measured under ambient pressure at 25 °C and 4 °C (Figure 69) resulted in much higher mean release rates at the higher temperature for the Cl1–Cl3 homologs and only slightly higher mean release rates for Cl4 and Cl5 than that measured at 4 °C. Release of Cl7 (PCB184) occurred initially during the 25 °C experiment but was not detected at 4 °C. The maximum release rate at 25 °C occurred within a few days probably due to predominant dissolution release at the SASA, while the release rate measured at 4 °C gradually increased to the maximum after about 75 days and then remained realatively stable for the remainder of the experiment. The release rates were dominated by the Cl4 and Cl5 homologs at both temperatures and releases of the heavier homologs (Cl6–Cl10) were not detected in the 4 °C, while Cl6, Cl8, Cl9, and Cl10 were not detected in the 25 °C experiment. The long-term leach rate endpoints for Cl4 and Cl5 were higher at 4 °C than 25 °C, while the long-term leach rate endpoints for the Cl1-Cl3 homologs were much lower at 4 °C than 25 °C.

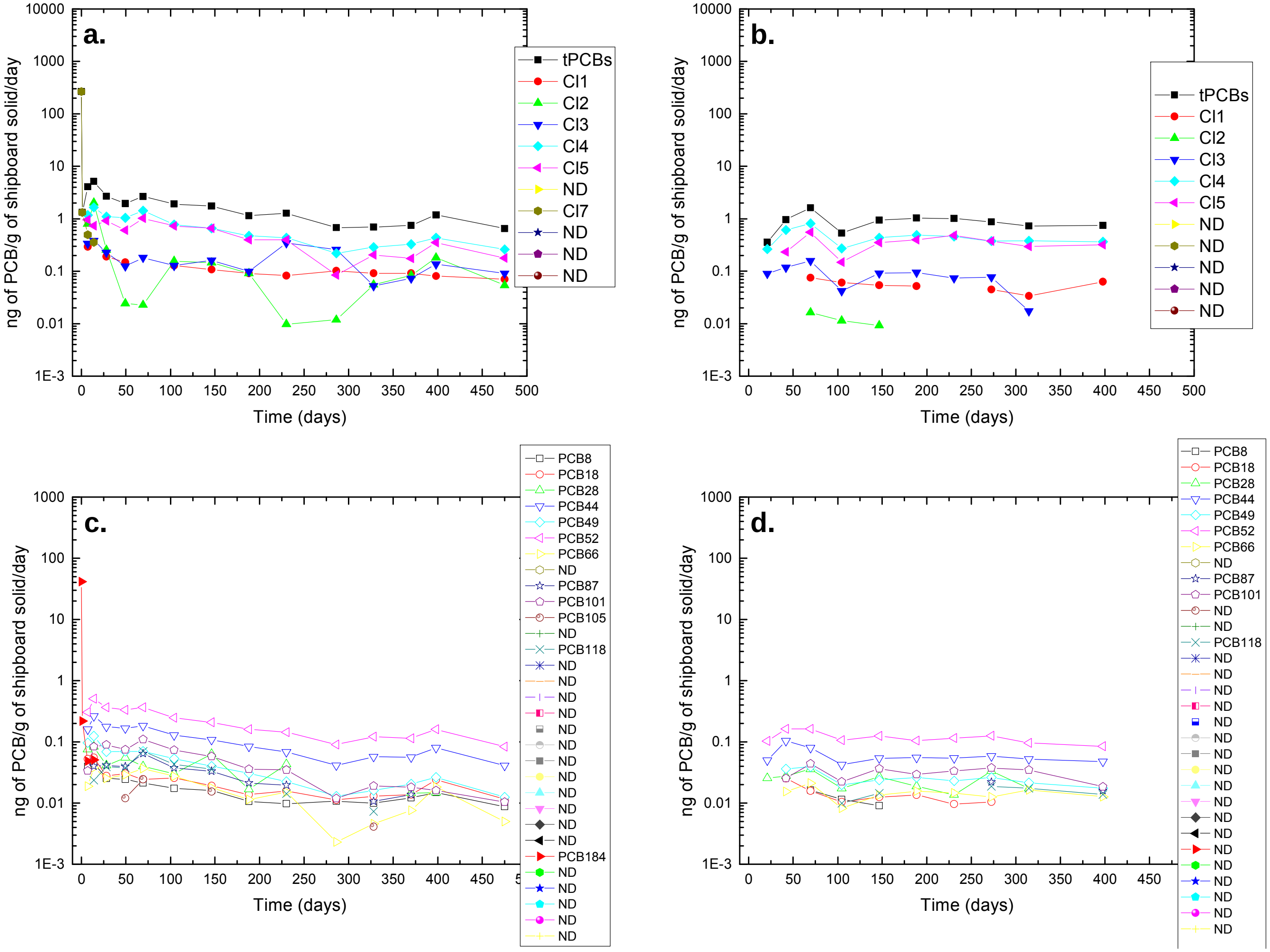

Figure 69. Comparison of BRPHL average leach rates at constant ambient pressure (~1 bar) and 25 °C (a, c), to 4 °C (b, d) for homologs and congeners.

Table 13. Release rates (ng PCB/g BRPHL-day) for BRPHL tested at 4 °C 1-bar and 25 °C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 69.

		4 °C 1-bar			25 °C 1-bar			(R) 25 °C/4 °C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
BRPHL	Cl1	0.0539	0.0547	0.0635	0.52	0.52	0.75	9.65	9.51	11.81
BRPHL	Cl2	0.0114	0.0122	0.00922	0.4	0.59	0.54	35.09	48.36	58.57
BRPHL	Cl3	0.0906	0.0847	0.0174	0.3	0.39	0.91	3.31	4.60	52.30
BRPHL	Cl4	0.407	0.446	0.365	0.57	0.75	0.26	1.40	1.68	0.71
BRPHL	Cl5	0.352	0.35	0.323	0.67	0.61	0.18	1.90	1.74	0.56
BRPHL	Cl6									
BRPHL	Cl7				0.5	0.73	0.35			
BRPHL	Cl8									
BRPHL	Cl9									
BRPHL	Cl10									
BRPHL	tPCBs	0.908	0.879	0.751	1.5	18	0.66	1.65	20.48	0.88

5.1.4. EC Temperature Dependence

The release rates of homologs and congeners from EC measured under ambient pressure at 25 °C and 4 °C (Figure 70) resulted in much higher mean release rates at the higher temperature for all homologs measured. The initial release of Cl2 occurred within a few days during the 25 °C experiment but was not detected until after 190 days at much lower concentrations during 4 °C experiment. The maximum release rate at 25 °C occurred within a few days, probably due to initial dissolution-dominated release of readily-available PCBs at the SASA, while the release rate measured at 4 °C remained relatively stable during the experiment. The mean release rates measured at 25 °C were similar for homologs measured (Cl5 ~ Cl4 > Cl6 ~ Cl2 > Cl7), and all homologs were detected except for Cl1 and Cl8. In the 4 °C experiment the Cl1, Cl3, and Cl7 – Cl10 homologs were not detected. The long-term leach rate endpoints for the homologs detected in both experiments were much higher at 25 °C than at 4 °C.

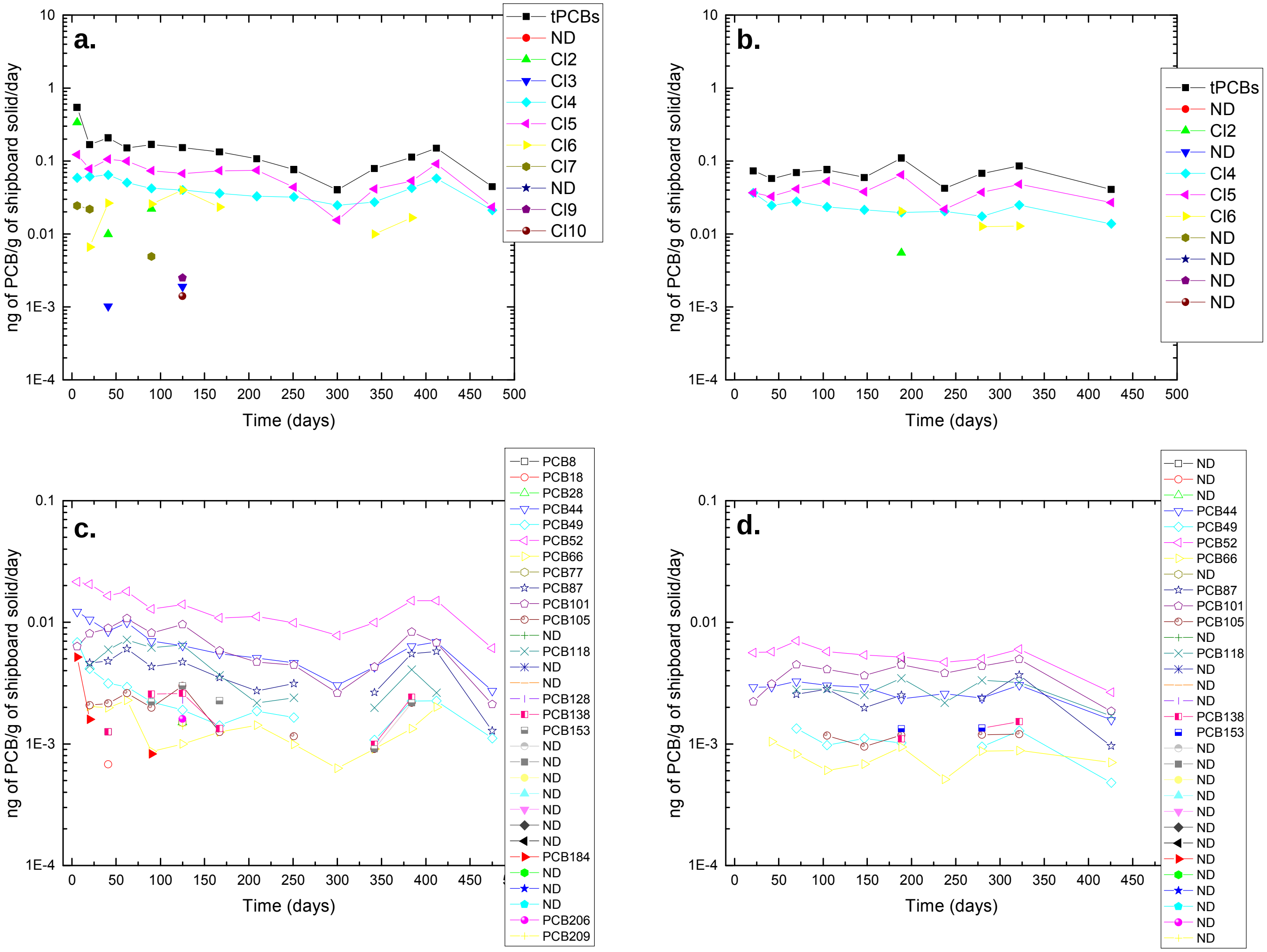

Figure 70. Comparison of EC average leach rates at constant ambient pressure (~1 bar) and 25 ^{o}C (a, c), to 4 ^{o}C (b, d) for homologs and congeners.

Table 14. Release rates (ng PCB/g EC-day) for EC tested at 4 ^{o}C 1-bar and 25 ^{o}C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 70.

		4 ^{o}C 1-bar			25 ^{o}C 1-bar			(R) 25 ^{o}C/4 ^{o}C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
EC	Cl1									
EC	Cl2	0.00549	0.00549	0.00549	0.34	0.52	0.22	61.93	94.72	40.07
EC	Cl3				0.16	0.16	0.2			
EC	Cl4	0.0222	0.023	0.0138	0.42	0.43	0.21	18.92	18.70	15.22
EC	Cl5	0.0376	0.0399	0.0269	0.6	0.55	0.23	15.96	13.78	8.55
EC	Cl6	0.0128	0.0153	0.0128	0.26	0.43	0.17	20.31	28.10	13.28
EC	Cl7				0.24	0.32	0.49			
EC	Cl8									
EC	Cl9				0.26	0.26	0.26			
EC	Cl10				0.15	0.15	0.15			
EC	tPCBs	0.0682	0.068	0.0407	0.12	0.13	0.044	1.76	1.91	1.08

5.1.5. FRE Temperature Dependence

The release rates of homologs and congeners from FRE measured under ambient pressure at 25 °C and 4 °C (Figure 71) resulted in higher mean release rates at the higher temperature for all homologs measured. For the 25 °C experiment, the maximum release rate occurred within 30 days followed by a general decrease in release rate, while the maximum tPCB release rate occurred after about 100 days followed by a relatively stable release for the 4 °C experiment. The mean release rates measured at 25 °C were similar for all homologs measured (Cl5 ~ Cl4 > Cl7 ~ Cl6 > Cl3 ~ Cl2), which were about twice as high as the release rates measured at 4 °C. The Cl8–Cl10 homologs were not detected in either of the experiments and Cl1 was only dectected in the 4 °C experiment. The long-term leach rate endpoints for the homologs detected in both experiments were equivalent or higher at 25 °C than 4 °C.

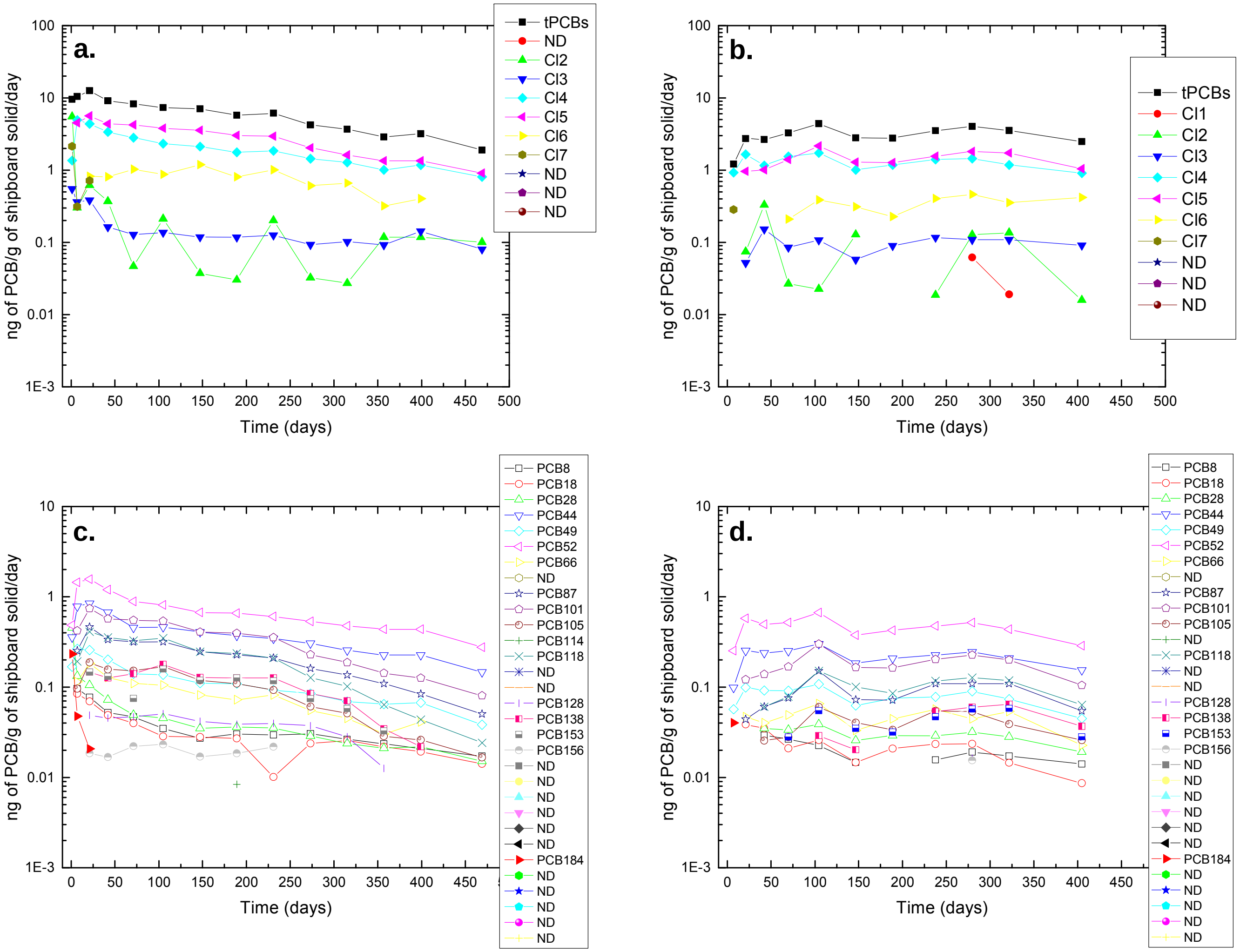

Figure 71. Comparison of FRE average leach rates at constant ambient pressure (~1 bar) and 25 ^{o}C (a, c), to 4 ^{o}C (b, d) for homologs and congeners.

Table 15. Release rates (ng PCB/g FRE-day) for FRE tested at 4 °C 1-bar and 25 °C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 71.

		4 °C 1-bar			25 °C 1-bar			(R) 25 °C/4°C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
FRE	Cl1	0.0404	0.0404	0.0191						
FRE	Cl2	0.0743	0.0977	0.0159	0.32	0.68	0.18	4.31	6.96	11.32
FRE	Cl3	0.0992	0.0969	0.0909	0.15	0.36	0.86	1.51	3.72	9.46
FRE	Cl4	1.18	1.28	0.909	1.9	2.3	0.86	1.61	1.80	0.95
FRE	Cl5	1.33	1.42	1.04	3.3	3.1	0.97	2.48	2.18	0.93
FRE	Cl6	0.371	0.347	0.418	0.87	0.9	0.43	2.35	2.59	1.03
FRE	Cl7	0.286	0.286	0.286	0.72	1.1	0.72	2.52	3.85	2.52
FRE	Cl8									
FRE	Cl9									
FRE	Cl10									
FRE	tPCBs	2.79	3.03	2.48	6.1	6.1	1.9	2.19	2.01	0.77

5.1.6. A1268 Temperature Dependence

The release rates of homologs and congeners from neat A1268 measured under ambient pressure at 25 °C and 4 °C (Figure 72) resulted in a much different release rate pattern for the two temperatures tested. At the higher temperature, the median release rate was dominated by Cl4 while at 4 °C Cl3 and Cl8 homologs dominated the median release rate. Release of Cl10 (PCB209), Cl9 (PCB206), Cl8, and Cl7 (PCB187 and PCB180) homologs occurred initially during the 4 °C experiment, while Cl10 was not detected at 25 °C and initial Cl7–Cl9 homolog dissolution rates were greater than 100 times less during the 25 °C experiment. The maximum release rate for both experiments occurred within a few days probably due to initial dissolution at the SASA, and could suggest that there are differences in the composition of PCBs available for dissolution at the surface of the A1268 sample tested in the study, and that temperature-dependent kinetics of dissolution may be dominating the process upon initial exposure to ASW. The latter may also be what makes the A1268 release curves at 4 ^{o}C appear flatter (release rates decreasing at slower rate), providing a steady release of PCBs over the course of the experiment, whereas the A1268 release rate curves at 25 ^{o}C appear to decrease more rapidly (release rates decreasing at faster rate), which may result in relatively fast depletion of those PCBs initially available for release over the course of the experiment. The long term leach rate endpoints for both temperatures support a complex combination of PCB availability and kinetics of dissolution versus kinetics of transport through the neat A1268 matrix to the SASA. The long term release rates were less variable, and PCBs measured from A1268 at 4 °C were much higher for Cl2, Cl3, Cl4, Cl6 and Cl8 homologs, while Cl1, Cl7, and Cl9 were higher at 25 °C, and Cl5 was about the same for both temperatures. These results suggest that the combined effects of dissolution and transport kinetics through the neat A1268 matrix, and perhaps heterogeneity of the neat A1268, to include the dynamically changing nature of the neat A1268 (matrix dissolution), may be more important in understanding the overall release, instead of a simple dependence of transport and dissolution on temperature.

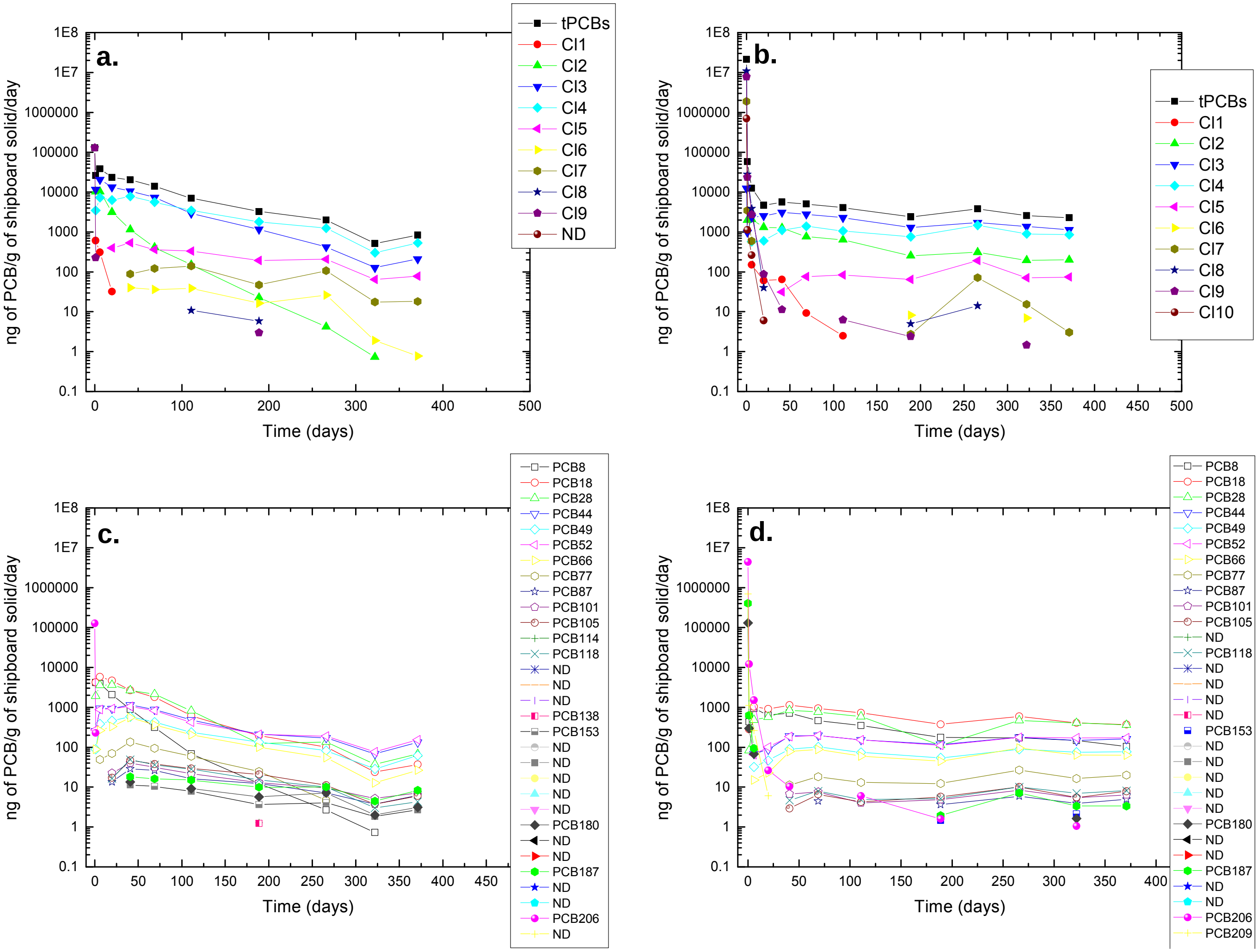

Figure 72. Comparison of A1268 average dissolution rates at constant ambient pressure (~1 bar) and 25 °C (a, c), to 4 °C (b, d) for homologs and congeners.

Table 16. Release rates (ng PCB/g neat A1268-day) for neat A1268 tested at 4 ^{o}C 1-bar and 25 ^{o}C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the dissolution rate curves shown in Figure 72.

		4^{o}C 1-bar			25^{o}C 1-bar			(R) 25^{o}C/4^{o}C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
A1268	Cl1	60.3	57.4	2.5	39	47	33	0.65	0.82	13.20
A1268	Cl2	700	899	200	150	700	0.73	0.21	0.78	0.00
A1268	Cl3	2280	2910	1140	960	3300	30	0.42	1.13	0.03
A1268	Cl4	894	971	858	1500	2400	530	1.68	2.47	0.62
A1268	Cl5	74.3	84.3	74.3	260	250	78	3.50	2.97	1.05
A1268	Cl6	7.6	7.6	6.99	16	18	0.77	2.11	2.37	0.11
A1268	Cl7	71.2	269000	3.05	19	46	19	0.27	0.00	6.23
A1268	Cl8	1950	1800000	14.2	3.8	3.8	5.8	0.00	0.00	0.41
A1268	Cl9	49.3	978000	1.46	230	43000	3	4.67	0.04	2.05
A1268	Cl10	690	175000	6.03						
A1268	tPCBs	4650	1930000	2280	14000	24000	840	3.01	0.01	0.37

5.1.7. BHI Temperature Dependence

The release rates of homologs and congeners from BHI measured under ambient pressure at 25 °C and 4 °C (Figure 73) resulted in a much different release rate pattern for the two temperatures tested. At the higher temperature, the median release rate was dominated by Cl4–Cl6, while at 4 °C the median release rate was totally swamped by the release of Cl2 and Cl7 homologs. The maximum release of Cl2–Cl7 homologs occurred at the beginning of the 4 °C experiment (initial dissolution-dominated release), while maxium releases occurred after about 30 days during the 25 °C experiment. Following the maximum release rates, the release rates remained relatively steady for both experiments. Releases of Cl1 and Cl8–Cl10 were not detected during either experiment. The rapid initial release of PCBs at 4 °C was similar to what was observed for A1268 at 4 °C, and is further evidence of initial release dominated by dissolution of readily available PCBs at the SASA interface, perhaps related to significant differences in the composition of initially readily available PCBs at the surface of the BHI sample tested in the study. The long-term leach rate endpoints for both temperatures were less variable, with the long term release rates of BHI at 4 °C much higher for Cl2 and Cl7 homologs, while long-term endpoint release rates for homologs Cl3–Cl6 were higher at 25 °C. These results provide further evidence that heterogeneity of PCB content at the SASA interface, in this case BHI, in addition to temperature may be important in determining the release rate.

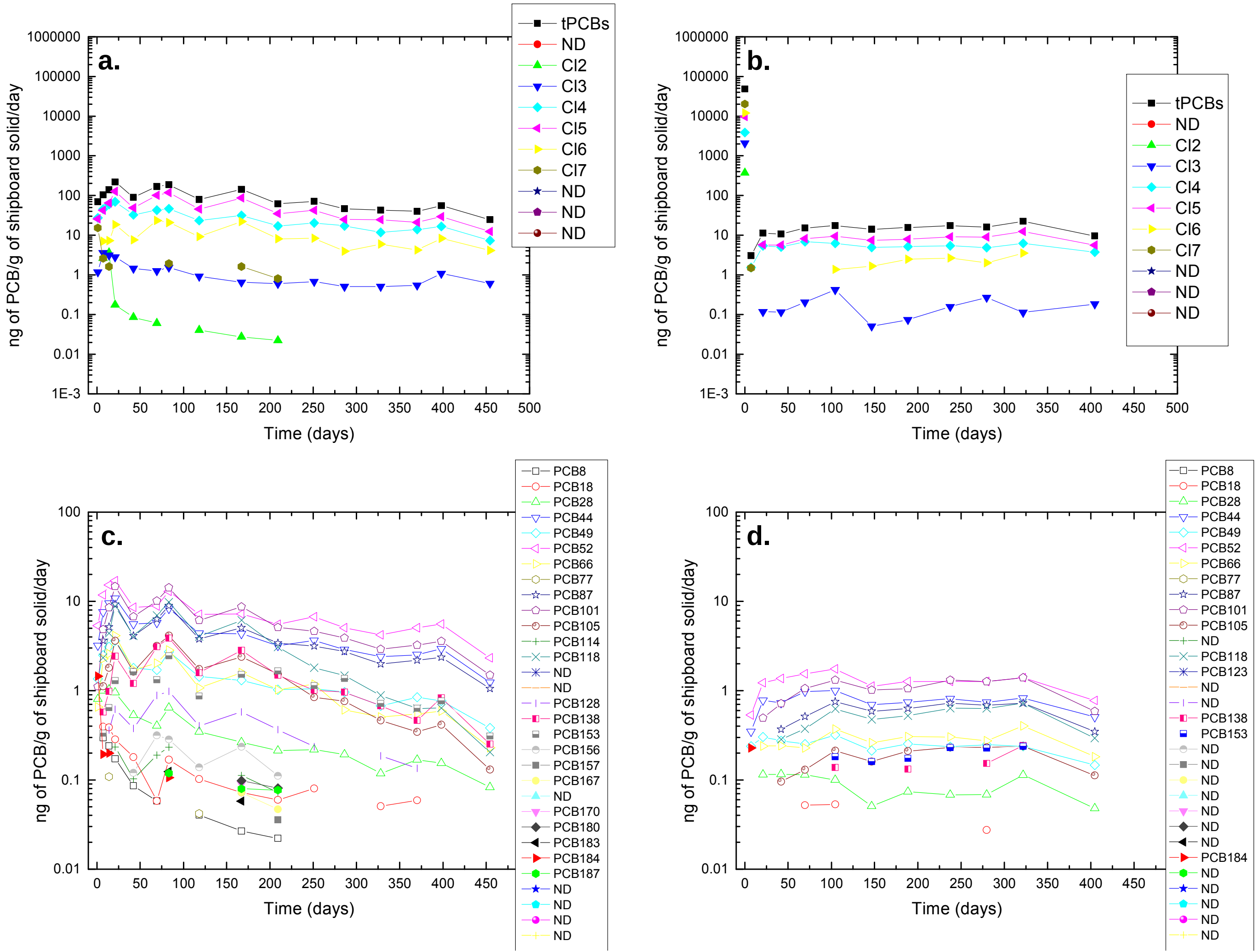

Figure 73. Comparison of BHI average leach rates at constant ambient pressure (~1 bar) and 25 ^{o}C (a, c), to 4 ^{o}C (b, d) for homologs and congeners.

Table 17. Release rates (ng PCB/g BHI-day) for BHI tested at 4 °C 1-bar and 25 °C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 73.

		4 °C 1-bar			25 °C 1-bar			(R) 25 °C/4 °C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
BHI	Cl1	0.114	0.114	0.114						
BHI	Cl2	371	371	371	0.55	1.1	0.22	0.00	0.00	0.00
BHI	Cl3	0.184	191	0.184	1	1.4	0.64	5.43	0.01	3.48
BHI	Cl4	5.28	327	3.74	25	29	7.3	4.73	0.09	1.95
BHI	Cl5	8	886	5.6	39	47	12	4.88	0.05	2.14
BHI	Cl6	2.48	1730	3.51	7.6	9.5	4.1	3.06	0.01	1.17
BHI	Cl7	10100	10100	1.51	1.8	4	0.89	0.00	0.00	0.59
BHI	Cl8									
BHI	Cl9									
BHI	Cl10									
BHI	tPCBs	15.3	4030	9.52	71	91	24	4.64	0.02	2.52

5.1.8. FGI Temperature Dependence

The release rates of homologs and congeners from FGI measured under ambient pressure at 25 °C and 4 °C (Figure 74) resulted in higher mean and median release rates at the higher temperature for all homologs measured. For the 25 °C experiment, the maximum release rate occurred initially, then decreased, followed by an increase to a secondary max within 50 days. This was followed by a general decrease in release rate over the rest of the experiment. For the lower temperature, the tPCB release rate remained relatively stable for the whole experiment, but there were some variations in the homolog release rates, especially for Cl2, Cl4, and Cl7. Cl10 was detected during the 25 °C experiment, but was not detected in the 4 °C experiment. The long-term leach rate endpoints for the homologs detected at 25 °C were similar (Cl4, Cl5, Cl7, Cl8), slightly higher (Cl2, Cl3, Cl6), or more that 10 times higher (Cl9 and Cl1) compared to 4 °C.

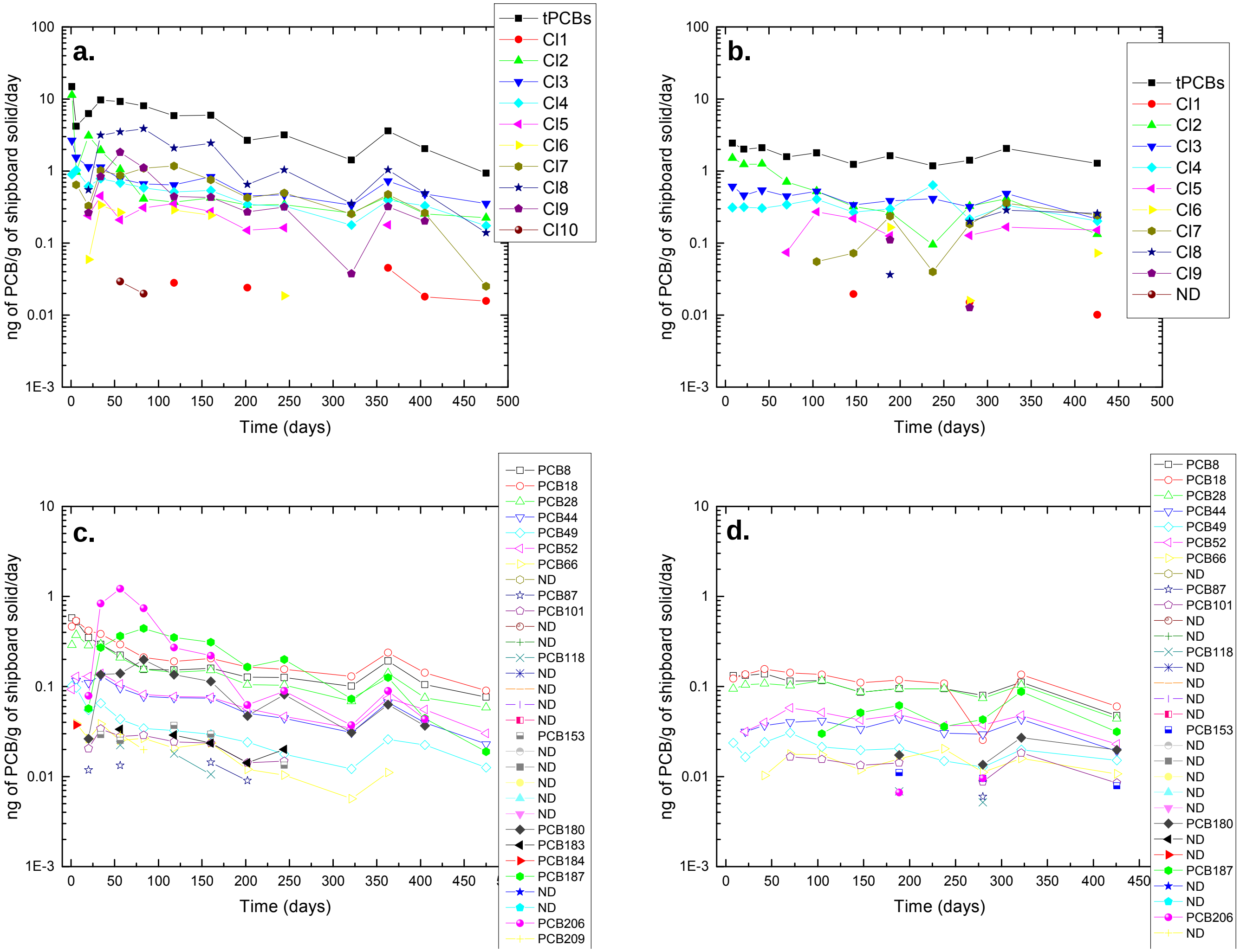

Figure 74. Comparison of FGI average leach rates at constant ambient pressure (~1 bar) and 25 °C (a, c), to 4 °C (b, d) for homologs and congeners.

Table 18. Release rates (ng PCB/g FGI-day) for FGI tested at 4 ^{o}C 1-bar and 25 ^{o}C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 74.

		4 ^{o}C 1-bar			25 ^{o}C 1-bar			(R) 25 ^{o}C/4 ^{o}C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
FGI	Cl1	0.0174	0.0174	0.0151	0.24	0.26	0.16	13.79	14.94	10.60
FGI	Cl2	0.413	0.617	0.132	0.43	1.6	0.22	1.04	2.59	1.67
FGI	Cl3	0.448	0.431	0.214	0.69	0.87	0.35	1.54	2.02	1.64
FGI	Cl4	0.313	0.33	0.201	0.53	0.55	0.17	1.69	1.67	0.85
FGI	Cl5	0.151	0.162	0.151	0.27	0.28	0.18	1.79	1.73	1.19
FGI	Cl6	0.0723	0.0845	0.0723	0.28	0.32	0.18	3.87	3.79	2.49
FGI	Cl7	0.183	0.169	0.242	0.5	0.69	0.25	2.73	4.08	1.03
FGI	Cl8	0.228	0.195	0.258	1.4	1.6	0.14	6.14	8.21	0.54
FGI	Cl9	0.0615	0.0615	0.0127	0.38	0.59	0.22	6.18	9.59	17.32
FGI	Cl10				0.25	0.25	0.2			
FGI	tPCBs	1.63	1.7	1.27	4.2	5.1	0.93	2.58	3.00	0.73

5.1.9. FGO Temperature Dependence

The release rates of homologs and congeners from FGO measured under ambient pressure at 25 °C and 4 °C (Figure 75) resulted in increased mean, median, and endpoint release rates at the higher temperature for all homologs measured. For the 25 °C experiment, the maximum release rate occurred after about 60 days followed by a general decrease in release rate, while the maximum release rate occurred within 50 days followed by a decreasing (until day 100) followed by a relatively stable release for the 4°C experiment. The mean release rates measured at 25 °C were similar for homologs measured (Cl3 ~ Cl4 > Cl2 > Cl7> Cl8 ~ Cl5 ~ Cl1 > Cl6), which were ~ 3 to 4 times higher than the mean release rates measured at 4 °C. The Cl9 and Cl10 homologs were not detected in either of the experiments, and Cl1, Cl5, Cl6, and Cl8 were not dectected in the 4 °C experiment. The long-term leach rate endpoints for the homologs detected in both experiments were much higher at 25 °C than at 4 °C.

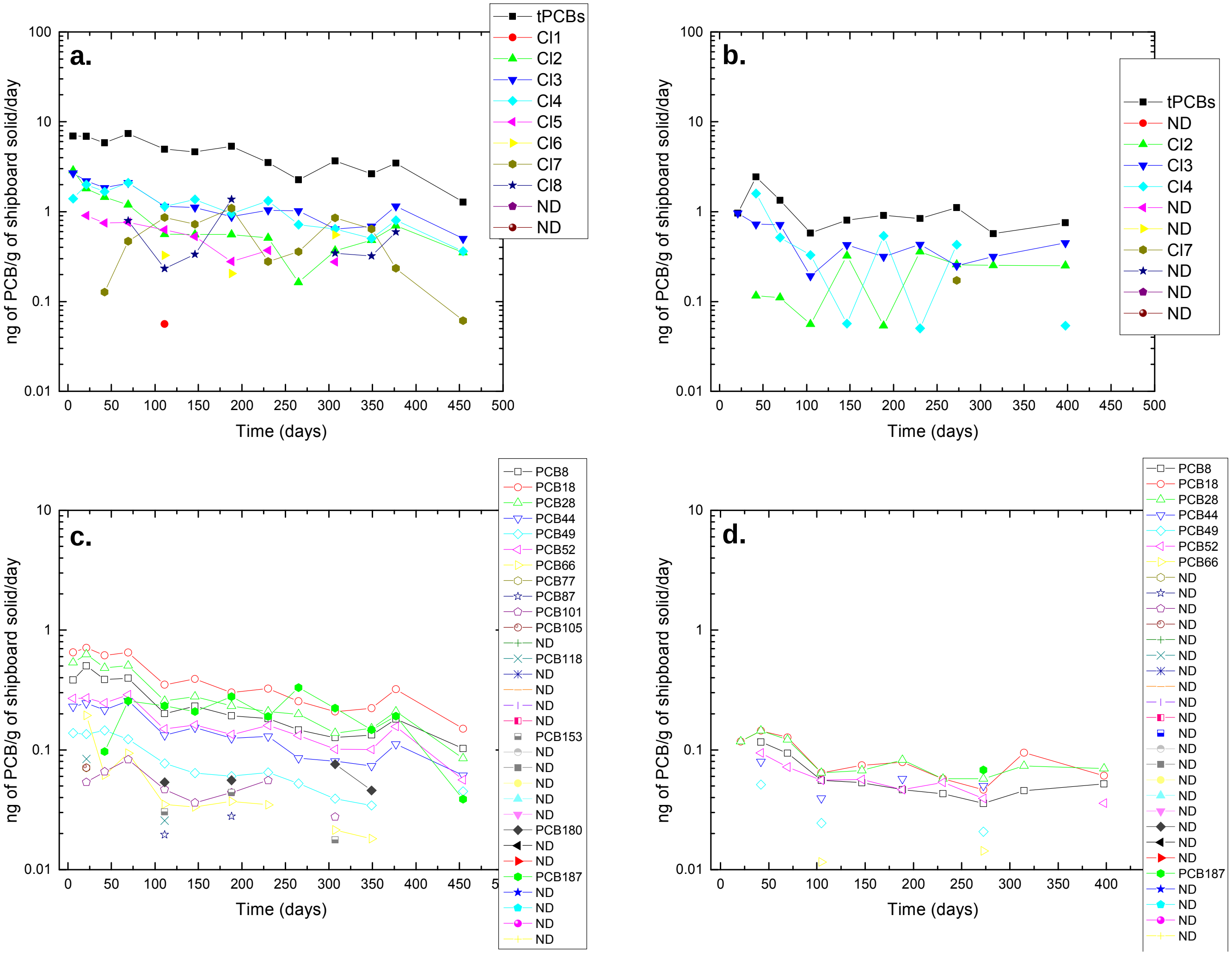

Figure 75. Comparison of FGO average leach rates at constant ambient pressure (~1 bar) and 25 ^{o}C (a, c), to 4 ^{o}C (b, d) for homologs and congeners.

Table 19. Release rates (ng PCB/g FGO-day) for FGO tested at 4 °C 1-bar and 25 °C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 75.

		4°C 1-bar			25°C 1-bar			(R) 25°C/4°C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
FGO	Cl1				0.56	0.56	0.56			
FGO	Cl2	0.251	0.197	0.251	0.56	0.9	0.35	2.23	4.57	1.39
FGO	Cl3	0.427	0.477	0.448	1.1	1.4	0.53	2.58	2.94	1.18
FGO	Cl4	0.379	0.444	0.0537	1.1	1.2	0.36	2.90	2.70	6.70
FGO	Cl5				0.58	0.56	0.28			
FGO	Cl6				0.33	0.37	0.55			
FGO	Cl7	0.172	0.172	0.172	0.61	0.64	0.61	3.55	3.72	3.55
FGO	Cl8				0.34	0.57	0.59			
FGO	Cl9									
FGO	Cl10									
FGO	tPCBs	0.871	1.03	0.752	3.7	3.9	1.3	4.25	3.79	1.73

5.1.10. AP Temperature Dependence

The release rates of homologs and congeners from AP measured under ambient pressure at 25 °C and 4 °C (Figure 76) resulted in higher release rates at the higher temperature for all homologs measured. For the 25 °C experiment, the maximum release rate occurred at initiation of the experiment due to the initial dissolution-release of Cl7 (PCB184), after which the release rate flucuated near 1 to 2 ng/g of shipboard solid until ~ 250 days, when the release rate decreased ~ tenfold, only to increase back up after about 320 days and then decline again. The release rates for the 4 °C experiment are best characterized as intermittant, with homologs Cl3–Cl5 appearing and disappearing throughout the experiment. The mean release rates measured at 25 °C were 2 to 6 times higher for homologs measured in both experiments (Cl3–Cl5). The Cl1, Cl2, and Cl8–Cl10 homologs were not detected in either of the experiments while Cl6 and Cl7 were only detected in the 25 °C experiment. The long-term leach rate endpoints for the homologs detected in both experiments were much higher at 25 °C than 4 °C, except for Cl5, which was similar for both temperatures.

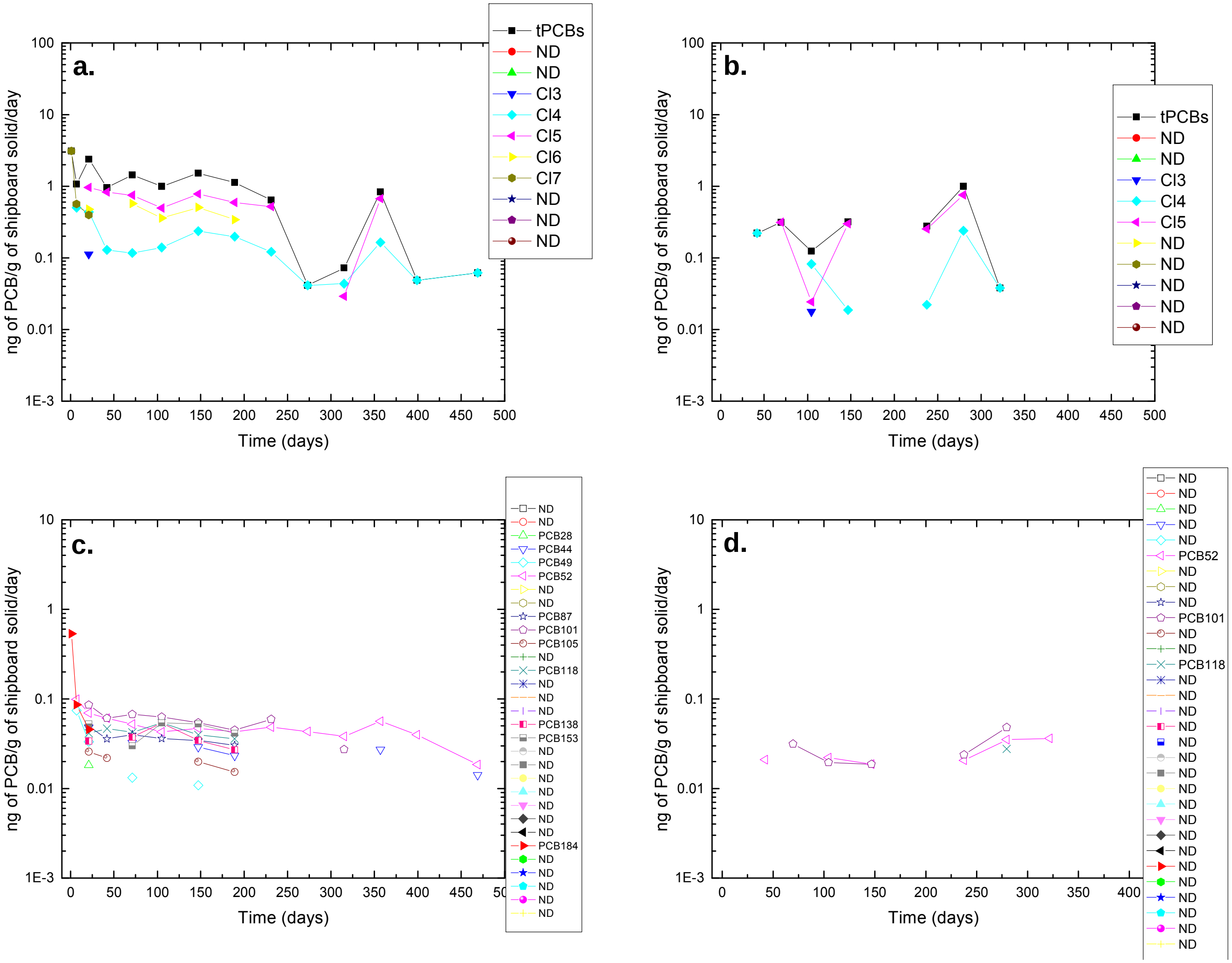

Figure 76. Comparison of AP average leach rates at constant ambient pressure (~1 bar) and 25 °C (a, c), to 4 °C (b, d) for homologs and congeners.

Table 20. Release rates (ng PCB/g AP-day) for AP tested at 4 °C 1-bar and 25 °C 1-bar and the ratio (R) between high and low temperature release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 76.

		4 °C 1-bar			25 °C 1-bar			(R) 25 °C/4°C		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
AP	Cl1									
AP	Cl2									
AP	Cl3	0.0177	0.0177	0.0177	0.11	0.11	0.11	6.21	6.21	6.21
AP	Cl4	0.0599	0.104	0.0379	0.24	0.32	0.62	4.01	3.08	16.36
AP	Cl5	0.298	0.328	0.756	0.67	0.65	0.67	2.25	1.98	0.89
AP	Cl6				0.48	0.47	0.35			
AP	Cl7				0.57	1.6	0.4			
AP	Cl8									
AP	Cl9									
AP	Cl10									
AP	tPCBs	0.276	0.326	0.0379	0.95	0.95	0.062	3.44	2.91	1.64

5.1.11. Leach Rate Pressure Dependence Summary

A subset of shipboard solids tested at low temperature/high pressure (4 ^{o}C/300 bar) were evaluated for pressure dependence, in addition to the dissoluton/leaching behavior temperature dependence evauation at constant ambient pressure (~1 bar) at the two temperatures (4 °C and 25 °C) described above. As with ambient pressure studies, leach rates were determined for all analytes in Table 4 and Table 5 (congeners, homologs, homolog-derived tPCBs) as a function of time. These low-temperature/variable pressure leach rate data are applicable to this study for purposes of demonstrating the behavior of leach rates as a function of hydrostatic pressure in a deep-ocean leaching scenario. Low temperature (4 °C) leach rates as a function of the two nominal pressures studied, 1 bar and 300 bar, are summarized below for comparing homolog-derived tPCB leaching behavior as a function of leaching time (Figure 77).

In general, mean release rates of tPCBs were much lower at high pressure for A1254 and BHI, whereas mean tPCB release rates for FGI were similar at both pressures. For EC, the mean release rates were similar, but the initial release was much higher and the endpoint was significantly lower at higher pressure (decreasing release rate at higher pressure compared to constant release rate at lower pressure across the experiment). Initial kinetics at lower pressure also appear suppressed for the solids, as indicated by a more gradual or sluggish leach rate increase up to the maximum leach rate, perhaps related to a shorter conditioning period (wetting action) upon exposure to high pressure seawater. The post-maximum leach rate decrease for solids tested at 1 bar generally also appear slower relative to what is observed at 300 bar, exhibiting flatter monotonically decreasing leach rates as a function of time. This slow decrease is probably related to less PCB depletion with time as dissolution at the seawater–solid interface progressed. Pressure appeared to affect leach rates for the shipboard solids EC and FGI to a greater extent than for the neat solid Aroclor® 1254 and the BHI, which both have minimal influence by the host matrix, i.e., BHI has an open structure relative to the other shipboard solids and is considered to have a much larger SASA, leading to much larger rates of PCB release under all conditions tested. In addition to these tPCB comparisons for each shipboard solid and the Aroclor dissolution control tested at a constant temperature 4 °C, at both ambient pressure (~1 bar) and high pressure (~300 bar), comparative behaviors of homologs and congeners, are similarly presented for these four materials below.

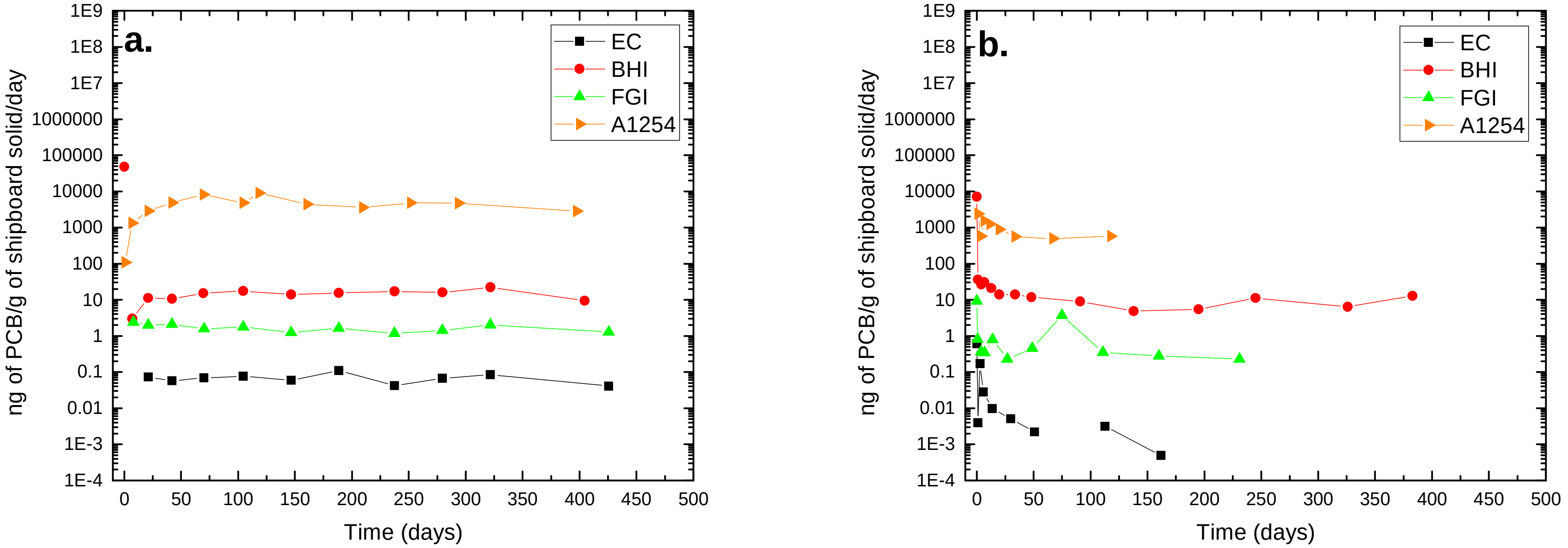

Figure 77(a-b). Overview of tPCB average leach rates at constant temperature (4 °C) and (a) 1 bar (nominal ambient) pressure, compared to (b) 300 bar (nominal high) pressure for the materials selected for pressure testing.

Table 21. Release rate (ng PCB/g shipboard solid- day) of tPCBs for solids tested at 4 ^{o}C 1-bar and 4 ^{o}C 300-bar and the ratio (R) between low and high pressure release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 77.

		4 ^{o}C 1-bar			4 ^{o}C 300-bar			(R) 1 Bar/300 Bar		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
A1254	tPCBs	5080	4760	3130	735	1030	580	6.91	4.62	5.40
BRPHL	tPCBs	0.908	0.879	0.751						
EC	tPCBs	0.0682	0.068	0.0407	0.0051	0.0922	0.000489	13.37	0.74	83.23
FRE	tPCBs	2.79	3.03	2.48						
A1268	tPCBs	4650	1930000	2280						
BHI	tPCBs	15.3	4030	9.52	13.4	524	12.9	1.14	7.69	0.74
FGI	tPCBs	1.63	1.7	1.27	0.364	1.53	0.229	4.48	1.11	5.55
FGO	tPCBs	0.871	1.03	0.752						
AP	tPCBs	0.276	0.326	0.0379						

5.1.12. A1254 Pressure Dependence

The release rates of homologs and congeners from A1254 measured at 4 °C with 1 bar and 300 bar pressure (Figure 78) resulted in higher mean release rates at the lower pressure for all homologs measured, except for Cl2, which was slightly higher at 300 bar. For the 1 bar experiment, the maximum release rate occurred after about 120 days followed by a relatively stable release. The release rates for the 300 bar experiment are characterized by a high initial release that rapidly decreased and stablized after about 60 days until the end of the experiment. The mean release rates measured for Cl1 and Cl2 for both pressures were similar while the mean release rates for Cl3–Cl5 were much higher at low pressure. The Cl8–Cl10 homologs were not detected in either of the experiments, whereas Cl6 and Cl7 were only detected in the low pressure experiment. The long-term leach rate endpoints for the dominant homologs (Cl4 and Cl5) detected in both experiments were much higher at 1 bar than 300 bar.

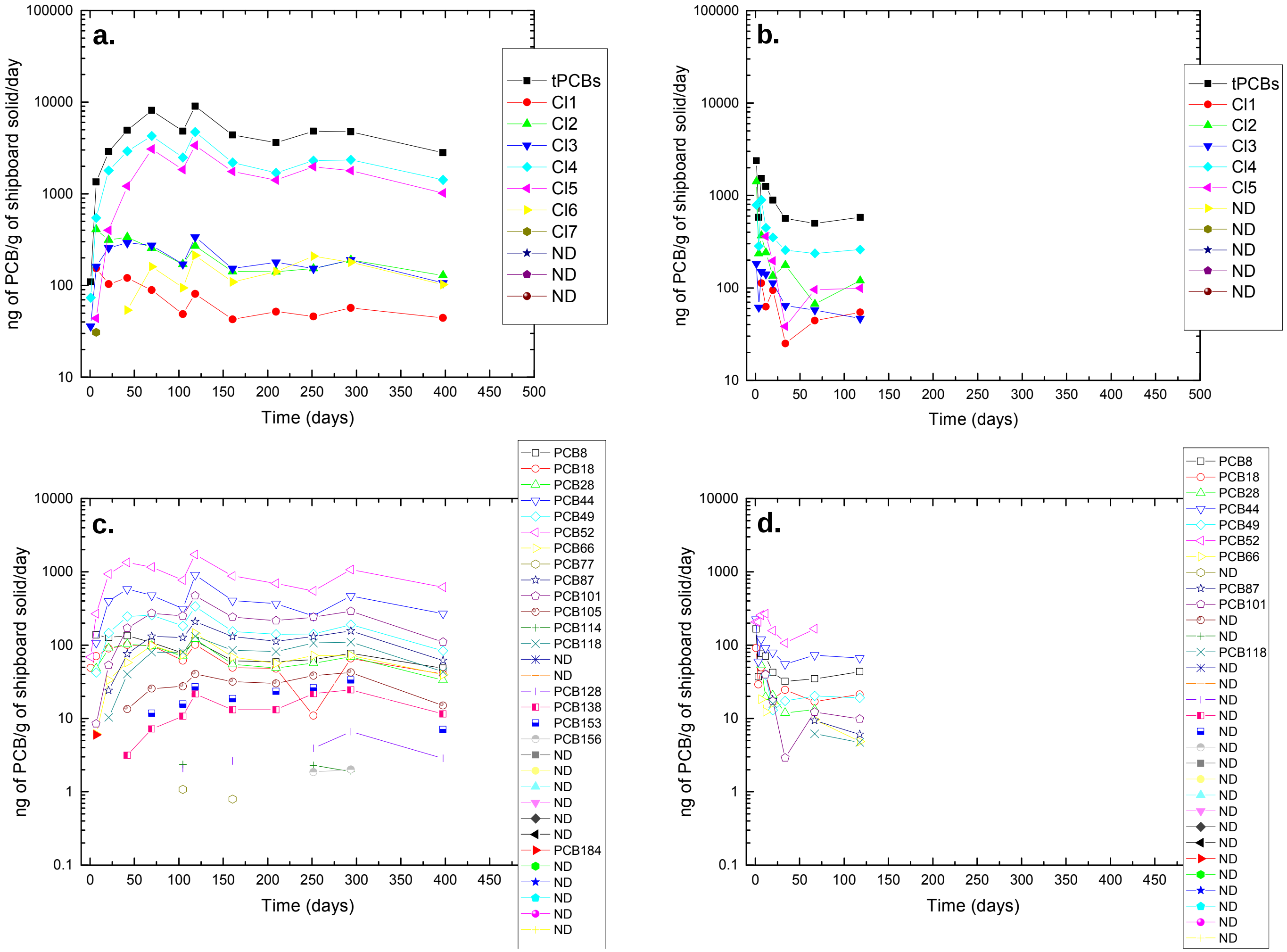

Figure 78. Comparison of A1254 average dissolution rates at constant temperature (4 ^{o}C) and 1 bar (nominal ambient) pressure (a, c), to 300 bar (nominal high) pressure (b, d) for homologs and congeners.

Table 22. Release rates (ng PCB/g neat A1254-day) for neat A1254 tested at 4 °C 1-bar and 4 °C 300-bar and the ratio (R) between low and high pressure release rates for the median, mean, and endpoint of the dissolution rate curves shown in Figure 78.

		4 °C 1-bar			4 °C 300-bar			(R) 1 Bar/300 Bar		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
A1254	Cl1	63.3	84.6	49.2	58.5	65.5	54.5	1.08	1.29	0.90
A1254	Cl2	211	253	143	206	344	120	1.02	0.74	1.19
A1254	Cl3	194	213	118	88.6	102	46.6	2.19	2.09	2.53
A1254	Cl4	2490	2470	1570	317	440	259	7.85	5.61	6.06
A1254	Cl5	1950	1800	1130	99.1	158	99.1	19.68	11.39	11.40
A1254	Cl6	157	155	113						
A1254	Cl7	34.3	34.3	34.3						
A1254	Cl8									
A1254	Cl9									
A1254	Cl10									
A1254	tPCBs	5080	4760	3130	735	1030	580	6.91	4.62	5.40

5.1.13. EC Pressure Dependence

The release rates of homologs and congeners from EC measured at 4 °C with 1 bar and 300 bar pressure (Figure 79) resulted in higher long-term endpoint release rates at the lower pressure for all homologs measured. The Cl1, Cl3, and Cl7–Cl10 homologs were not detected in either of the experiments, and the Cl2 homologs were only dectected in the low pressure experiment. For the 1 bar experiment, the maximum release rate occurred after about 180 days followed by a slightly fluctuating release. The release rates for the 300 bar experiment showed a high initial release that rapidly decreased and disappeared, then returned after ~ 120 days. The mean and median release rate measured for Cl6 at both pressures were similar, while the mean release rates for Cl4 and Cl5 were lower at low pressure. The median release rates at 1 bar were higher for Cl4 than at 300 bar. The long-term leach rate endpoints for the homologs (Cl4–Cl6) detected in both experiments were much higher at 1 bar than 300 bar.

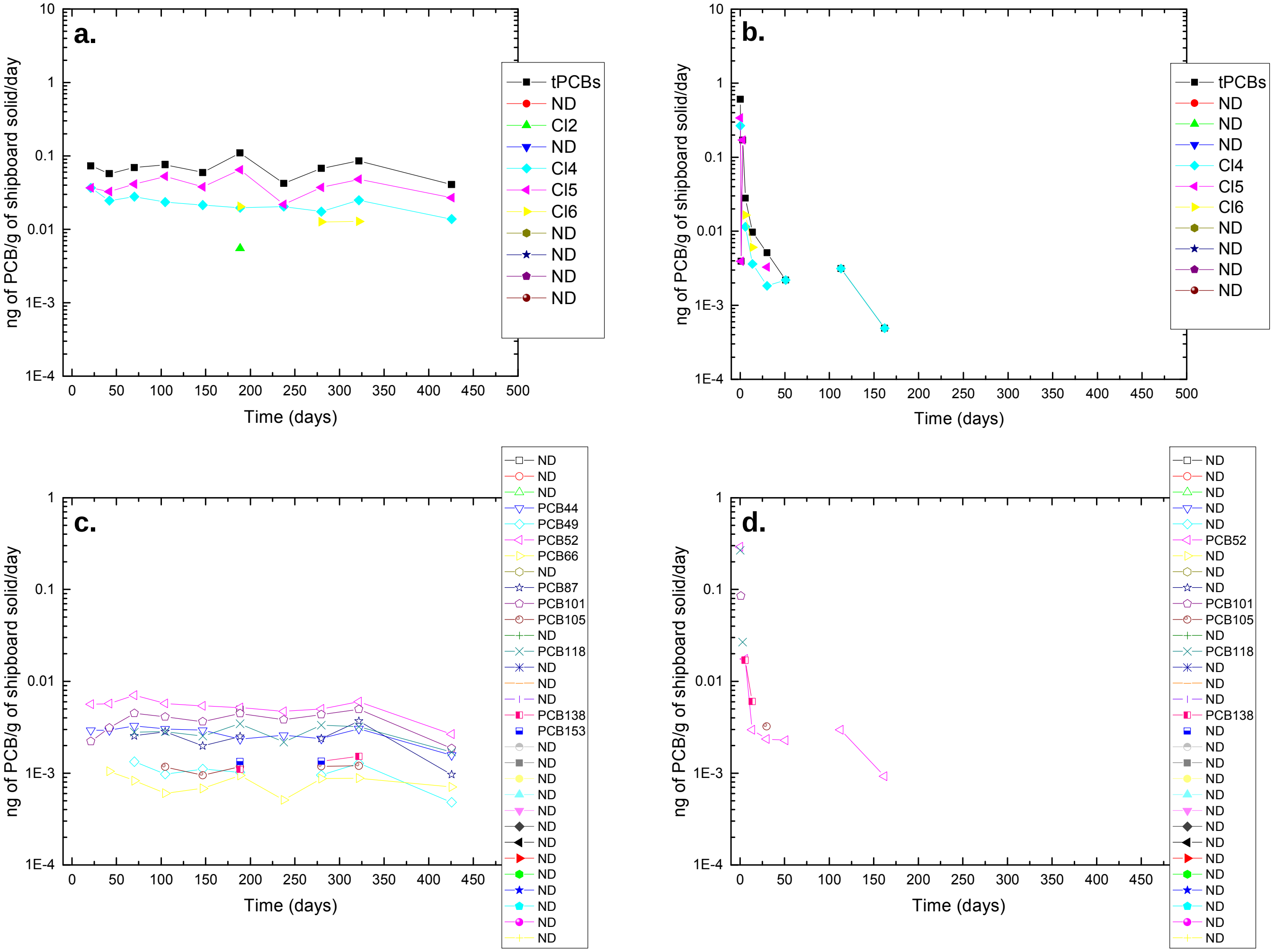

Figure 79. Comparison of EC average dissolution rates at constant temperature (4 ^{o}C) and 1 bar (nominal ambient) pressure (a, c), to 300 bar (nominal high) pressure (b, d) for homologs and congeners.

Table 23. Release rates (ng PCB/g EC-day) for EC tested at 4 °C 1-bar and 4 °C 300-bar and the ratio (R) between low and high pressure release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 79.

		4 °C 1-bar			4 °C 300-bar			(R) 1 Bar/300 Bar		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
EC	Cl1									
EC	Cl2	0.00549	0.00549	0.00549						
EC	Cl3									
EC	Cl4	0.0222	0.023	0.0138	0.00313	0.0414	0.000489	7.09	0.56	28.22
EC	Cl5	0.0376	0.0399	0.0269	0.0872	0.129	0.00326	0.43	0.31	8.25
EC	Cl6	0.0128	0.0153	0.0128	0.0113	0.0113	0.00607	1.13	1.35	2.11
EC	Cl7									
EC	Cl8									
EC	Cl9									
EC	Cl10									
EC	tPCBs	0.0682	0.068	0.0407	0.0051	0.0922	0.000489	13.37	0.74	83.23

5.1.14. BHI Pressure Dependence

The release rates of homologs and congeners from BHI measured at 4 °C with 1 bar and 300 bar pressure (Figure 80) resulted in higher mean release rates at the lower pressure for all homologs measured, except for Cl1. The Cl9 and Cl10 homologs were not detected in either of the experiments, while the Cl7 and Cl8 homologs at 300 bar were only detected once (at the beginning of the experiment). For the 1 bar experiment, the maximum release rate occurred after about 100 days followed by a relatively stable release rate. The release rates for the 300 bar experiment showed a high initial release that rapidly decreased and then stablized after about 30 days. The mean release rate at 1 bar was dominated by Cl7 homologs released early in the experiment, and was lower by nearly 9 times in the high pressure experiment. The long term leach rate endpoint for Cl7 at high pressure was more than 100 times higher than for the 1 bar experiment, but occurred at the beginning of the experiment and was not detected beyond that. This dissolution-dominated behavior is indicative of readily available Cl7 release at the SASA interface at high pressure and readily available Cl7 and Cl8 release at low pressure.

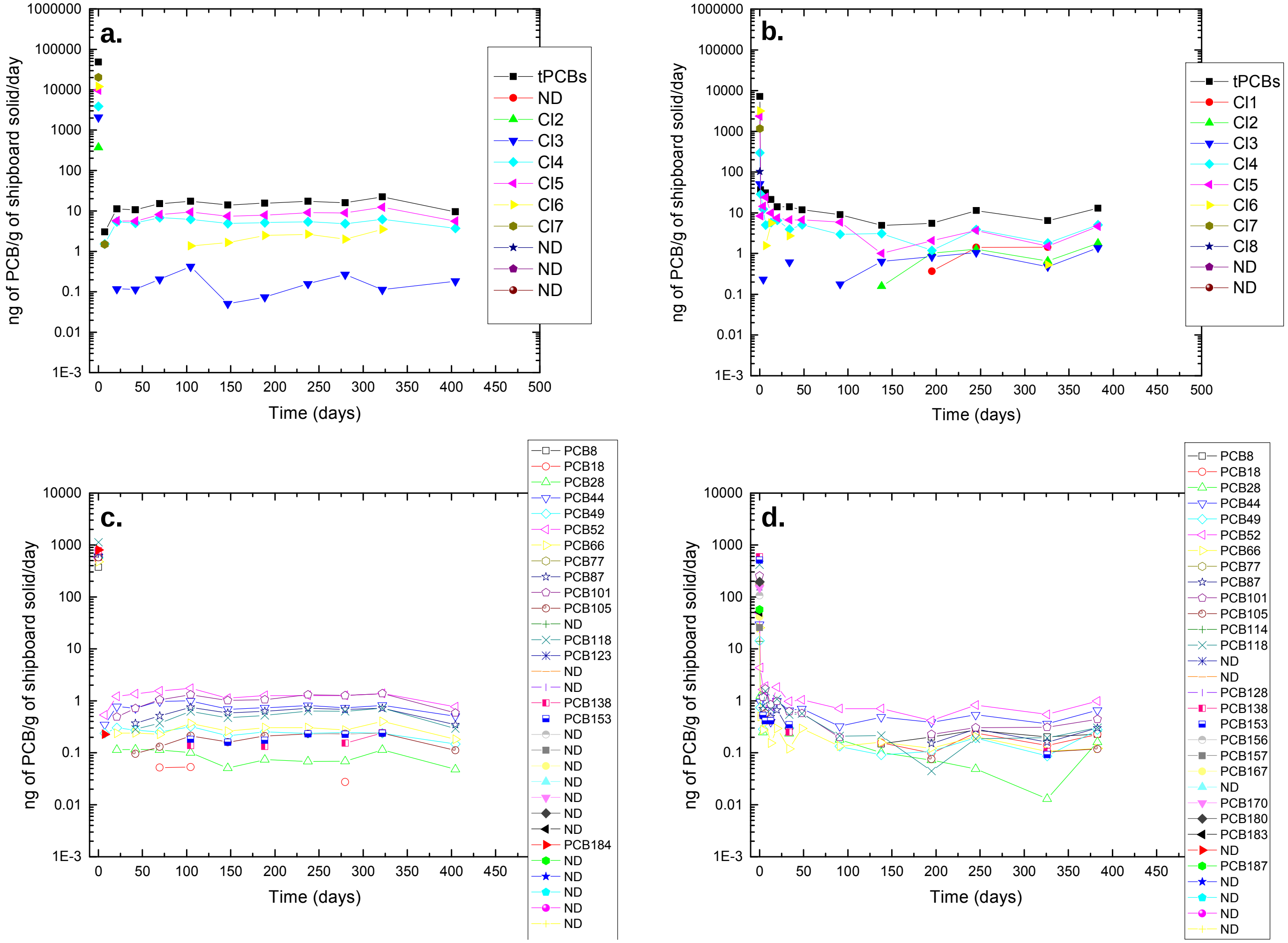

Figure 80. Comparison of BHI average dissolution rates at constant temperature (4 ^{o}C) and 1 bar (nominal ambient) pressure (a, c), to 300 bar (nominal high) pressure (b, d) for homologs and congeners.

Table 24. Release rates (ng PCB/g BHI-day) for BHI tested at 4 ^{o}C 1-bar and 4 ^{o}C 300-bar and the ratio (R) between low and high pressure release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 80.

		4 ^{o}C 1-bar			4 ^{o}C 300-bar			(R) 1 Bar/300 Bar		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
BHI	Cl1	0.114	0.114	0.114	1.41	1.07	1.43	0.08	0.11	0.08
BHI	Cl2	371	371	371	1.02	0.978	1.79	363.73	379.35	207.26
BHI	Cl3	0.184	191	0.184	0.638	6.29	1.38	0.29	30.37	0.13
BHI	Cl4	5.28	327	3.74	5.02	27.2	5.07	1.05	12.02	0.74
BHI	Cl5	8	886	5.6	6.7	176	4.63	1.19	5.03	1.21
BHI	Cl6	2.48	1730	3.51	2.73	633	0.526	0.91	2.73	6.67
BHI	Cl7	10100	10100	1.51	1160	1160	1160	8.71	8.71	0.00
BHI	Cl8				102	102	102			
BHI	Cl9									
BHI	Cl10									
BHI	tPCBs	15.3	4030	9.52	13.4	524	12.9	1.14	7.69	0.74

5.1.15. FGI Pressure Dependence

The release rates of homologs and congeners from FGI measured at 4 °C with 1 bar and 300 bar pressure (Figure 81) resulted in higher long term endpoint release rates at lower pressure for all homologs measured. All the homologs except for Cl10 were measured during the low pressure experiment but only Cl2, Cl3, and Cl4 were measured in the high pressure experiment. For the 1 bar experiment, the tPCB release rate remained relatively constant even though the different homologs varied throughout the experiment. The release rates for the 300 bar experiment showed a high initial release of Cl4 that rapidly decreased and was followed by spikes of Cl3 at about 30 days and Cl2 at about 75 days. The median and mean release rates for homologs at 1 bar (Cl2–Cl3) were all higher. The long term leach rate endpoint estimated for Cl4 was more than 12 times higher at 1 bar than 300 bar, while the long term leach rate endpoints for Cl3 and Cl2 from the 1 bar experiment were 1.5 and 1.8 times higher than the 300 bar experiment, respectively.

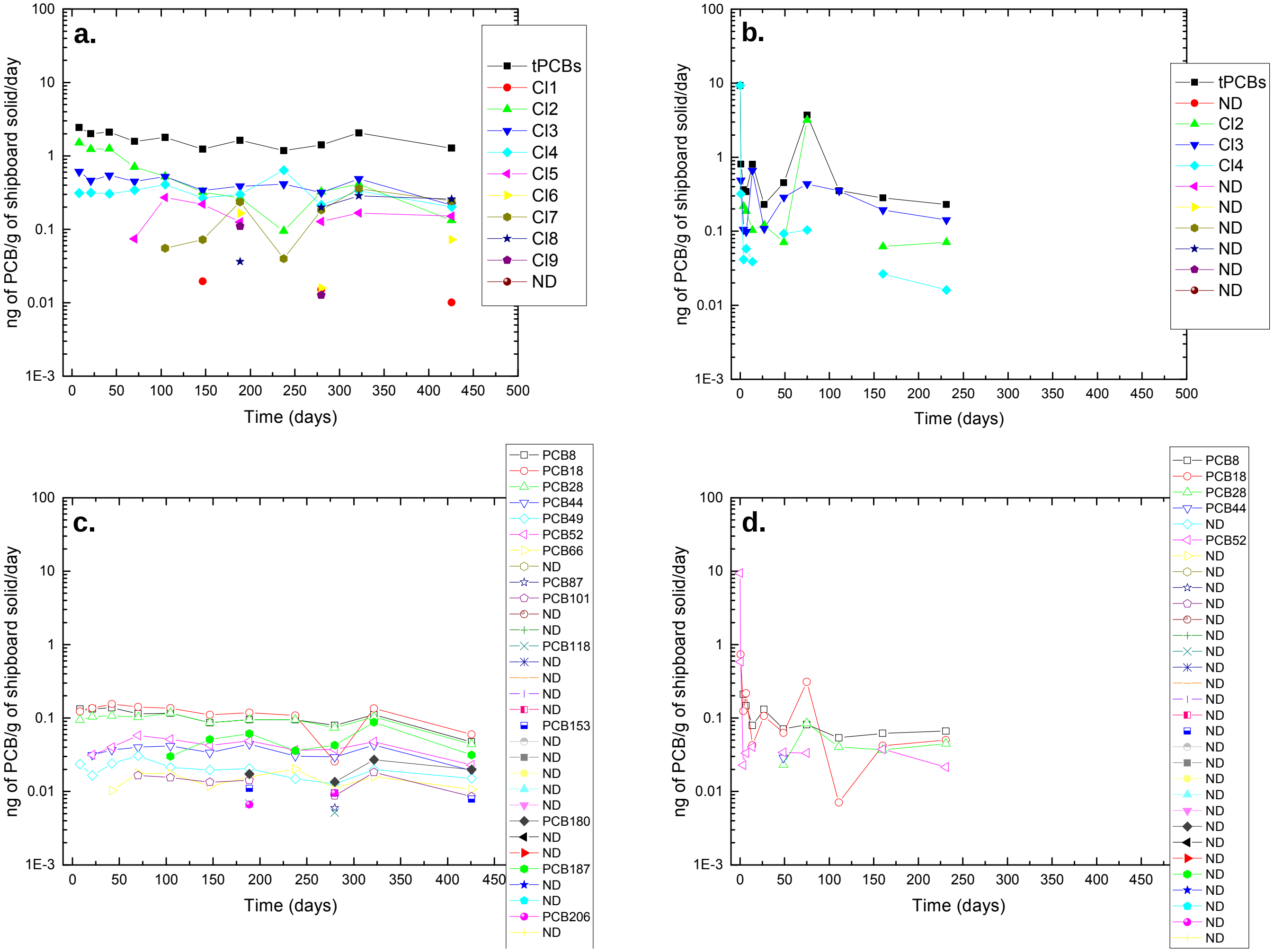

Figure 81. Comparison of FGI average dissolution rates at constant temperature (4 ^{o}C) and 1 bar (nominal ambient) pressure (a, c), to 300 bar (nominal high) pressure (b, d) for homologs and congeners.

Table 25. Release rates (ng PCB/g FGI-day) for FGI tested at 4 °C 1-bar and 4 °C 300-bar and the ratio (R) between low and high pressure release rates for the median, mean, and endpoint of the leach rate curves shown in Figure 81.

		4 °C 1-bar			4 °C 300-bar			(R) 1 Bar/300 Bar		
Solid	Parameter	Median	Mean	Endpoint	Median	Mean	Endpoint	MedianR	MeanR	EndpointR
FGI	Cl1	0.0174	0.0174	0.0151						
FGI	Cl2	0.413	0.617	0.132	0.112	0.5	0.0709	3.69	1.23	1.86
FGI	Cl3	0.448	0.431	0.214	0.241	0.287	0.142	1.86	1.50	1.51
FGI	Cl4	0.313	0.33	0.201	0.058	1.11	0.0161	5.40	0.30	12.48
FGI	Cl5	0.151	0.162	0.151						
FGI	Cl6	0.0723	0.0845	0.0723						
FGI	Cl7	0.183	0.169	0.242						
FGI	Cl8	0.228	0.195	0.258						
FGI	Cl9	0.0615	0.0615	0.0127						
FGI	Cl10									
FGI	tPCBs	1.63	1.7	1.27	0.364	1.53	0.229	4.48	1.11	5.55

5.2. LEACH RATE STUDY UNCERTAINTY AND CONFIDENCE IN LEACH RATE STUDY RESULTS

This section describes uncertainties and limitations encountered during the study. This description provides an adequate level of confidence in the leaching results to objectively select aspects of the leach rate study results that are applicable to any potential application, including but not limited to risk assessment, Aroclor® dissolution behaviors, and PCB congener and homolog leaching behavior(s) in ASW under varied pressure and temperature conditions. The following discussion focuses on different components of the leach rate study to provide a reasonably comprehensive summary of critical issues in study design/ approach, shipboard solids containing PCBs, analytical chemistry, leach rate results, and leach rate uses/applications. With the exception of analytical chemistry, many issues are not readily quantified, but will be presented in a quantitative manner whenever possible, if necessary, by using reasonable assumptions to estimate any potential impacts.

5.2.1. Leachate Saturation Evaluation.

To evaluate the shipboard solid leaching results against Aroclors® as analytical controls, the maximum concentrations observed in each shipboard solid leaching experiment at 4° C were compared to the corresponding maximum concentrations observed for Aroclor® 1254 and Aroclor® 1268 dissolution experiments (Table 26). Also shown is the maximum observed tPCBs concentration in a single sample (calculated as sum of homologs). For comparison as a potential upper experimental limit (effective saturation), the sum of the homolog maxima across all leachate samples is shown for each dissolution and shipboard solid experiment.

All tPCB concentrations in shipboard solids were lower than A1254 and A1258, demonstrating that the overall goal of not exceeding saturation under the experimental leaching conditions was achieved. Upon close inspection of Table 26, most analyses are indeed lower, but on an analyte basis vice a tPCBs basis, several of the homologs and congeners that comprise the tPCBs number (generally Cl6 and above), are slightly higher for the shipboard solid leaching experiments compared with their respective Aroclor® results. In samples where a particular analyte in the shipboard solid experiment was higher, the value is shown in Table 26, with parentheses, and double parentheses further indicating which of these were J-flagged/estimated below MRL.

The explanation for these observations includes one or more of the following:

1. Concentration was a very low value near the detection limit with higher uncertainty.
2. 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 satisfactorily.
3. Differences in analyte concentrations were within the expected analytical precision of each other.
4. Concentration could not be explained using the Aroclor® results reported here, which assumes the leachable PCBs are distributed similar to the bulk Aroclor® PCB distribution. (The PCB-ISM may have contained a different PCB distribution that was different from the Aroclor tested.)

Item 4 indicates the possibility of localized regions of readily leachable PCBs at the interface (SASA), which is particularly evident for the shipboard solid BHI. For high pressure experiments, the most concentrated BHI sample was considered to be an effective surrogate for A1268, as only A1254 was tested under high pressure.

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 for 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, i.e., that particular sample could be approaching a potential saturation limit for that analyte, meaning suppression was a possibility. This assumption cannot be confirmed without having performed an experiment under the same conditions for that specific analyte (homolog or congener instead of using an Aroclor® selected to match the bulk PCB distribution as was done in this study). Nonetheless, the congener and homolog levels were well below published saturation levels reported in the literature. Leach rates derived from the highest concentration values, in those samples only, could potentially have been influenced by saturation of that analyte in solution. The impact of these individual leach rate values on the overall empirical leach rate curve behaviors is minimal, and none of the suggested long-term leach rate values were affected (observed leachate concentration maxima did not correspond to the endpoints of leach rate curves). Note that samples exhibiting maximum concentrations did not generally correspond to the maximum leach rates because the leach rates, by definition, are related to the change in concentration as a function of time (time over which a concentration change occurs), not simply the concentration magnitude.

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 homologs in that sample. A summation of all maximum homolog values across all samples is also included, which represents a reasonable maximum tPCBs concentration one might expect for a material containing A1254 or A1268, if tested under the leaching conditions of this study.

Table 26. Comparison of Aroclor dissolution and shipboard solid leaching experiment concentration maxima at a) 4 ^{o}C/1 bar, and b) 4 ^{o}C/300 bar. 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).

a) 4 ^{o}C /1 bar 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	6360	6384	140	404	42	442.2	54	142	545.5
Cl1–10 (Max Sum)	6364	7925	160	486.5	65.8	487.66	54.8	152.7	571.4
Cl1	100	29	0	2.5	0	2.2	0	12	6.8
Cl2	290	590	7	78	14	0.46	0	1	18
PCB8	110	320	6.3	15	2.9	0.46	0	1	3.1
Cl3	240	2900	0	68	25	12	0.8	9.7	20
PCB18	91	1000	0	19	3.4	0.85	0	1.3	3
PCB28	75	790	0	14	3.9	2.2	0	3.2	4.2
Cl4	3200	2500	43	94	22	140	13	69	200
PCB44	610	300	4.9	6.1	1.6	19	0	9	34
PCB49	190	150	1.6	4.8	0.71	5.5	0	3.3	10
PCB52	1400	300	8.3	7.3	2	29	2	16	63
PCB66	89	160	2.2	3.4	0.4	7.8	0	2.4	7.3
PCB77	0.82	45	0	0	0	0.79	0	0	0
Cl5	2300	320	84	48	0	240	41	61	230
PCB87	140	10	4.6	0.75	0	(16)	0.51	3	14
PCB101	260	14	6.2	2.7	0	(29)	2.6	3.6	28
PCB105	38	17	1.5	0	0	5.1	0	0	7
PCB114	2.1	0	0	0	0	0	0	0	0
PCB118	98	17	5.3	0.87	0	14	1.5	2.6	15
PCB123	0	0	0	0	0	((0.84))	0	0	0
PCB126	0	0	0	0	0	0	0	0	0
Cl6	230	14	26	(23)	0	(68)	0	0	92
PCB128	6.5	0	0	0	0	0	0	0	1.8
PCB138	26	0	1.9	0	0	((4.7))	0	0	8.1
PCB153	30	2.6	1.7	2.5	0	()5.1))	0	0	6.4
PCB156	1.8	0	0	0	0	0	0	0	1.7
PCB157	0	0	0	0	0	0	0	0	0
PCB167	0	0	0	0	0	0	0	0	0
PCB169	0	0	0	0	0	0	0	0	0
Cl7	4	140	0	77	4.8	25	0	0	(4.6)
PCB170	0	0	0	0	0	0	0	0	0
PCB180	0	9.7	0	6.3	0	0	0	0	0
PCB183	0	0	0	0	0	0	0	0	0
PCB184	0.78	0	0	0	0	((1.0))	0	0	0.65
PCB187	0	30	0	11	1.9	0	0	0	0
PCB189	0	0	0	0	0	0	0	0	0
Cl8	0	800	0	82	0	0	0	0	0
PCB195	0	0	0	0	0	0	0	0	0
Cl9	0	580	0	14	0	0	0	0	0
PCB206	0	330	0	1.2	0	0	0	0	0
PCB209	0	52	0	0	0	0	0	0	0

b) 4°C / 300 bar ng/L	A1254 MAX Value	EC MAX Value	FGI MAX Value	BHI MAX Value
tPCBs	443	5.9	134.8	361.8
Cl1–10 (Max Sum)	443	8.9	140.8	545.2
Cl1	40	0	0	40
Cl2	87	0	(110)	35
PCB8	32	0	8.7	6.4
Cl3	40	0	26	27
PCB18	16	0	12	5
PCB28	6.5	0	5.8	2.7
Cl4	200	1.8	4.8	99
PCB44	53	0	0.84	14
PCB49	15	0	0	5.3
PCB52	76	1.7	3	21
PCB66	4.4	0	0	4
PCB77	0	0	0	0
Cl5	76	5.9	0	(120)
PCB87	5	0	0	(7.9)
PCB101	8	1.1	0	(13)
PCB105	0	((0.9))	0	(9.1)
PCB114	0	0	0	((.71))
PCB118	3.7	1.1	0	(21)
PCB123	0	0	0	0
PCB126	0	0	0	0
Cl6	0	((1.2))	0	(160)
PCB128	0	0	0	(7.7)
PCB138	0	((1.2))	0	(30)
PCB153	0	0	0	(26)
PCB156	0	0	0	(5.4)
PCB157	0	0	0	(1.3)
PCB167	0	0	0	(2.1)
PCB169	0	0	0	0
Cl7	0	0	0	(59)
PCB170	0	0	0	(7.6)
PCB180	0	0	0	(9.9)
PCB183	0	0	0	(2.6)
PCB184	0			
PCB187	0			
PCB189	0			
Cl8	0			
PCB195	0			
Cl9	0			
PCB206	0			
PCB209	0			

5.2.2. Leach Rate Study Design/Approach

Before the study by George et al (2006), 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). This effort sought 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 reduced the number and types of samples to be analyzed, increased the defensibility of selected variable dependencies in the simulated environment, and also provided significant control and QA/QC of fundamental parameters.

Given these 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 deep ocean 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 release not inhibited or enhanced by external processes, attenuated only by the shipboard solid matrix itself. This design required the simulation of completely advective conditions, meaning no suppression of leaching by PCB leachate concentrations, a very conservative approach, considering that most PCB-containing shipboard materials inside the vessel hulk and would be protected from advective currents. (An evaluation of how well this simulation was accomplished is included in Subsection 5.2.5) The empirical study was limited to what is known and could be parameterized; data are evaluated in the context of the empirical study, and potential effects of shipboard material degradation were subsequently addressed in the context of uncertainty.

Secondary effects from processes such as biotic or physical degradation in natural environments are considered part of the site-specific scenario that would typically be addressed as a component or bounding assumption at the end-use/application, e.g., site characteristics for risk assessment. These degradation processes should exert only a minimal impact on the leaching behaviors of shipboard solid materials as the following analysis demonstrates.

5.2.3. Potential Degradation—Bounding Analysis

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 degrade with time to produce a porous solid. From the surface area perspective, this process is conceptually similar to producing a porous solid (envisioned as a highly localized hydrodynamically isolated assemblage of many, much smaller particulates) with an increased surface area defined by particle size. This treatment was used to estimate an effective upper bound for leach rates in a general context, using only the scalar effect of surface area, deliberately not including other possible dependencies and effects expected to be minimized under the expected reef conditions.

An effective or functional surface area dependence (see Equation 7) is used in this evaluation to provide a solution that is applicable to the hypothetical perturbation of an expected leach rate for a realistic leaching scenario under realistic artificial reef conditions instead of the conservatively biased conditions under which the leaching experiments have been initially conducted. Admittedly, the leach rate study sought to quantify leaching behaviors that are inherently dependent upon leaching surface area, although the study did not attempt to evaluate/quantify specific surface area parameters. In the leaching study timeframe, the effect of surface area on leaching was only captured as part of the measured macroscopic release of PCBs; it was not explicitly quantified. However, it is unlikely that quantitation of active leaching surface area alone would have been sufficient to adequately address potential degradation issues and related effects. Such an assessment would still require a detailed understanding of the microscopic/molecular properties of the system as a function of systematically varied leaching conditions. The elucidation of microscopic/molecular properties for PCB-containing materials was beyond the scope of this effort because the experimental approach focused on macroscopic behaviors and properties under simulated deep ocean conditions. This was part of the experimental design to provide a conservative estimate of the macroscopic physical environment in which the shipboard solid would reside by slightly overestimating the magnitude of leach rates relative to a leaching scenario in the natural environment.

An increase in surface area caused by degradation would be expected to occur largely within the material, initially starting from the outer macroscopic surface, and progressing inward at microscopic (pore) scales. For a porous solid, particularly in a hydrodynamically isolated environment such as might be expected in the bowels of a vessel (minimal or no dispersion), the fluid-filled pores of a shipboard solid would be relatively stagnant, and nearly isolated. In this scenario, transport of PCBs from newly formed degraded surface areas inside the solid would be limited by diffusion through the pore fluid in the innermost regions to the outermost regions and would eventually be advected away at the pore openings on the outer surface of the solid. It would be expected that this diffusive behavior would also inhibit and control the release and transport of PCBs diffusing through depletion of the surface layer (SASA interface) expected to form at the inner pore interfaces. Concurrently, degradation would originate at the outermost portion of the developing porous solid where the surfaces would be first and most depleted, leading to a lower magnitude leaching behavior for PCBs in exfoliated particulates. It is important to note that exfoliation is unlikely to occur spontaneously, i.e., the process of exfoliation would probably require physical damage/ perturbation to produce particulates. Ultimately, the degradation process would be expected to occur over significantly long time periods (minimally, many decades to several centuries), given the inherent resistances of xenobiotic (man-made) materials to degradation and persistence of materials such as plastics and polymers in the marine environment (Alexander, 1981; Andrady, 2000; Atlas and Bartha, 1998; Colton, Knapp, and Burns, 1974; Cundell, 1974; Gregory and Andrady, 2003; Heap and Morrell, 1968; Hetherington et al., 2005; Paustian, 1998; Pruter, 1987; The Ocean Conservatory and U.S. Environmental Protection Agency, 1993; U.S. Environmental Protection Agency, 1991b).

While the knowledge and treatment of leaching surface area is empirically limited in this study, the following is considered a realistic treatment of degradation for the available data, physical model, and site-specifics for a deep ocean environment. In this degradation scenario, the potential effects of increasing pore surface area were evaluated by considering the dynamics of a hypothetical assemblage of hydrodynamically isolated (no fluid dispersion) localized particulates. These particulates were representative of a porous degraded solid. In the absence of quantitative microscopic and molecular descriptors to accurately describe the behavior at the surfaces formed within the pores of the solid as degradation proceeds, this functional model was used to estimate an upper limit for the combined effects of the new diffusive behaviors that would be associated with a newly formed surface area in the material’s internal pores. These effects were approximated using the observed bulk macroscopic diffusive behavior (empirical leach rates) applied to the expected incremental surface area increase, over realistic degradation timeframes, to conservatively represent the upper bound for an incremental increase in macroscopic leach rate. This approach was used to represent a porous solid produced by degradative means at conditions under which properties that control microscopic inner pore structure diffusion parameters were considered very small or minimal, and thus deliberately not included (e.g., diffusion pathlength/ depletion layer, hydrodynamically isolated/minimal or no pore fluid dispersion, fluid saturation/diffusion, and magnitude of exfoliated particulate leaching).

These results are generally applicable to any shipboard solid leaching curve, and for any analyte. The underlying premise is that a shipboard solid, possessing a given leaching behavior related to the surface area defined by the seawater leachate exposure can be adjusted to reflect a-percentage 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 under the isolated/stagnant conditions described above, and an assemblage of small particles with the same total mass as one large particle will possess a higher surface area and thus potentially release at a higher rate.

It is assumed that a generic piece of shipboard solid such as FRE to be of size 1 cm x 1 cm x 1 cm, with empirically observed leach rates in units of ng PCB/g-shipboard solid-day, and that single piece of FRE is allowed to degrade into an increasingly larger number of localized hydrodynamically isolated particles (simulating a porous solid). 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 1-cm^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, 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 shipboard solid leach rate results for the example (FRE) using the analysis presented in Table 28.

Equation 7 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 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 units of active-surface area (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 28 illustrates this type of analysis to perform bounding calculations at different degradation rates (over variable degradation times, with decreased particle sizes, and/or increased particle numbers, and/or increased SASA).

Equation 7 – Surface area dependent AvgLR

$$AvgLR(implicit) = \frac{V}{\left(\frac{M_S}{SASA}\right)} \frac{[PCB]_f}{(t_f - t_i)},$$

where AvgLR(implicit) represents the inherent functional dependence on surface area and is calculated in a manner similar to Equation 5, but instead of normalizing only to mass (M_S), the AvgLR is normalized to mass per unit of seawater accessible surface area (M_S/SASA). The units in this functional form are ng PCB/(g shipboard solid/1 SASA unit)-day.

The shipboard solid FRE was used in this example because:

1. The solid tested was intact as a single piece of material
2. The material could be easily broken into smaller particles by natural processes
3. The material was less dense than other shipboard solids so it would be more likely to disentegrate over time.

For the calculations in Table 28. , the data treatment is non-dimensional (x-units), i.e., the increase in leach rate is based on a %-increase in surface area that is based on a %-decrease in particle size, and an increase in the number of particles. The treatment is mass-independent and can be applied to any shipboard solid leach rate under any experimental condition for any PCB analyte reported in this study, as the increase in leaching calculation is simply a scalar multiplier.

Table 27. (A and 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 a porous solid simulated by 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 that the degradation process is expected to take place: (1) and (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.

(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 (25°C/1 bar)	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
AvgLR [ng PCBs/g SS-day]	tPCBs	0	9.5	1.0	1.3	9.1	8.2	7.3	7.0	5.7	6.1	4.2	3.7	2.9	3.2	1.9
Case 1)	73000 days (200 years)	SA Increase Timeframe														
Additional Release AvgLR incl SA increase timeframe (x 10^{-2})		0	1.3	1.4	1.8	1.2	1.1	0.99	0.95	0.77	0.83	0.57	0.50	0.39	0.43	0.26
Case 2a)	73000 days (200 years)	SA Increase Timeframe														
Additional Release AvgLR incl SA increase timeframe (x 10^{-2})			13	14	18	13	11	10	9.6	7.8	8.4	5.8	5.1	4.0	4.4	2.6
Case 2b)	36500 days (100 years)	SA Increase Timeframe														
Additional Release AvgLR incl SA increase timeframe (x 10^{-1})		0	2.6	2.7	3. 6	2.5	2.2	2.0	1.9	1.6	1. 7	1.2	1.0	0.79	0.88	0.52
Case 2c)	18250 days (50 years)	SA Increase Timeframe														
Additional Release AvgLR incl SA increase timeframe (x 10^{-1})		0	5.2	5.5	7.1	5.0	4.5	4.0	3.8	3.1	3.3	2.3	2.0	1.6	1.8	1.0

5.2.4. Potential Effects of Biotic Processes on Leach Rates

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, before the majority of biotic processes could occur. Additionally, the influence of biotic processes is expected to 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, compared to shipboard solid degradation as demonstrated above, resulting in decreases and increases in effective PCB leach rate, but with a smaller magnitude relative to the early release.

Biological factors such as biofouling and encrustation could influence the long-term release of PCBs from shipboard solids. The laboratory leach rate study did not address such issues empirically because of inherent difficulties with experimental complexities, concerns with data interpretability, and subsequent applicability of results to site-specific reef environments. Clearly, biological factors are an uncertainty; however, one can speculate very generally about the possible effects of biological organisms on leaching, including, but not limited to the following:

- Potentially enhanced release caused by an increase in leaching surface area
- Potentially decreased leaching caused by protection of the leaching surface from seawater by marine organic/biological matter and enhanced sorption of PCBs from the aqueous phase
- Potentially decreased leaching by biological breakdown of PCB-ISM.

As an example, for antifouling paints in marine environments, a decreased leach rate caused by biofilm presence is well-documented for organometallic and inorganic contaminants leaching into seawater (Caprari, Slutzky, Pessi, and Rascio, 1986; Haslbeck et al., 2000; Mihm and Loeb, 1988; Schatzberg, 1996; Seligman et al., 2001; Thomas, Raymond, Chadwick, and Waldock, 1999; Valkirs, Seligman, Haslbeck, and Caso, 2003). Additionally, other authors have reported that PCBs can be sequestered by lipids as PCBs in water pass through membranes in cell walls of various types of microbial organisms (Kujawinski, Farrington, and Moffett, 2000). Such a process could decrease the concentration of PCBs in seawater near the leaching surface, thus potentially enhancing the release by increasing the concentration difference between the solid and seawater. Conversely, PCB sorption into an extra-cellular matrix (biopolymer) and/or organic/biological matter (e.g., previously suspended in water column) (Baier, 1984; Little, 1984; Mitchell and Kirchman, 1984; White and Benson, 1984) in intimate contact with the leaching surface could also inhibit the release. The presence of organic matter at the SASA might provide a significant diffusional barrier to direct exposure over the residence time or lifetime of the microbial population prior to the onset of higher order colonization in the macrofouling organism settlement/long-term encrustation process. Such diffusional barrier mechanisms could also contribute to decreases in PCB leach rates that might occur in a manner analogous to that commonly observed to decrease performance of antifouling coatings.

Since biotic processes leading to degradation are not instantaneous/short-term processes, as noted in the bounding analysis above, the empirical leach rates in the study timeframe should closely reflect the initial 1 to 2 years of release. Another important concern is what one chooses to use as a long-term leach rate. The long-term AvgLR could be affected by biotic or physical degradation conditions, although the magnitude of such an effect would be comparatively small as shown in Table 27.

These factors were considered during the experimental design phase and are also reflected in the suggested applicability/use of the empirical results. Specifically, it is not advisable to adopt and use an extrapolated curve leach rate value beyond ~2 years as a long-term (>>2 years) leach rate value without first performing an extrapolation of post-maximum leach rate data and evaluating a long-term endpoint at the 95% UCL and UPI. Extrapolated data beyond ~2 years should only be used to demonstrate that the statistical upper limits of regressions performed on the empirical AvgLR curves beyond their maxima either decrease or remain constant. This approach can be used to provide confidence in using a constant leach rate from the decreasing portion of the AvgLR curve or regression (1.5 to 2 years) as a reasonable maximum rate to use beyond the initial release timeframe. However, using the regression analysis results to extrapolate back to a time point before the maximum rate on the empirical curve would not be valid.

5.2.5. Shipboard Solid Sources

The selection of shipboard solids investigated in this study presented a serious technical and logistics challenge during the field sample collection phase. Most 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 were either anecdotal or historical, described materials that had already been remediated, or were for a vessel was no longer available for sampling. This reality presented the leach rate study with a unique challenge in terms of locating and collecting existing materials as source material with known quantities and PCB distributions. Ultimately, the necessary approach consisted of evaluating shipyard databases to focus on the major classes of materials in Table 3, and then attempting to collect those materials with the highest concentrations available in the inactive vessel inventory (1999), prior to imminent shipyard remedial action. As a lower concentration limit requirement, a material with sufficient PCB concentration was needed such that, given a substantial amount of time to release, PCBs could be detected in seawater leachate (e.g., thus avoiding situations where the tPCB concentration in the solid would be diluted to below detection in the laboratory leaching vessel minimum volume (1 L), even if all the PCBs came out of the solid instantaneously). This requirement generally meant that a minimum of hundreds of ppm in the solid was needed to realistically expect to see a measurable PCB concentration, below 10- to 20-ppb seawater saturation limits in leachate samples over a reasonable amount of time.

From the PCB database for the inactive fleet inventory used during the study, it was clear that finding and collecting materials with specific PCB distributions was beyond the scope of the study, as it would have required a dedicated/robust random sampling and analysis effort similar to the decades-old NAVSEA sampling program be performed in real time. Instead, the database was evaluated to identify the most common Aroclors® for the leach rate study classes of materials in the database, followed by subsequent targeted field collection events to obtain materials expected to have a similar distribution, if the materials were still available for sample collection. This approach resulted in the samples with distributions in Table 3, which when compared with the NAVSEA PCB program summary statistics in Table 2, exhibited significant overlap to effectively provided an increased confidence in a) assuming a similar distribution in shipboard solids on board other vessels, and b) applying the empirical leach rate results to those materials.

In addition to the PCB content issues in shipboard solids described above, each shipboard solid was tested in a manner designed to conservatively emulate the worst-case physical form of the solid initially on board a vessel during a typical natural leaching scenario. This means 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 are in the field sampling descriptions in Section 2 and shipboard solids descriptions in Section 3, and summarized here.

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 exposure represents only a small fraction of the cable typically on board 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. The leaching surface area to mass ratio for most EC in its native state on board a typical vessel is expected to be significantly lower than that tested in this study, resulting in a much larger empirical EC leach rate than expected on board a vessel in a realistic sunken ship environment.

Bulkhead Insulation (BHI). This sample was tested intact, without the outer lagging (painted pressboard backing), behind which, is the man-made vitreous fiber (MMVF or fiberglass) BHI material. The material as-tested was likely similar to that on board most vessels except that the as-tested sample had no paint on its outer surfaces, unlike many materials on board, which would reduce the leach rate caused by 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 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. Most BHI material in its native state on board a typical vessel is expected to have a leaching surface area to mass ratio is less than or equal to that tested in this study. The BHI empirical leach rate slightly overestimates that expected on board a vessel in a realistic sunken ship environment.

Black Rubber (BRPHL). This sample was tested intact, but unlike most materials on board vessels, without the presence of paint on its outer surfaces. The presence of outer painted surfaces would reduce the leach rate caused by sorptive processes, acting as a barrier to PCB release, and thus the leach rate study is evaluating a more conservative leach rate process. Most BRPHL material in its native state on board a typical vessel is expected to have a leaching surface area to mass ratio less than or equal to that tested in this study. The BRPHL empirical leach rate slightly overestimates that expected on board a vessel in a realistic sunken ship environment.

Paint (AP). This sample was tested in a significantly different form than what is on board 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 well beyond that found for most paints on board in a natural leaching scenario. Consequently, 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 paint flakes are 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, except for antifouling hull paint, which is not a PCB-containing material found on board Navy or commercial vessels. The leaching surface area to mass ratio for most AP in its native state on board a typical vessel is expected to be significantly lower than that tested in this study. This results in a much larger empirical AP leach rate than that expected on board a vessel in a realistic sunken ship environment.

Foam Rubber/Ensolite® (FRE). The FRE sample was basically what one would expect to find leaching in a natural environment, except 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 cut/exposed by the subsampling process. The lack of paint on >75% of the available surface allowed a conservative measurement of PCB release. Most FRE in its native state on board a typical vessel is expected to have a leaching surface area to mass ratio less than or equal to that tested in this study. The FRE empirical leach rate slightly overestimates that expected on board a vessel in a realistic sunken ship environment.

Felt (FGI). Felt gasket material is similar to other types of felt components on board vessels and in this study is the same gasket material that was protruding out of an HVAC duct flange, which was 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; it was removed from the flange and tested with most of its surfaces exposed, resulting in a more open, advective condition during the test than would be found on board a vessel in a natural leaching scenario, 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, rather than exposed instantaneously in its entirety as tested. Leaching of exposed surfaces after loss (corrosion/dissolution) of the metal flange would continue uninhibited in a manner similar to what was measured in the laboratory but any fresh surface would be small and exposed only incrementally over time. The leaching surface area to mass ratio for most of the FGI in its native state on board a typical vessel is expected to be significantly lower than that tested in this study, resulting in a much larger empirical FGI leach rate than that expected on board a vessel in a realistic sunken ship environment.

Felt (FGO). This sample, as mentioned above, is part of the same flange gasket as the tested FGI. The sample was tested essentially intact and its surface approximately 30% painted, with the remainder exposed because of the material was cut off of the intact flange during the field sample collection and subsampling event in the laboratory. The 30% painted surface probably contributed a smaller fraction to leach rate and the unpainted portion, a larger fraction. Most felt material of this type on board 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, 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 on board a vessel. The leaching surface area to mass ratio for most FGO in its native state on board a typical vessel is expected to be significantly lower than that tested in this study, resulting in a much larger empirical FGO leach rate than that expected on board a vessel in a realistic sunken ship environment.

Shipboard Solid Surface Areas. This study did not focus on evaluating the molecular properties of the interfaces each of these materials makes with seawater, probably a dynamic/changing property of each shipboard solid. However, this study did capture the resultant effect of such properties on the magnitude and variability of the leaching process by quantifying the release in each case, and with normalization to shipboard solid mass instead of surface area. From a practical (data-use) standpoint, this effort was 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 urged if using an initial surface area approach, simply because it represents only the starting surface area and not necessarily the seawater accessible surface area (SASA), a parameter likely to be dynamic temporal variable, which could increase or decrease over time.

5.2.6. Analytical Chemistry

The choice to use homolog 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 homolog 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. Detailed uncertainty and confidence issues concerned with the analytical chemistry methods is provided in the QA/QC sections of Appendix C, including data quality objectives (DQO), in addition to analytical chemistry-related subsections included in Section 2 and standard laboratory operations/methods described in Appendix B.

In general, analytical data quality exceeded DQOs 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, one could have performed experiments longer in an attempt to perhaps observe leaching for analytes that were never detected in this study. However, one must know very precisely and at very low or trace levels, what is present in and on the leachable surfaces of the solid source materials and 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, and it was beyond the study scope to determine what molecular level composition was present at each shipboard solid interface (SASA), which was likely changing with time, as noted in the shipboard solid discussion above.

As can be seen in Table 3, all Aroclors® in all shipboard solids did not have a corresponding analytical (Aroclor®) control. Evaluating the dissolution behavior under the leaching conditions for all possible neat Aroclors® as analytical controls was beyond the scope of this study. As a result (as noted in Table 11 for each shipboard solid), an analyte was occasionally detected for a shipboard solid leaching experiment, but a corresponding measure of that analyte in seawater from Aroclor® analytical control was unavailable for comparison. These compounds usually only made up a small fraction of the PCBs quantified. For reasons of scope, this study was unable to examine every possible perturbation of Aroclor® loading possibilities. For similar reasons, samples occasionally did not have corresponding Aroclor® analyte maxima against which to compare to evaluate the Aroclor® analyte. The impact of this was minimal because many other lower incremental leaching sample concentration data were collected during the leaching experiment. Regardless, in these rare instances, the analyte maxima in those samples must be interpreted as a possibility (not certainty) that it may have potentially been influenced somewhat by possible saturation conditions. In general, these cases occurred earlier rather than later in the leaching process for a given experiment, exerting minimal impact on long-term leach rates at the curve endpoint or extrapolation beyond empirical data. Furthermore, while steps were taken to avoid the release of PCB-rich shipboard solid particulates into the leachate, it is possible, though not probable, that an occasional very small particle made it through the glass fiber filter and SS 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 relates to availability of PCB analytes at the seawater interface (SASA), as briefly described below.

5.2.7. Leach Rate Data/Results

Leachate Saturation. With few exceptions, all shipboard solid PCB leachate concentration maxima were lower compared with Aroclor® analytical controls (see Table 11). For the non-Aroclor® analyte maxima, the shipboard solid interface (SASA) could probably release more of that particular PCB than the A1254 or A1268 matrix. Unfortunately, without more detailed information about the interfacial PCB compositions of shipboard solids, vice assuming that it is composed 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 leaching maxima can be considered the effective saturation limit in seawater for each analyte. Other concentrations for analytes across the experimental series were below that maximum and still comprise a valid leach rate dataset.

Sampling Interval. Maintaining a non-saturated condition was a primary component of the study approach, which ensured that leaching results reflect a truly uninhibited release process. The sampling time was also a critical variable in the leaching studies. This variable 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 leach rates could be determines was entirely dependent on the rate of release from the solid, with the result that the time intervals in the leaching experiments were large and not truly differential. This relatively large time interval was out of necessity, 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 (resulting in 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, instead of 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 much lower detection limits to observe potentially lower magnitude release in a shorter time, and the sampling interval might have been minimized further within similar criteria. Regardless, the 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 (faster/slower) leaching that could be occurring within each sampling/leaching interval. AvgLR, as described by Equation 5, captures the total behavior and is numerically correct, reflecting an average change in concentration over a time-period interval, Δt. As mentioned above, the underlying issue is one of time resolution. This calculation is numerically dependent on t_f and t_i, and defines an average for any value of Δt. It does not provide any information about instantaneous values of leach rate within the time-period; however, the sum of all instantaneous rates within the time-period must equal the average rate defined by Equation 5. While it is correct to consider this AvgLR a low-resolution value, it is not an underestimation. The AvgLR can be composed of low and high values within the sampling interval that must sum to the AvgLR.

Adsorption Loss. The leach rate study was designed to avoid PCB adsorption on leaching vessel walls using weekly leaching vessel exchange. PCB adsorption is a function of the concentration of PCBs in the glass container and the condition of the inner surfaces of the glass bottles used, which were cleaned to full EPA cleaning and quality assurance standards to include custody seals and labeled with lot number for traceability to certificate of analysis. Because adsorption was intentionally minimized in the experimental approach, only an insignificant level of adsorption would occur in the bottles, and as a result, the analysis of used leaching vessels would probably fall below the limits of detection. To verify this, leaching vessels were selected for analysis from each solid leaching experiment based on high concentration in the leaching vessel during that leaching experiment. The intent was to apply corrections for adsorption to the experiments by using these results. This approach did not yield detectable levels of PCBs analyzed over a range of concentration values observed in the leachate solutions. These results are included in Appendix C and provide confidence in earlier predictions that it would be difficult to even detect adsorbed PCBs at such low levels in leaching vessels, which contained PCB concentrations in ASW significantly below saturation.

While it is probable that loss caused by PCB adsorption on leaching vessel walls was insignificant during the experiments, based on the empirical data described above, supplementary data for PCBs detected in similarly selected leaching vessels during Aroclor® dissolution experiments were evaluated to estimate the amount of adsorption. This approach significantly over-predicted adsorption values on shipboard solid leaching vessel walls for which PCBs were not detected. Similarly, using ½ MDL as an alternate approach led to even higher over-predictions.

The prediction of unrealistic estimated values for both of these approaches is likely related to the approximation of an adsorption factor (mass-adsorbed/PCB concentration in seawater) assuming a linear rather than nonlinear dependence on seawater PCB concentration. Figure 82 illustrates the observed adsorption behavior graphically, showing that adsorption was only detectable at very high PCB concentrations in leachate, significantly higher than the levels measured in shipboard solid leaching experiments. At the much lower concentrations typically observed for shipboard solid leachate (e.g., <10^3 ng/L), an insignificant level of adsorption (at or below detection limits) would be expected.

As shown in Figure 82, the leaching vessel analysis for FGI, also shown in red, is an artifact associated with source material, i.e., corresponds to the source material distribution (homologs Cl7 – Cl9) rather than the corresponding leachate distribution (homologs Cl2–Cl7). The predominant homolog distributions found in other leaching vessel analyses are composed of homologs Cl2–Cl7. Adsorption values indicated above for shipboard solid leaching vessels and the Aroclor® 1268 leaching vessel were derived from sample-specific minimum detection limits in those analyses. Most shipboard solid leaching vessels in the leach rate study were exposed to concentrations below 1,000 ng/L, where adsorption was not detected on leaching vessel walls and is estimated to be minimal.

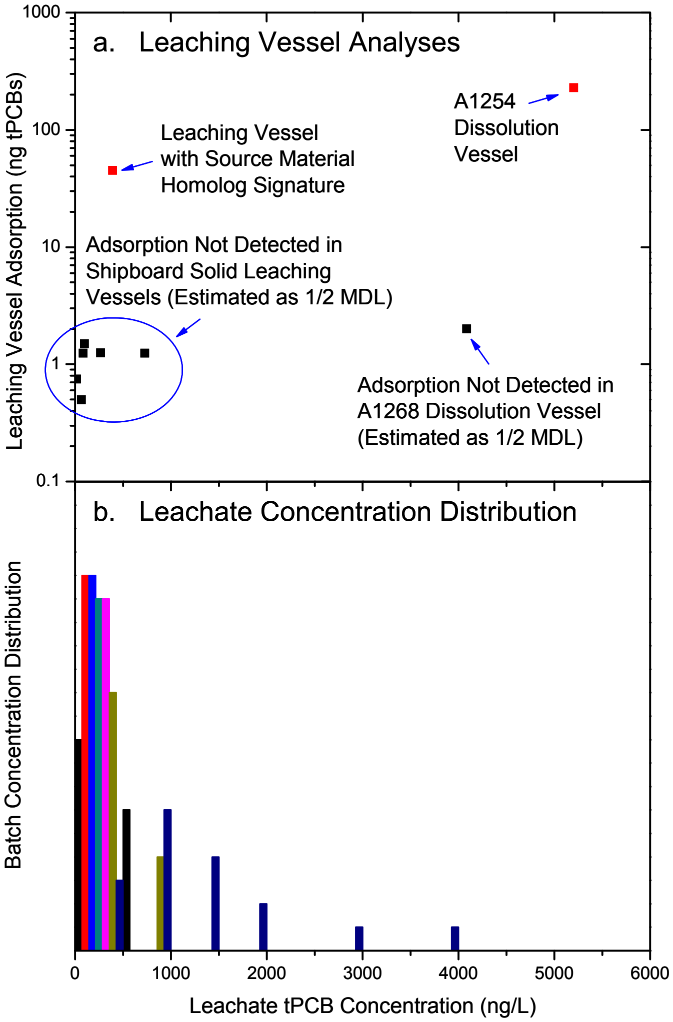

Figure 82. (a) PCB mass associated with leaching vessel walls as a function of leachate concentration, and (b) leachate concentration distribution across all shipboard solid leaching experiments. The Aroclor® 1254 dissolution vessel analysis in (a) provided the only measure of adsorbed PCBs above detection limits, but at significantly higher leachate concentrations than typical leachate concentrations for shipboard solid leaching vessels.

Replicate Leaching Results. The leaching curves are unique results for each solid and do not represent a statistical result in the sense of replicate experiments and analyses to provide statistics (error bars) on each leach rate data point (beyond only the expected variance in analytical precision, as demonstrated in the raw concentration data evaluation). It is improbable that such a set of experiments could provide results considered interpretable, simply because commonality in PCB source content is insufficient, even within a given solid sample (subsamples of a field sample have been generally shown to contain very different concentrations and distributions of PCBs/Aroclors®). However, subsamples of the same solids, tested at low (4°C) and high (25°C) temperature, as described in subsection 5.1.1, and presented in Appendix E, were qualitatively similar. Further analyses of these low-temperature data are discussed below to address the issue of replicate leaching samples at either temperature (4 or 25 °C). Low-temperature leaching results at 4°C were corrected for temperature and compared to results at 25 °C to provide confidence that quantitative results are sufficiently representative. This evaluation is based on enthalpy of solution data from the literature to correct for temperature effects on dissolution properties (Dickhut, Anders, and Armstrong, 1986) and uses the integrated form of the van't Hoff equation for dilute solutions (Equation 8), which can be used to calculate the concentration of a soluble chemical species (e.g., a PCB congener) at a given temperature.

Equation 8 – van't Hoff equation for dilute solutions

$$\Delta H_{ss} = RT(C - \ln(x)),$$

where ΔH_{ss} is the enthalpy of solution of the solid, C is an experimentally determined integration constant, x is concentration, T is temperature, and R is the universal gas constant. Requirements for using this approach included identifying a PCB congener, for which ΔH_{ss} and C were known/reported, and that was consistently detected in most of the leaching experiments for all shipboard solids at both temperatures. Fortunately, a congener was identified (one of the few noted), PCB101 (2,2',4,5,5'-pentachlorobiphenyl), that met all of these requirements. Using temperature-dependent solubility parameters for PCB101, in which C was experimentally determined to be −8.0159, and ΔH_{ss} determined to be 31.9 kJ/mol, the respective concentrations for each of the leaching temperatures (4 °C and 25 °C) were calculated. The ratio of these (4 °C concentration to 25 °C concentration) was then used to initially correct for the temperature dependence of the dissolution component in the 4°C A1254 dissolution curve, which is the experiment in the leach rate study that should bear a close similarity to a solubility study.

The result provided a very good correspondence upon comparison to the 25 °C curve for A1254. Similarly, this approach was then used to correct the 4 °C EC (electrical cable) experiment, and it compared well with EC at 25 °C. By assuming that the behavior of PCB101 was representative of the other congeners in the pentachlorobiphenyl homolog group and similar corrections were performed for the congener and the homolog leach rate curves for A1254 and EC at 4 °C and compared them with the A1254 and EC curves at 25°C. All of these results described for A1254 and EC are included in Appendix E for comparison, in addition to similar corrections and comparisons of leaching results for other shipboard solid materials and Aroclor® 1268 (A1268) at 4 °C.

While this approach probably cannot be extrapolated to the other homologs in each sample, the data treatment and close correspondence between temperature-corrected 4 °C and the corresponding empirical 25 °C curves provide a reasonable level of confidence in using the empirical leach rate study results to represent mass release for materials onboard a vessel.

Leaching Nondetection. Ultimately, regression analyses performed on leach rate curves can be 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 maxima or the statistical means and standard deviations in the observed empirical leach rates can provide an estimation of the release and perhaps the variance in the data. Additionally, for leaching behavior non-detect (ND) data, evaluated in the study as part of the regression approach and homolog data quality analysis, were treated conservatively. Specifically, ND data (reported as zero) were not included in leach rate calculations or plots, and should not be used in regression analyses, as described below.

Throughout the leach rate study, at times, for all of the materials leached, concentration data were encountered that were intermittent, that is, release was detected in one leaching interval, then not detected in the subsequent interval, then detected again in the following interval. Occasionally, the non-detection would remain a non-detect for several leaching intervals and then a detection, then nothing for the remainder of the experiment, and so on. Certainly, these observed behaviors make the data credible, i.e., if the study had always detected every analyte, it may have not appeared believable. However, this issue was evaluated as part of data quality analyses performed on all of the concentration data collected, realizing that because a process was being measured, the concept of data distribution should be in the context of variability around a given behavioral pattern or trend (i.e., leaching curve) rather than a distribution in samples randomly collected in the environment from contaminated sites, for example.

In environmental sample analyses, a standard method of treating nondetects as ½ MDL, while perhaps applicable, needs to be applied in the context of a behavioral trend represented by a leaching curve, as PCBs are diffusively transported from a region of high concentration to a region of low concentration in the shipboard solid, and then dispersed in the external fluid medium. This type of treatment was relatively straightforward for PCB congeners, but laborious for treatment of homolog data, which were quantified as the sum of all detectable congeners within a homolog group. An example of such a homolog evaluation was included in the SW-LRS (George et al (2006)). Essentially, during that evaluation, it was demonstrated that relatively few cases existed where the detection of homolog data was significantly low enough to be classified as an uncertainty issue, and in those cases, omitting a low value was more conservative than including a value based on MDL, which would have resulted in a lower magnitude leaching curve regression. In several cases, where data for regression analyses was insufficient, a significant number of nondetect values could have been replaced with values based on MDL, but in such cases, the validity of the curve itself was in question for evaluation in context (where no behavioral trend really existed). Ultimately, the maximum leach rate can be used as a conservative measure, negating the need for having MDL-based values assigned for nondetects. The overall result of this approach is a bias towards a more conservative rate, which in the case of regression analyses, effectively interpolates across regions where nondetects occur in the leaching curves. Furthermore, in scenarios where release was not observed, assigning MDL-based values to the homolog group is considered invalid for use in modeling release from a vessel because such an approach arbitrarily assumes a low constant level of release.

5.2.8. Alternative Uses of Leach Rate Data

A detailed analysis and description of confidence, limitations, assumptions, and uncertainties associated with using these leach rate data to describe the source component in a vessel-sinking scenario is best described by using the example vessel (the ex-Lawe) discussed in Subsection 5.3. However, providing broad, general guidance on what the data ultimately represent is also prudent because situations may arise where the data are being evaluated/explored for another use. Examples 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 needed to estimate what the release could be as a worst-case scenario. For this reason, one must know or obtain information on PCB content (concentration and type of PCBs) for the source material in question. Once this information 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 method is only valid under certain circumstances, one of which is described for the example vessel. The primary caveat is that the type of material must possess similar physico-chemical properties. In particular, using Aroclor® results to rationalize the mechanism or model the complete leaching behavior of an inert solid material containing PCBs is invalid because the Aroclor® matrix, even if it is a solid or semi-solid material, is not inert to dissolution in seawater. 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.

5.2.9. Leach Rate Data Regression Uncertainty

Understanding and describing the uncertainties associated with the use of (1) empirical leach rates, (2) statistical means of empirical leach rates, or (3) leach rates calculated using regression analysis results is also important. 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 where the confidence in the regression value is significantly lower than using the empirical data, even to the point of an unacceptable confidence level. These approaches should be evaluated on a case-by-case basis and the user should verify that the decision to use any particular approach can be rationalized in some reasonable, defensible manner.

In general, for analytes exhibiting stable leaching curves, the final empirical leach rate should be used unless it is shown to be outside of an extrapolated regression curve with sufficient statistical confidence as was illustrated in the SW-LRS (George et al., 2006). A 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., $\leq$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 perform 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 support a regression analysis.

Unless the data are used to fit a model over the entire time course of the experiment regression analysis results are only applicable to calculating a post-maximum leach rate, as regression analyses for the decreasing portion of leach rate curves are not statistically related to points on an empirical leach rate curve prio to the maximum leach rate. In cases where a regression value is selected as a long-term leach rate, it is advisable to compare that value to the upper prediction interval (UPI) of the regression analysis to ensure that the selected value is greater than or equal to it and that the p-value for the regression is of high predictive power. This defensible approach will ensure the use of a conservative value in which one can place a high degree of confidence.

5.3. RECOMMENDATIONS FOR USING LEACH RATE DATA

The leaching data and leach rates presented in this work are useful for 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., leaching for a shallow artificial reef or deep ocean environment. The portion of a given leaching curve to use as a source term in such a model depends on what assumptions are considered reasonable within the risk assessment framework used. However, to help illustrate the process of choosing and using leach rate data such as presented in this report, an example evaluation previously reported for potential sinking of a vessel as an artificial reef in shallow water (George et al., 2006) is included here for demonstration purposes. This example uses the regression analysis approach described above and compares that to using the long-term empirical leach rate (endpoint) as the PCB source release to model the time to depletion for a decommissioned U.S. Navy vessel, the ex-William C. Lawe (NavSource Online Destroyer Photo Archive, 2006e). This vessel was the subject of a report prepared for NAVSEA, in which PCBs-ISM were thoroughly evaluated to provide source information (PCBs-ISM on board) 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 intense oceanographic and environmental sampling effort for subsequent risk assessments.[6] The ex-Lawe, although not the typical type of vessel used for artificial reef-building, was used as a surrogate reef vessel and considered a valid approach from the PCB leaching perspective, considering that the same types of PCBs-ISM evaluated in this study were found on board the ex-Lawe. The total estimated amount of each type of PCBs-ISM on board (JJMA, 1998) will be used to demonstrate how one would apply 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 used to varying degrees of complexity, depending on 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 was used in the prospective risk assessement model (PRAM), as part of the human health and ecological risk assessment for the ex-Oriskany [NEHC, 2003b; Johnston et al., 2005]), as part of in the U.S. Navy's Artificial Reef program. The former approach, using only the final empirical leach rate for each shipboard solid over the entire risk assessment timeframe, was originally used in a screening ecological risk assessment (Johnston et al., 2005.) with the ex-Agerholm as a surrogate reef-vessel. The constant average leach rates for such an approach was reported(George et al., 2006) and is reproduced here in Table 29A as the "(b) Long-term" column of values for use in the ex-Lawe mass loading example. In that report, extrapolated leach rate curves supported this choice of long-term upper limit leach rate by demonstrating that the leach rates do appear to continue decreasing with time. Table 29 also summarizes those reported data for the case where the empirical leach rate (a) applies over the shipboard solid-specific experimental leaching timeframe, and the long-term upper limit (b) applies over the remaining timeframe of interest.

In Table 29B, the quantities and high estimates for PCB concentrations of each shipboard solid are adopted from the ex-Lawe report, and the leach rates for the materials tested at 25 ^{o}C/1 bar were used to calculate depletion times. For this shallow water sinking scenario, note that the leaching amounts and times to depletion for each solid are much different because of the very different amounts of each material onboard and with varied concentrations. This leads 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-releasing 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. In this scenario, all PCBs are assumed to be mobile and leach in their entirety. This is very conservative, as it is highly likely that some PCBs in the solid would remain permanently bound within the solid matrix. As previously stated, the neat Aroclor® dissolution 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 risk assessment for a hypothetical sinking of the ex-Lawe as a reef at a shallow-water site. If we were to model a hypothetical sinking of this vessel in a deep ocean environment, we would use the leach rate data reported in Section 4 of this study for materials tested at 4 ^{o}C/1 bar or 4 ^{o}C/300 bar, and develop a similar table to be used as the source release term.

Alternatively, regression results could be derived from 4 ^{o}C/1 bar or 4 ^{o}C/300 bar leach rate curves and used to support using a constant long-term leach rate value for regression analyses of PCBs that indicate leach rates will continue to decrease. In general, the leach rate behaviors in this study can be described in a manner similar to that previously reported (George et al., 2006), i.e. by the power function in Equation 9, where y is the average leach rate and x is time. The leach rate data are subsequently fit using the logarithmic form of this power function (in "y = mx + b" form), shown in Equation 10.

Equation 9 – Power function

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

Equation 10 – Logarithmic power function

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

The tail or decreasing portion of the leach rate curves can be plotted on a log-log scale, for which a linear regression can then be performed (only on data points at leaching times beyond and including the observed curve maximum).

If regression analyses are used, it is suggested that an approach similar to how experimental leaching results were treated in Table 29, "(a) Empirical," be used for the source release over the short-term (experimental) leaching period, beyond which, functions derived from regression analyses could be used for estimating the long-term source parameter, or to support using the final empirical value as a conservative upper limit leach rate.

Further, the use of regression functions should 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 very long-term extrapolation endpoints (times). Because of this, it is highly recommended that the more conservative, upper prediction interval curve/data be used at such endpoints if this approach is chosen. In cases where the predicted upper limit (prediction interval) is nearly equivalent to the final empirical data value, the curve-fit is most useful in providing confidence in using the final empirical leach rate value as a long-term upper limit leach rate.

Table 28. (A and 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 a porous solid simulated by 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 that the degradation process is expected to take place: (1) and (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.

(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	

(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 homologs)	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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14. ABSTRACT

The deep ocean simulated leaching provided empirical data that are useful for characterizing the time- and temperature-dependent leaching behaviors of PCBs from different shipboard solid materials under physical and chemical conditions similar to a deep ocean (SINKEX) environment. In addition, the deep ocean experiments provided additional information on the effect of pressure and temperature on PCBs leaching from PCB-ISM in the marine environment. The acceptable leach rate source term in the context of a release and exposure model for risk assessment depends on what assumptions are considered reasonable within the appropriate risk assessment framework. Shipboard solid-specific leach rate data provides a means of estimating the releases from shipboard sources that can range from (1) assuming a single, mean leach rate over the entire period of time to (2) using the leaching curves for the empirical release, followed by a long-term leach rate, as an extrapolated (changing) rate based on the leaching curve, or an assumed constant rate as an upper limit (conservative case). The regression analysis and extrapolated curves reported in George et al. (2006) are examples of using a long-term leach rate described in (2) by demonstrating that leach rates continued to decrease with time. Alternatively, the regression analysis itself can be used as a source term function to predict a continued decreasing release. In general, the empirical leaching results can be used to characterize the early release beyond which, empirical curve endpoints or regression functions from curve analyses can be used for estimating a long-term source parameter or to support using a conservative constant leach rate. Furthermore, the use of regression functions should 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). Thus, it is recommend that the statistically-derived upper prediction interval curve data be used at such endpoints if this approach is chosen.

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