PCBs in Caulk:
Evaluation of Mitigation Methods and Source Characterization

Final Draft Research Plan

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National Risk Management Research Laboratory
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1. BACKGROUND

In recent years, EPA has learned that caulk containing potentially harmful polychlorinated biphenyls (PCBs) was used in many buildings, including schools, in the 1950s through the 1970s. In response to concerns about the public health impacts of PCBs in buildings, EPA announced on September 25, 2009 a series of steps that building owners and school administrators should take to reduce exposure to PCBs that may be found in caulk in many buildings constructed or renovated between 1950 and 1978. EPA also announced that it would conduct new research to better understand the risks posed by caulk containing PCBs. This research will guide EPA in making further recommendations on long-term measures to minimize exposure as well as steps to prioritize and carry out actions to remove the caulk to better protect public health. Specifically, the EPA National Exposure Research Laboratory (NERL) and National Risk Management Research Laboratory (NRMRL) have been charged to conduct research in the following areas:

- Characterize potential sources of PCB exposures in schools (caulk and other materials).
- Investigate the relationship of these sources to PCB concentrations in air, dust, and soil.
- Evaluate mitigation methods to reduce exposures to PCBs in caulk and other sources.

This document describes NRMRL's research plan for evaluating mitigation methods and characterizing PCB sources.

2. RESEARCH OBJECTIVES

This study has two major objectives: (i) support the development of risk reducing strategies and decision-making tools by evaluating the mitigation measures that reduce or eliminate available PCBs on building surfaces and, consequently, in indoor air and dust, and (ii) support exposure/risk assessment for PCBs in schools by characterizing PCB sources to better understand the transport and distribution of PCBs in buildings.

3. STUDY SUMMARY

3.1 Research Tasks

NRMRL's research effort consists of two tasks and six subtasks, as summarized in Table 1.

Table 1. NRMRL Research Tasks

Task	Title	Subtask
1	Evaluation of mitigation methods to support risk management decision-making for PCBs in schools	1.1 PCB Encapsulation
		1.2 Evaluation of NASA's activated metal treatment system (AMTS) for PCB destruction
		1.3 Review of mitigation methods for PCBs in buildings
2	Source characterization to support exposure/risk assessment for PCBs in schools	2.1 PCB off-gassing from primary and secondary sources
		2.2 PCB partition among indoor media
		2.3 PCB migration from sources to house dust

3.2 Investigators

Researchers and staff members for this study include:

NRMRL

Zhishi Guo	Team leader, co-principal investigator
James Jetter	Principal investigator for evaluation of mitigation methods
Xiaoyu Liu	Principal investigator for source characterization
Kenneth Krebs	Chemist
Robert Wright	QA officer
Ivan Dolgov	Laboratory technician
Dale Greenwell	Laboratory technician

NERL

Kent Thomas	Collaborating investigator

ARCADIS (in-house contractor for laboratory support)

Nancy Roache	Environmental scientist and task manager
Andrew Stinson	Chemist
Corey Mocka	Laboratory technician

3.3 Study Limitations

ORD is directed to complete this study in 18 months including reporting, data quality review and peer review. One key factor for the encapsulation study is to determine how the encapsulating capability deteriorates over time, which can be done under either natural or accelerated weathering (i.e., aging) conditions. Because of the time limitation, the encapsulants can only be tested under accelerated aging conditions (i.e., intense UV irradiation, elevated temperature, and perhaps the

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presence of ozone). A disadvantage of accelerated weathering is that only rough correlations with actual indoor or outdoor weathering are possible due to multiple variables. However, accelerated weathering is suitable for comparing encapsulant durability in relative terms [1].

Because of the time limitation and legal issues related to testing encapsulants in occupied buildings, the encapsulation study is limited to laboratory experiments only. We will make recommendations to the agency after the completion of this study on the needs for further investigation including field testing.

The mitigation study will review available mitigation methods and provide recommendations on the usefulness, applicability, and feasibility of different mitigation methods. The results will support the development of guidelines and decision-making tools. However, it is not the goal of this study to write mitigation guidelines or develop decision-making tools.

PCB transfer from sources (caulk and contaminated building materials) to house dust is an important factor for human exposure. There are three mechanisms that may lead to pollutant migration from the source to dust: (i) evaporation and subsequent partitioning, (ii) direct partitioning on source surfaces, and (iii) dust generation due to abrasion on source surfaces [2]. This study will investigate the first two mechanisms. The third mechanism will not be investigated because the dust generation rate due to abrasion is difficult to determine in quantitative terms.

4. EVALUATION OF MITIGATION METHODS TO SUPPORT RISK MANAGEMENT DECISION-MAKING FOR PCBS IN SCHOOLS (TASK 1)

4.1 Introduction

An EPA fact sheet provides the following guidance under Cleanup Requirements [3]:

> "Caulk containing PCBs at levels > 50 ppm is not authorized for use under the PCB regulations and must be removed. Caulk containing PCBs at levels < 50 ppm may remain in place. PCBs in caulk are known to contaminate adjacent building material (e.g. masonry, wood, concrete) and soil surrounding the building. Therefore, any surrounding building material that is contaminated by > 50 ppm PCB-containing caulk, such as through leaching of PCBs is considered PCB remediation waste and must be cleaned up using 40 CFR § 761.61. Safely removing the PCB-containing caulk, while preventing further contamination and cleaning up surrounding materials, should be the focus of cleanup projects."

Although various mitigation measures have been applied to PCBs in schools and other types of buildings, these measures have not been thoroughly tested, and further evaluation is needed. This study attempts to address the following science question: *What is the performance and cost effectiveness of various mitigation measures for reducing availability of PCBs from caulk in contaminated buildings?*

Preliminary exposure analysis by NERL indicates that inhalation, dermal contact, and ingestion all may be important routes of exposure to PCBs (internal communications). Thus, further exposure analysis by NERL will inform and direct mitigation efforts by NRMRL.

4.2 Evaluation of PCB Encapsulation Methods (Subtask 1.1)

4.2.1 Technical Approach

Encapsulation is one of the commonly used methods for mitigation. It has been used for lead paint, asbestos, indoor contamination associated with clandestine methamphetamine manufacturing and, more recently, PCB contamination in buildings. The ability to encapsulate PCBs in contaminated building materials may lead to reduced human exposure for building occupants while awaiting ultimate removal of PCB-contaminated materials consistent with regulatory requirements. Because of the widespread use of PCB caulk in the 1950s through the 1970s, the cost for complete removal of the sources from the existing building stock in the U.S. is high. One estimate puts the cleanup cost at $150 to $200 billion [4]. Thus, encapsulation may provide a short-term solution to protecting building occupants and give building owners more time to find permanent solutions.

This study will take a two-step approach: (i) conduct fast screening tests for a wide range of coating materials and application methods to identify the most promising coatings and application methods for further evaluation, and (ii) conduct more rigorous testing for several of the most promising coating materials and methods. These evaluation methods are fully described below.

Performance evaluation will be based on short- and long-term encapsulation abilities, cost, and feasibility for use in schools.

4.2.2 Selection of PCB Congeners or Aroclors

This evaluation of encapsulation will be based primarily on individual congeners. At least 15 PCB congeners commonly found in the caulk samples will be included for encapsulation evaluation. Aroclors will be considered as a secondary measure. Selection of PCB congeners or Aroclors will be determined by analyzing caulk samples obtained from the field and by considering the following factors:

- Congeners specific to the common Aroclor formulation.
- Congeners with wide range of boiling points and different structures (e.g., #Cls = 1 to 8).
- Congeners' toxicity (e.g., World Health Organization identified 12 dioxin-like congeners).
- Consideration for analytical complexities (e.g., coelusion).

To minimize generation of PCB wastes, PCB surrogates will be used to develop screening test methods.

4.2.3 Screening Tests

Summary

At least ten coating systems will be evaluated for (i) ability to resist migration of PCBs and (ii) cost per square meter of application area. Coating types will include epoxy, acrylic, polyurethane, polyurea, oil-base, and latex.

Coating systems will be evaluated for (i) ability to resist migration of PCBs as follows. Known concentrations of specific PCB congeners or surrogates will be mixed with an oil-base primer. The primer will be applied to aluminum sheets using a precision applicator to maintain a uniform dry-film thickness. Test coatings will be applied over the primer following manufacturer instructions for application. Half of these test specimens will be aged in an accelerated weathering chamber. The accelerated weathering chamber will be operated at a 340 nm irradiance of 0.89 W/(m^2·nm) at a temperature of 60 ± 2.5 ºC, and the appropriate test duration will be estimated according to Equation 1:

$$ D_E = D_C \, \frac{I_C}{I_0} \times 2^{\left(\frac{T_C - T_0}{10} \right)} \tag{1} $$

where D_E = equivalent aging duration under natural environmental conditions (days),
D_c = aging (weathering) duration in the weathering chamber (days),
I_C = total irradiation energy in the weathering chamber (J/m^2/day),
I_0 = average total irradiation energy under natural environmental conditions (J/m^2/day),
T_C = temperature in the weathering chamber (°C),
T_0 = temperature inside buildings (°C).

Equation 1 assumes that the rate of material degradation is proportional to the intensity of UV irradiance and that the degradation rate doubles when the temperature increases by 10 °C.

At least three replicate test specimens will be prepared for each coating system and aging condition. Wipe sampling, on specimens with and without weathering, will be used to measure PCB/surrogate concentrations on the surfaces of the test coatings. A milling machine will be used to remove approximately 2 mils (0.05 mm) thickness of the test coatings, and the milled material will be analyzed for bulk PCB/surrogate concentration. Concentrations of PCBs/surrogates in wipe samples and milled samples will be measured to indicate the test coatings' resistance to migration of PCBs.

Coating systems with an indicated resistance to migration of PCBs will be evaluated for (ii) cost per square meter of application area as follows. Typical ranges of costs will be estimated for each coating system evaluated. Costs will include primer, coating, surface preparation, application, finishing, and any other special requirements. The service life for each coating system will be considered based on existing data.

Note: In the initial screening tests, coating systems will be tested on PCB-containing paint applied to metal sheets. Although this substrate is not the same as substrates found in the field, it has many advantages. The metal sheets can be easily mounted in an accelerated weathering chamber. The PCB-containing paint will have known concentrations of specific PCB congeners. The test substrates will be identical, and will enable good comparison of performance among test coatings. The test substrates will use minimum amounts of PCBs and will minimize PCB waste."

Coating Materials and Application Methods

At least ten coating systems will be selected for screen testing their encapsulating capability according to the following criteria:

- Selected coatings represent a variety of binder systems such as epoxy, acrylic, silicone, one- and two-component polyurethane, polyurea, alkyd, and latex.
- Selected coatings are commercially available "off the shelf" products.
- Selected coatings are suitable for the substrates of concern.
- A coating may be selected if it has been advertised as a PCB encapsulant, or used in the field as a PCB encapsulant, or used as an encapsulant for other contaminants (e.g., lead, asbestos, and methamphetamines).

Application methods (as recommended by manufacturers for each product tested) may include:

- Surface preparation techniques.
- Spray-on versus roller.
- Single coat versus multiple coats.
- Combination of coating materials (e.g., primer + paint).
- Curing methods (e.g., duration between two applications).

Evaluation Criteria

The ability of a coating material/application method to encapsulate PCBs will be evaluated based on one or more of the following methods:

- Wipe sampling.
- Migration of PCBs or surrogates into coatings (milling sampling method).
- Alternative extraction (leaching out) tests.

Evaluation Methods

Screening tests for coatings will be conducted by using a standard PCB source with the following characteristics:

- Has known PCB congeners and/or surrogates.
- Has known PCB/surrogate concentrations.
- PCBs/surrogates are uniformly distributed in the source.

- Can create many identical samples for testing.
- Can create large surface area for coating application and surface sampling.
- Needs minimum amounts of PCBs to develop.
- Relatively convenient for waste disposal.

A standard PCB source will be prepared as follows:

- Mix a known quantity of PCB congeners or surrogates with an oil-base primer that will be used as a standard source. Test the PCB content in the primer before mixing to ensure PCB content is below the level of quantification.
- Mix a known quantity of PCB congeners and/or surrogates (to be determined) in oil-based primer to obtain a concentration of at least 100 ppm for each congener/surrogate.
- Apply the PCB (or surrogate)-containing primer to an aluminum or stainless steel sheet designed to fit the sample holders in the QUV accelerated weathering chamber.
- Apply the PCB (or surrogate)-containing primer to an aluminum or stainless steel sheet using a 3-inch wide, precision wet-film applicator to produce a dry film thickness of 2 mils (≈ 0.05 mm).
- Allow the primer to dry for 24 hours.

The main goal of the screen testing is to determine how well they can resist PCB penetration through the encapsulant film with and without accelerated aging. Thus, difference in physical properties between oil paint and caulk is not a key factor because the PCB availability on the source surface is the only parameter that matters.

Each coating (from list above) and application method (recommended by manufacturer for each product tested) will be screened using the standard PCB source as follows:

- Test coatings will be applied over the standard source (primer) following the coating manufacturer's instructions.
- Test coatings will be tested with or without primers/sealers specified by the manufacturers
- Application methods may include spraying, rolling, or brushing.
- Coatings will be applied to provide a dry-film thickness of at least 4 mils.
- Test coatings will be allowed to dry following manufacturer's instructions.
- Make 7 (6 specimens required, 1 extra) test specimens for each coating evaluated with the wipe method, described below.
- Make 7 (6 specimens required, 1 extra) test specimens for each coating evaluated with the milling method, described below.

Accelerated weathering of test coatings:

The purpose of accelerated weathering tests is to evaluate coating systems in a relatively short period of time under artificial conditions (elevated temperature and exposure to UV light and ozone) that simulate real conditions that may cause failure of the coating systems over a longer period of time. The accelerated weathering tests will be conducted at elevated temperatures, and this is expected to have a larger effect on PCB migration through the coatings than ultraviolet light

exposure. The UV light exposure is expected to have a larger effect on deterioration of some coatings.

- Test specimens (three for each coating evaluated) will be placed in the QUV accelerated weathering chamber.
- Two field blanks will be placed in the QUV accelerated weathering chamber with each batch of test specimens. Evaluation of field blanks will indicate if any cross-contamination occurs due to volatilization of PCBs.
- The QUV accelerated weathering chamber will be operated without water/mist to avoid cross-contamination between samples.
- The accelerated weathering chamber will be operated at a 340 nm irradiance of 0.89 $W/(m^2 \cdot nm)$ at a temperature of 60 ± 2.5 ºC, and the appropriate test duration will be experimentally determined. Test conditions are based on ASTM D 4587-05 Standard Practice for Fluorescent UV-Condensation Exposures of Paint and Related Coatings, Table 1, Cycle Number 2. Regarding Cycle Number 2, ASTM D 4587-05 states: "Historical convention has established this as a very commonly used test cycle."
- The UV light exposure area for specimen is 2.50" (6.35 cm) x 3.75" (9.52 cm) = 9.37 in^2 (60.5 cm^2).

The following weathering conditions will be recorded for aging tests: temperature, UV light intensity, humidity, and ozone concentration.

Wipe sampling method:

PCB-containing caulk was manufactured with PCB congeners with a wide range of boiling points and different structures. Data from the field show that PCB congeners migrate from the caulk into adjoining materials, to the surfaces of the caulk and adjoining materials, and into the air. The more volatile congeners are less likely to be present on the surface of materials, but PCBs have been measured on surfaces in many locations in the field. The wipe method will be used in screening tests to detect PCBs on the surface of encapsulants. Screening tests will be used to select encapsulants for more rigorous testing (to be described in a subsequent QAPP or QAPP revision) that will include testing in sealed chambers to evaluate an encapsulant's ability to prevent off-gassing of the more volatile PCB congeners.

- A template will be used to wipe the 60.5 cm^2 area (6.35 cm x 9.52 cm) of test specimens exposed to the standard (PCB) source, as described above.
- Wipe sampling will be done following the standard method listed in Table 2-1 and developed SOPs for this project.
- Wipe sampling will be done on three tests specimens that have been exposed to accelerated weathering (as described above), and on three test specimens that have not been exposed to accelerated weathering (The actual sample number may be greater, dependent on the variability of replicate samples).
- PCBs and/or surrogates in the wipes will be quantified by the GC/MS/ECD methods described below and in the related QAPP entitled *PCBs in Caulk: Source Characterization to Support Exposure/Risk Assessment for PCBs in Schools.*

Milling method:

- Test specimens, described above, will be held flat in a vacuum chuck on a milling machine
- An end mill will be cleaned and rinsed in solvent to remove any PCB or surrogate contamination.
- The end mill will be installed in the milling machine.
- The clean end mill will be used to remove 2 mils ($\approx$ 0.05 mm) from the top surface of the test coating.
- The removed coating material will be collected on a clean filter with a micro-vacuum sampler and sample weight will be determined.
- Material will be collected from three tests specimens that have been exposed to accelerated weathering (as described above), and on three test specimens that have not been exposed to accelerated weathering.
- PCBs and/or surrogates in the collected material will be quantified by the GC/MS/ECD methods described below and in a related QAPP entitled *PCBs in Caulk: Source Characterization to Support Exposure/Risk Assessment for PCBs in Schools.*

Alternative method:

If the wipe method or the milling method does not provide adequate performance, then other alternatives will be explored. The screening test must provide a way to differentiate the effectiveness of various coatings. It is expected that some coatings will be more effective than others as encapsulants, and the screening test must show differences in effectiveness. An alternative method that may be explored is extraction (or "leaching out"), described as follows:

- Test specimens, described above, will be submerged in a mild solvent (to be determined) for a period of time (to be determined) to enable PCBs (or surrogates) to leach from the test coating to the solvent.
- The solvent must not penetrate through the test coating to contact the PCB (or surrogate) source coating.
- After extraction, the solvent will be concentrated, if necessary.
- PCBs and/or surrogates in the solvent will be quantified by the GC/MS/ECD methods described below and in the related QAPP entitled *PCBs in Caulk: Source Characterization to Support Exposure/Risk Assessment for PCBs in Schools.*

4.2.4 Further Evaluation of Selected Coating Materials and Application Methods

Coating Materials, Application Methods, and Substrates

Three to five most promising combinations of coating materials and application methods will be selected based on the screening tests.

Masonry materials (concrete and brick) will be substrates for testing the selected coating materials and application methods, because these are the materials of most concern. Other building materials, such as wood and gypsum wall board, are more easily removed, so they are usually

removed and disposed of." A standard method will be developed for applying PCBs to these materials.

Additionally, polysulfide and polybutene caulks will be prepared in the laboratory for testing encapsulants. It is known that PCBs were once used as a plasticizer in polysulfide and polybutene caulks [5-7]. The caulk will be made based on the formulations used between the 1950s and the 1970's [5-9] and the binding requirements of the substrate to be tested. Aged caulk samples collected from the field may also be included, if an adequate quantity of caulk with relatively uniform PCB bulk concentration can be obtained.

To simulate realistic conditions for caulk application, lab-mixed PCB caulk will be applied to a grove on a masonry substrate (Figure 1).
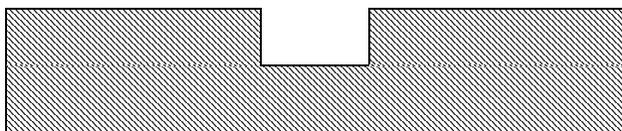
Figure 1. Cross section of the masonry substrate for caulk application (not to scale)

Evaluation Criteria

The encapsulation effectiveness will be evaluated based on the following criteria:

- PCB availability on surface measured by the wipe method (The acceptance criteria is <10 ng/100 cm^2).
- PCB emissions (off-gassing) measured in small or micro environmental chambers (The acceptance criteria will be set by means of indoor air quality modeling).
- PCB leaching out.
- Coating resistance to aging.
- Coating resistance to abrasion.
- Potential new health concerns caused by encapsulation, such as the emission of hazardous chemicals.
- Cost.

Evaluation methods

A method will be developed to test encapsulants applied to aged caulk samples prepared in the laboratory or obtained from the field. The choice of whether to use lab-prepared caulk or caulk samples from the field (or both) will depend on the availability of suitable field caulk with good integrity, relatively consistent PCB concentrations, adequate surface area, and sufficient available quantity
.
Testing of encapsulants on masonry substrates will be conducted as follows:

- Use solid, aged, concrete bricks and solid, clay bricks as test specimens.
- Obtain all bricks from the same batch(es).
- Measure PCBs (if any) in some bricks from each batch, as received.
- Apply PCBs to solid, aged concrete bricks and solid, clay bricks using a standard method, to be developed.
- Make 15 test specimens for each coating evaluated (14 specimens required as shown in Table 2, 1 extra).

Table 2. Minimum numbers of test specimens required for wipe, off-gassing and leaching tests [a]

Test	Before aging	After aging
Wipe	3	3
Off-gassing	2	2
Leaching	2	2

[a] Actual sample numbers may be greater, dependent on the variability of replicate samples.

For wipe sampling:

- Apply a coating material (following manufacturer instructions).
- Allow the coating to dry (following manufacturer instructions).
- Measure availability of PCBs on 3 test specimens immediately after drying, then dispose of the 3 specimens.
- Measure availability of PCBs on 3 test specimens after accelerated aging (roughly equivalent to 10 years of natural aging under outdoor conditions or up to the limit of the equipment), then dispose of the 3 specimens.

Evaluation of the encapsulation ability to reduce PCB off-gassing will be conducted by following ASTM 5116 Standard Guide for Small-scale Environmental Chamber Determination of Organic Emissions from Indoor Materials/Products, and as described below under Section 5.3.

Evaluation of the encapsulation effectiveness to reduce PCB leaching out will be conducted by a standard test method (e.g., solvent extraction). Coating resistance to impact, scratching, and abrasion will be tested by using masonry materials without PCBs and by following a standard test methods such as ASTM D6905 -03(2008) Standard Test Method for Impact Flexibility of Organic Coatings and similar standard methods.

4.3 Evaluation of NASA's AMTS (Activated Metal Treatment System) for Surfaces Contaminated by PCB-containing Caulk (Subtask 1.2)

The AMTS method, also known as the bimetallic treatment system (BTS), is based on the use of zero-valent magnesium (ZVM) to remove and rapidly degrade polychlorinated biphenyls (PCBs) found in structural coatings [10]. The BTS technology consists of elemental or ZVM coated with a

small amount of palladium in a solvent solution capable of hydrogen donation, and has two functions: (i) to extract PCBs from weathered, decades-old coating material such as paint; and (ii) to degrade the extracted PCBs. The technical details of this method are currently proprietary.

According to a NASA website (http://nasaksc.rti.org/Bimetallic.cfm), the AMTS can be used to "remove and destroy PCBs in painted surfaces," and its benefits include:

- Effective at removing and destroying PCBs from surfaces.
- Non-destructive to the surface being treated.
- Safer for end-user and environment than current alternatives.
- Useful for a variety of applications.
- Cost-competitive.
- In situ or ex situ.

The application areas of this method include:

- Painted structures such as buildings and ships.
- Concrete surfaces contaminated by PCB-laden transformer oil.
- Caulks and other adhesives.
- Electrical equipment.
- Soils.
- Other PCB-contaminated debris.

The NASA scientists who developed the method have expressed an interest in collaborating with EPA/ORD to test the AMTS for buildings contaminated by PCBs from caulk. The main application in the field for the AMTS would be to treat masonry materials that have been contaminated with PCBs from old caulk. The AMTS will be tested in the laboratory at the same time that coatings are tested using methods similar to those described above in Section 4.2.4. In the EPA/ORD laboratory, the AMTS will be applied to the PCB-contaminated masonry substrates and aged caulk samples described above in Section 4.2.4. NASA personnel or trained EPA personnel will apply the AMTS. After application of the AMTS, masonry substrates and aged caulk samples will be evaluated for residual PCBs.

The NASA scientists have indicated an interest in doing a preliminary field test to evaluate the AMTS for effectiveness in mitigating PCBs in contaminated building materials, such as concrete, brick, and mortar. NASA staff may do the field test on their own, because EPA/ORD is limited to laboratory testing.

Evaluation Criteria

The AMTS effectiveness and usefulness will be evaluated based on the following criteria:

- PCB availability on surface measured by the wipe method.
- PCB residual contamination of porous materials by grinding method.
- PCB emissions (off-gassing) measured in small environmental chambers.

- Potential effects of the chemical agents, reaction products, and by-products on indoor air quality.

The evaluation criteria for this method will include its performance for removing PCBs, cost, and the need for hazardous waste disposal.

Evaluation methods

A method will be developed to test the AMTS applied to aged caulk samples. Caulk samples will be treated with the AMTS, and the effectiveness of the AMTS will be evaluated with surface wipes and bulk analysis of the treated caulk.

The AMTS will be tested on the same masonry substrates used for encapsulation testing, as described above in Section 4.2.4 and as follows:

- Use solid, aged, concrete bricks and solid, clay bricks as test specimens.
- Obtain all bricks from the same batch(es).
- Measure PCBs (if any) in some bricks from each batch, as received.
- Apply PCBs to solid, aged concrete bricks and solid, clay bricks using a standard method, to be developed.
- Make 15 test specimens for each application of the AMTS evaluated (14 specimens required as shown in Table 3, 1 extra).

Table 3. Minimum numbers of test specimens required for wipe, grinding, and off-gassing tests [a]

Test	Before aging	After aging
Wipe	3	3
Grinding	2	2
Off-gassing	2	2

[a] Actual sample numbers may be greater, dependent on the variability of replicate samples.

For wipe sampling:

- Apply the AMTS (following NASA recommendations).
- Allow the AMTS time to treat materials (following NASA recommendations).
- Remove AMTS residue (following NASA recommendations).
- Measure availability of PCBs on 3 test specimens immediately after treatment, then dispose of the 3 specimens.
- Measure availability of PCBs on 3 test specimens after accelerated aging (roughly equivalent to 10 years of natural aging under outdoor conditions or up to the limit of the equipment), then dispose of the 3 specimens.

For grinding sampling:

- Apply the AMTS (following NASA recommendations).
- Allow the AMTS time to treat materials (following NASA recommendations).
- Remove AMTS residue (following NASA recommendations).
- Remove a top layer of 3 mm of masonry material by grinding.
- Measure bulk concentration of PCBs in grinding samples taken from 2 test specimens immediately after treatment, then dispose of the 2 specimens.
- Measure bulk concentration of PCBs in grinding samples taken from 2 test specimens after accelerated aging (roughly equivalent to 10 years of natural aging under outdoor conditions or up to the limit of the equipment), then dispose of the 2 specimens.

Evaluation of the AMTS ability to treat PCB contamination, and thereby reduce PCB off-gassing, will be conducted by following ASTM 5116 Standard Guide for Small-scale Environmental Chamber Determination of Organic Emissions from Indoor Materials/Products [11], and as described below under Section 5.3.

4.4 Review of Mitigation Methods for PCBs in Buildings (Subtask 1.3)

A literature review will be conducted for mitigation methods for PCBs in buildings. An EPA report will summarize the existing mitigation methods, analyze the pros and cons of each method, and compare the performances, costs, and feasibilities to be used in schools. This report will support the development of guidelines and decision-making tools. It is not the goal of this study, however, to write mitigation guidelines or develop decision-making tools.

5. SOURCE CHARACTERIZATION TO SUPPORT EXPOSURE/RISK ASSESSMENT FOR PCBs IN SCHOOLS (TASK 2)

5.1 Introduction

Understanding the source of PCBs is a critical step for risk assessment and the very first step for developing risk management options. Several predicative models have been developed in recent years for the emissions (i.e., off-gassing) of volatile and semi-volatile organic compounds from building materials. For PCBs in caulk, preliminary simulation results (see the Appendix) suggest the following:

- After several decades off-gassing, the majority of PCBs still remain in the source.
- Although the rates of gas-phase transfer from the source to the indoor environment are expected to be low, the contribution of PCB off-gassing to the PCB levels in indoor air may still be a factor.
- The off-gassing rates vary greatly among individual congeners.

Task 2 is intended to serve two purposes: (i) provide data and methods to improve understanding of PCB contamination sources in schools, and (ii) provide source and sink data to reduce uncertainty in NERL's Stochastic Human Exposure and Dose Simulation (SHEDS) model and to reduce the reliance of the SHEDS model on field measurements. In particular,

- Currently, the SHEDS model does not have a source module for PCB off-gassing. If the test results show that PCB off-gassing is a significant contributing factor for inhalation exposure, NRMRL will develop an off-gassing module for SHEDS model for PCBs.

- Provide NERL modelers with data for PCB distributions among indoor media (source, air, interior surfaces, etc.). Such data can be used by the SHEDS model as default values in case field measurements are absent.

- Provide NERL modelers with data for PCB transfer from sources to dust for use in estimating inhalation and dermal exposures.

5.2 Technical Approach

Research will focus on three areas:

(i) Determination of PCB off-gassing rates from PCBs and contaminated building materials through chamber testing. The results can be used to determine whether gas-phase PCBs contribute significantly to inhalation exposure. PCBs are classified as semi-volatile compounds, as their vapor pressures vary greatly from congener to congener, ranging from 10^{-12} to 10^{-4} atm (approximately 8×10^{-10} to 8×10^{-2} mm Hg). Rough calculations based on existing mass transfer models suggest that PCB off-gassing from caulk may still be contributing to PCB concentrations in air after initial application of PCB caulk decades ago. See the appendix for model predictions.

(ii) Distributions of PCBs between sources, air, settled dust, and interior surfaces. If correlations exist, the results can be used by the SHEDS model and also can lead to improved indoor environmental monitoring strategy.

(iii) Migration of PCBs from sources to settled dust. A preliminary assessment conducted by NERL indicates that inhalation of dust is an important exposure route (internal communications). Recent studies suggest that pollutants can migrate from sources to dust by volatilization, direct partitioning, and particle formation due to mechanical forces such as abrasion. This study is directed toward generating semi-quantitative data for PCB migration rates from sources to settled dust.

In this project we propose to use both field samples and lab-mixed samples for source characterization because each type has its advantages and disadvantages (Table 4). We believe that a combination of two types of PCB sources will produce most useful results.

Table 4. Comparison of two types of PCB samples for source characterization

PCB Sample Type	Advantages	Disadvantages
PCB-containing samples collected from schools	– Realistic samples – Test results are more useful for measurement-based exposure estimation	– Caulk is in irregular shapes – Surface area is too small for wipe sampling and testing PCB transfer to dust – Difficult to determine surface area for calculating emission factor ($ug/m^2/h$) – Unknown PCB distribution in sample, which is an error source for determining partition coefficient
Lab-mixed PCB samples	– PCB content in sample is well defined – Excellent PCB uniformity, which reduces the errors in emission factor and partition coefficient – Well defined flat surface for swipe sampling and testing PCB transfer to dust	– Physical properties may be different from field samples – Test results are less useful for measurement-based exposure estimation

5.3 PCB Off-gassing from Primary and Secondary Sources (Subtask 2.1)

Several mass transfer models have been developed to predict chemical emissions from building materials [12]. At a given temperature, the emission rate is determined by several factors: the initial concentration of the chemical in the source, the diffusivity in the solid material, the solid/air partition coefficient, the surface area of the source, and the age of the source. Currently there are no diffusivity and partition coefficient data for PCB emissions from caulk. Thus, the PCB off-gassing tests will serve two purposes: (i) provide emission data to determine whether gas-gassing is a significant contributor to indoor PCBs, and (ii) provide data to estimate the parameters (such as diffusivity and partition coefficient) in the emission models (including empirical models) for use by NERL's SHEDS model.

5.3.1 Materials

PCB sources to be tested for off-gassing will be obtained from NERL's environmental measurements study in a limited number of schools (<10). Approximately 10 primary sources (caulk) and 5 secondary sources (adjacent materials and settled dust) will be tested. Three lab-mixed PCB sources will also be tested as references.

5.3.2 Test Methods

Conventional method:

Emissions testing will be conducted in small or micro environmental chambers by following ASTM 5116 Standard Guide for Small-scale Environmental Chamber Determination of Organic

Emissions from Indoor Materials/Products [11], literature [13], and the project-specific standard operation procedures (SOPs). Because of the low vapor pressures of PCBs, elevated temperature may be needed for these tests. For each PCB source, tests will be conducted at a minimum of three different temperatures. We will start at the lowest feasible temperature then up to 80 °C to allow the results to be extrapolated to room temperature (22 °C or 72 °F). The testing protocol will be as follows:

- Create subsamples of materials.
- Measure surface area.
- Determine the PCB content by using one set of three to five subsamples.
- Conduct chamber testing.
- Collect multiple air samples from chamber outlet at different elapsed times.
- Remove test specimen from chamber.
- Collect wipe samples from chamber walls.
- Determine the PCB emission rates according to ASTM 5116.

Alternative method:

An alternative method currently under evaluation is to conduct the chamber tests without air exchange flows [14, 15]. The advantage of this new method is its ability to determine the partition and diffusion coefficient, from which the off-gassing rate can be determined by using the existing mass transfer models (see the appendix as an example).

The PCB off-gassing rates for individual congeners will be reported in ($ng/m^2/h$). The experimentally determined off-gassing rates will be used to evaluate the existing emission models for potential use by the SHEDS model.

5.4 PCB Partitioning Among Indoor Media (Subtask 2.2)

PCB partitioning among indoor media will be studied by using both standard sources developed in the lab and source materials obtained from the field. The numbers of tests needed (including duplicate tests) are as follows:

Source/air partition   6
Source/sink partition   4 (multiple sink materials in each test)
Source/dust partition (gas-phase)   6

According to the literature, PCBs were once used between the 1950s and the 1970s to make two-part polysulfide polybutene caulk [5-9]. The lab-mixed PCB caulk will be prepared by mixing PCB standards with PCB-free polysulfide or polybutene caulk. Scouting tests will be performed to prepare the lab-mixed PCB caulk. Selection of PCB congeners or Aroclors will be based on analyses of PCB caulk taken from schools. Both new and aged lab-mixed PCB caulk will be tested. The resemblance of the lab mixed and aged caulk to naturally aged caulk will be evaluated by comparing the PCB congener profiles and physical properties of the caulk (e.g., brittleness). In general, the degree of resemblance between the lab-mixed caulk and the naturally aged caulk

found in schools depends largely on the availability of the polymers used 40 to 50 years ago and the accelerated aging process.

5.4.1 Source and Air Partition

PCB partition between sources and indoor air is an important parameter in emission models. For a given type of source material, the partition coefficient is a function of vapor pressure of the chemical as shown in Eq. 1 [16]:

$$K = \frac{B}{P^n} \tag{1}$$

where K is the dimensionless air/solid partition coefficient; P is the vapor pressure; B and n are constants.

Several methods have been developed for determination of partition coefficients of volatile organic compounds for building materials (refs [17, 18], for example). However, they may not be sensitive enough for semi-volatile or non-volatile compounds. In this study, PCB partition between PCB sources and air will be determined in static chambers or by headspace sampling. This method is essentially a static chamber method [14, 15]. Tests at elevated temperatures may be considered (see Section 5.3.2). The testing protocol will be as follows:

- Conduct a scouting test to find out the time for PCBs reaching steady state in the static chamber.
- Determine PCB content in the source.
- Place test specimen in the chamber.
- Allow the chamber to operate under the static mode until steady state is reached.
- Take air samples at the end of test.
- Determine the PCB concentrations in air samples.

The air/source partition coefficients for individual congeners will be reported as dimensionless numbers (i.e., the ratio of PCB concentration in the air and the source).

5.4.2 Source and Sink Partition

PCB partition between PCB sources and interior surfaces is an important parameter in both source and sink models. It determines how the PCBs distribute inside the building. PCB partition between sources and interior surface materials (paint, gypsum wallboard and carpet) will be determined by placing the source and surface materials in the same chamber:

- Determine PCB content in the source and surface materials.
- Place the source on the floor of the chamber.
- Place eight surface material coupons on the rack and at half the chamber height.
- Allow the chamber to operate under static mode.
- Remove two surface material coupons at 48 elapsed hours.
- Determine PCB content in the coupons.

- Repeat the two steps above at 96, 148 and 240 elapsed hours (at least one test will last for 1000 hours).

The source/sink partition coefficients for individual congeners will be reported as dimensionless numbers (i.e., the ratio of PCB concentrations in the sink material and source per unit area).

<u>5.4.3 Source and Dust Partition Due to PCB Off-gassing</u>

Inhalation of re-suspended indoor dust and ingestion of indoor dust may play an important role in human exposure to PCBs. However, no data is available for the transfer rates of PCBs from PCB sources to indoor dust. There are three mechanisms that may lead to pollutant migration from the source to dust: (i) evaporation, (ii) direct partitioning on source surfaces, and (iii) dust generation due to abrasion on source surfaces [2]. Tests described below are aimed to determine the importance of the first mechanism (partition due to evaporation). The second mechanism will be investigated in Subtask 2.3. The third mechanism will not be investigated in this research plan because the dust generation rate due to abrasion is difficult to determine in quantitative terms.

PCB gas-phase partition between sources and dust will be determined by using NIST standard house dust (PCB-free) [19] or Arizona Test Dust (≤ 10 µm diameters). Two experimental methods will be evaluated.

Methods 1 (Using the 53-L environmental chamber)

- Apply a thin later of PCB-free dust on six stainless steel panels (500 cm^2 each) either manually or by aerosol deposition; the target dust loading is 0.2 to 0.4 mg/cm^2.
- Placed two dust laden panels on chamber floor.
- Place the source with known PCB content on a rack in the chamber.
- Allow the chamber to operate under static mode.
- Remove the panels at 336 elapsed hours (2 weeks).
- Collect house dust with a micro vacuum dust sampler.
- Determine the PCB content in collected dust.
- Repeat the test for 4 and 6 weeks.

Method 2 (Using the 27-m^3 Environmental Chamber)

The experimental method is described above. To evaluate gas-phase transfer, the dust laden panels will not contain PCB sources. PCB sources will be present in the chamber but not in contact with dust laden panels.

The source/dust partition coefficients for individual congeners will be reported as dimensionless numbers (i.e., the ratio of PCB concentrations in the dust and source).

5.5 PCB Migration from Sources to Settled Dust (Subtask 2.3)

The purpose is to determine the rates by which PCBs are transferred from the source (e.g., caulk) to settled dust due to direct partitioning on the source surface and PCB gas-phase emissions. Tests

will be conducted in a 27-m^3 stainless steel chamber equipped with aerosol generators and aerosol injection ports:

- Create 19 PCB standard source panels by applying a thin layer of lab-mixed PCB caulk (or paint), which contains approximately 0.1% (by weight) of each target PCB congeners, on concrete or gypsum board; each panel should be at least 1000 cm^2 in size.
- Use three panels to determine PCB availability on surface in (ng/cm^2).
- Place the remaining 16 panels, including 4 backups, on the bottom of the chamber.
- Place three blank panels (the same type substrate, but without PCB sources) on the bottom of the chamber.
- Turn on the ceiling fan.
- Introduce approximately 120 g of Arizona Test Dust ($\leq$ 10 μm diameters) into the chamber with a TSI 3400 Fluidized Bed Aerosol Generator (> 60% mass is expected to settle on the chamber floor).
- Stop the ceiling fan to allow the airborne dust to settle for 24 hours. The targeted dust load on PCB panels is 0.1 to 0.2 mg/cm^2.
- Place six passive air samplers on chamber walls and at half height of the chamber.
- Start the test with low air change flow rate (to be determined by conducting scouting tests).
- Remove 4 panels and two passive air samplers after one week.
- Collect dust with a micro vacuum dust sampler.
- Determine the PCB content in the dust samples and air sampler.
- Repeat the three steps above at elapsed time of 2, 4, and 6 weeks.

The PCB transfer rates for individual congeners will be reported in (ng/m^2/ppm PCB in source/h) and (ng/g dust/ppm PCB in source/h).

6. SAMPLE COLLECTION AND ANALYSIS

6.1 Sampling Methods

The air and dust sampling will follow the standard methods listed in Table 5 and the SOPs specifically developed for this project.

Table 5. Standard Sampling Methods for This Project

Method	Method ID	Method Title	Reference
Wipe Sample	ASTM D6661	Field Collection of Organic Compounds from Surfaces Using Wipe Sampling	[20]
	40CFR 761.123	Wipe Sample	[21]
Air Sample	EPA Method TO-10A	Determination Of Pesticides and Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD)	[22]
	EPA Method TO-4A	Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)	[23]
Dust Sample	ASTM D5438	Standard Practice for Collection of Floor Dust for Chemical Analysis	[24]

6.2 Sample Analysis

The GC/MS/ECD will be used to determine the concentrations of PCBs as individual PCB congeners or "Total PCBs" in the air or in extracts from polyurethane foam (PUF) sampling or other solid materials. Compound identification will be performed on MS detector and quantification will be conducted on either MS or ECD. The sample extraction will be conducted using sonicator, Soxhlet system or other methods. The ultrasonic method will enhance contact of the sample matrix with the extraction solvent. The analytical sample preparation will follow methods listed in Table 6 and SOPs. In case interferences are encountered from sample medium after extraction, selected cleanup procedures will be applied. Table 7 lists standard methods we will follow for analytical procedures.

Table 6. Standard Sample Preparation Methods for This Project

Method	Method ID	Method Title	Reference
Extraction	EPA Method 3541	Automated Soxhlet Extraction	[25]
	EPA Method 3550B	Ultrasonic Extraction	[26]
Cleanup	EPA Method 1668B	Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids and Tissue by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)	[27]

Table 7. Standard Analytical Methods for This Project

Method Number	Method Title	Reference
EPA Method 8082A	Polychlorinated Biphenyls (PCBs) by Gas Chromatography	[28]
EPA Method 1668B	Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids and Tissue by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)	[27]
EPA method TO-10A	Determination Of Pesticides and Polychlorinated Biphenyls In Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed By Gas Chromatographic/Multi-Detector Detection (GC/MD)	[22]
EPA method TO-4A	Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD)	[23]
NIOSH Method 5503	Polychlorobiphenyls	[29]
EPA Method 680	Determination of Pesticides and PCBs in Water and Soil/Sediment Gas Chromatography/Mass Spectrometry	[30]

7. QUALITY ASSURANCE AND QUALITY CONTROL

7.1 Quality Management Plan and Quality Assurance Category

This study will be guided by the NRMRL Quality Management Plan (http://www.epa.gov/nrmrl/qa/) and conducted under category II QA requirements. Two quality assurance project plans (QAPPs) have been approved by the QA Officer:

- Screening tests of coatings for encapsulating building materials contaminated by polychlorinated biphenyls (PCBs).

- Polychlorinated biphenyls (PCBs) in caulk: source characterization to support exposure/risk assessment for PCBs in schools.

To complement the QAPPs, fifteen project-specific standard operating procedures (SOPs) have been developed. At least 25% of the data collected from this study will be audited.

7.2 Data Quality Indicators

Data quality indicator (DQI) goals for critical measurements during this project are based on historical data obtained in similar studies and from laboratory evaluations of sampling methods and analysis. To the extent possible, standardized methods will be followed. The DQIs for the measurement parameters and validation methods are listed in Table 8.

Table 8. Data Quality Indicator Goals for Critical Measurements

Measurement Parameters	Methods	Accuracy/Bias	Precision
PCB content in lab-mixed sources	Gravimetric	≥ 90%	Not applicable
Amount of PCB source applied to substrate	Gravimetric	≥ 80%	20%
Temperature	Thermocouple, RTD probe [a]	± 0.5 °C	± 2 °C
Relative humidity (RH)	RTD Probe, thin film capacitance sensor	± 5% RH	10%
Air exchange rate (ACH) for small chamber	Mass flow controller/meter	± 0.05 ACH	10%
Air flow rate	Mass flow controller	± 5% of full scale	10%
Weight of materials	Gravimetric	± 2 mg	± 2 mg
Recovery of PCB concentration	GC/MS/ECD [b]	75 - 125%	25%

[a] RTD is Resistance Temperature Detector.

[b] GC/MS/ECD is gas chromatography/ mass spectrometry/ electron capture detection.

7.3 Chamber Operation Parameters

In addition to the DQI goals for the critical measurement parameters, objectives established for the control of operating parameters for the 53-liter small chamber, accelerated weathering chamber, and μ-CTE micro chamber are presented in Tables 9 to 11, respectively.

Table 9. Small Chamber Operating Parameters

Operating Parameters	Control Methods	Typical set point	Accuracy
Chamber temperature	Incubator	23 °C	± 1.0 °C
Chamber inlet air RH	Water vapor generator / dilution system	20 - 70%RH	± 5% RH
Air exchange rate	Mass flow controllers/meters	0.5 or 1 ACH	± 0.05 ACH
Air velocity	Fan	10 cm/s	Not defined
Individual PCB congeners	Clean air system	< 10 ng/sample	Not applicable
Total PCB congeners	Clean air system	< 100 ng/sample	Not applicable

Table 10. Accelerated Weathering Chamber Operating Parameters

Operating Parameter	Control Method	Typical Set Point	Accuracy
UV temperature	UV cycle temperature control	50 - 75 °C	± 2.5 °C
Irradiance	UVA-340 lamps	0.68 - 1.38 W/m^2/nm [1]	± 5%
Total PCB congeners	Filtered ambient air in enclosure	<100 ng/sample	Not applicable

[1] at 340 nm

Table 11. µ-CTE Micro Chamber Operating Parameters

Operating Parameter	Control Method	Typical Set Point	Accuracy
Chamber temperature	Air supply temperature control	28 - 120 °C	± 0.5 °C
Low inlet air flow	Gas tank regulator	10 - 70 mL/min	± 10%
High inlet air flow	Gas tank regulator	50 - 500 mL/min	± 10%
Total PCB congeners	Clean air system	< 100 ng/sample	Not applicable

8. LABORATORY SAFETY AND HAZARDOUS WASTE MANAGEMENT

To ensure occupational safety and health precautions and proper handling of PCB wastes, a Health, Safety and Environmental Research Protocol (HSRP) for Hazardous Agent Research has been developed by the research team and approved by the ORD Safety, Health and Environmental Management (SHEM) Office.

9. REPORTING

The complete results from this study will be compiled in four EPA reports:

- Evaluation of encapsulants for PCB sources in buildings.
- Evaluation of the NASA Activated Metal Treatment System for destruction of PCBs in contaminated building materials.
- Literature review on PCB mitigation methods.
- Laboratory characterization of PCB sources in buildings.

Except for the literature review, these reports will be externally peer reviewed and will be available to the EPA program offices and regions and other stakeholders. It is anticipated that several peer reviewed journal articles will be prepared based on this study.

10. STUDY TIMELINE

This study is to be completed in an 18-month period, starting from September 25, 2009 when EPA made a public announcement that it would conduct new research to better understand the risks posed by caulk containing PCBs. The tentative timeline proposed below assumes that we can obtain field samples for testing in early summer of 2010.

Laboratory preparations and method development	October 2009 - February 2010
External review of research plan	February 2010
QAPP approval	February 2010
Laboratory testing	March – November 2010
QA technical system audit	August 2010
Data quality audit	September 2010
Report preparation	December 2010 – January 2010
Report review	February 2011
Final reports	March 2011

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APPENDIX. PREDICTING PCB EMISSIONS FROM AGED CAULK

A1. Purpose

This appendix presents the model predictions for PCB off-gassing rates from aged caulk. The sole purpose is to help develop hypotheses and design test protocols. The predictions are based solely on theoretical calculations without the support of any real emission data.

A2. Summary

PCBs comprise a class of 209 individual compounds. As a group, they are classified as non-volatile compounds with vapor pressures ranging from 10^{-12} to 10^{-4} atm (approximately 8×10^{-10} to 8×10^{-2} mm Hg). Because PCB-containing caulk was made long ago (in the 1950s through the 1970s), it is expected that the composition of the PCB congeners in the source today is somewhat different from that several decades ago due to different off-gassing rates. The calculations do show, however, that the majority of PCBs still remain in the source. Although the rates of gas-phase transfer from the source to the indoor environment are expected to be low, the contribution of PCB off-gassing to the PCB levels in indoor air may still be a factor.

The models used consider only gas-phase transfer. They do not consider PCB transfer from sources to house dust.

A3. Model Description

The emissions of PCBs from aged caulk can be predicted by diffusion-based emission models. About a half dozen such models have been developed, but they perform more or less the same.

The following parameters are required for the source material:

> Exposed area of the material
> Thickness of the material
> Initial pollutant concentration in the source
> Material/air partition coefficient
> Diffusivity in the material

The model used here (Eqs. a1 and a2) is from Huang and Haghighat [A1]:

$$\frac{M(t)}{M_0} = 2 \sum_{n=1}^{\infty} \frac{\sin^2 \beta_n b}{\beta_n^2 b^2 + \beta_n b \sin \beta_n b \cos \beta_n b} \times \left(1 - e^{-\beta_n^2 D_m t}\right) \tag{a1}$$

$$\frac{h}{K D_m} = \beta_n \tan(\beta_n b) \tag{a2}$$

where $M(t)$ = total amount of a PCB congener that has left the caulk at elapsed time t (μg),
   M_0 = initial amount of a PCB congener in the caulk (μg),

β_n = the nth eigenvalue determined by Eq. a2 (m^{-1}),
h = gas-phase mass transfer coefficient (m/s),
K = solid/air partition coefficient (dimensionless),
D_m = diffusivity in material (m/s), and
b = material thickness (m).

A4. Estimation of Model Parameters

A4.1 Estimation of Diffusivity in the Solid Material

Diffusivity data for PCBs in dry caulk is not available. They have to be estimated based on data for other chemicals and materials. According to Bodalal and his co-workers [A2], the following correlation exists for diffusivities in a given solid material:

$$\frac{D_1}{D_2} = \left(\frac{m_2}{m_1} \right)^n \qquad\qquad (a3)$$

where D_1 and D_2 = diffusivity for compound 1 and 2 (m^2/s) and

m_1 and m_2 = molecular weight for compound 1 and 2 (g/mole)

For aromatic compounds the reported values of n ranges from 6.0 to 8.6 [A3]. An average of 7.39 is used for this estimation. Diffusivity data for two aromatic compounds and two polymer materials are shown in Table A1 and the estimated diffusivities for PCBs are shown in Figure A1.

Table A1. Experimentally determined diffusivity for aromatic compounds in vinyl flooring and PVC carpet backing.

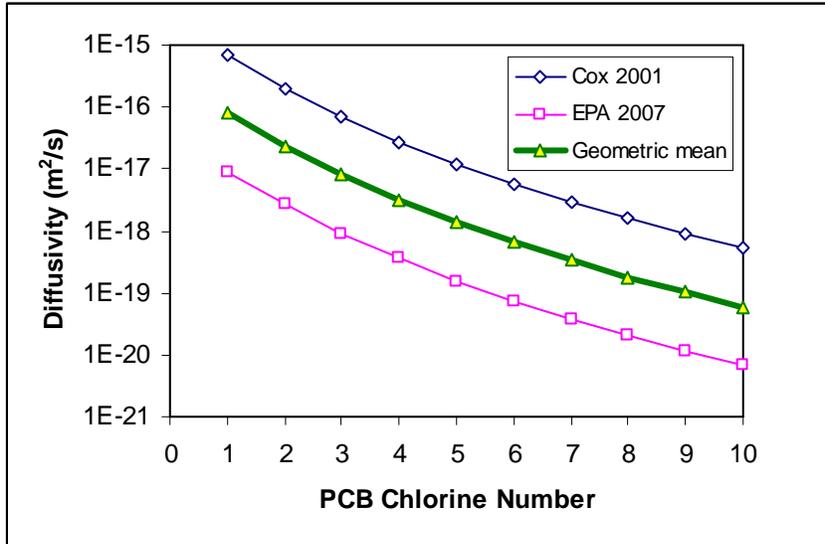| Compound	Material	Diffusivity	Source
Phenol	Vinyl flooring	1.2×10^{-13} m^2/s	[A4]
Ethylbenzene	PVC carpet backing	2.3×10^{-12} m^2/h	[A5]

Figure A1. Estimated diffusivities for PCBs in vinyl flooring and PVC carpet backing

A4.2 Estimation of Partition Coefficient

The soli/air partition coefficient is estimated from the following equation [A3]:

$$\ln K = 8.78 - 0.785 \ln P \tag{a4}$$

where   K = partition coefficient (dimensionless)

P = vapor pressure (mm Hg).

For PCBs, the vapor pressures range from 8×10^{-2} down to 8×10^{-10} mm Hg, and the calculated partition coefficients range from 4.6×10^{4} to 8.8×10^{10} depending on the degree of chlorination.

A4.3 Estimation of gas-phase mass transfer coefficient

Several methods are available for estimating gas-phase mass transfer coefficient the indoor environment [A3]. In this work h = 2 m/h (0.056 cm/s) is used.

A5. Percent of PCBs Remaining in the Aged Caulk after 30 Years

Simulations were based on Equations a1 and a2 for over a 30-year period with diffusivities and partition coefficients parameters shown in Table A2. The material thickness is assumed to be 1 cm.

Table A2. Diffusivity (D_m) and solid/air partition coefficient (K) used for simulation

PCB Chlorine Number	D_m[1] (m^2/s)	K[2] (dimensionless)
1	7.98×10^{-17}	4.63×10^4
5	1.38×10^{-18}	6.39×10^7
10	5.99×10^{-20}	8.82×10^{10}

[1] Geometric mean in Figure A1.
[2] Calculated from Eq. a3.

The fractions of PCBs remaining in the caulk [i.e., $1 - M(t)/M_0$] for three PCB congeners (chlorine number = 1, 5, and 10) are shown in Figures A2. The results suggest that PCBs tend to stay in caulk, and that only a small fraction has been emitted into air over the 30-year period.
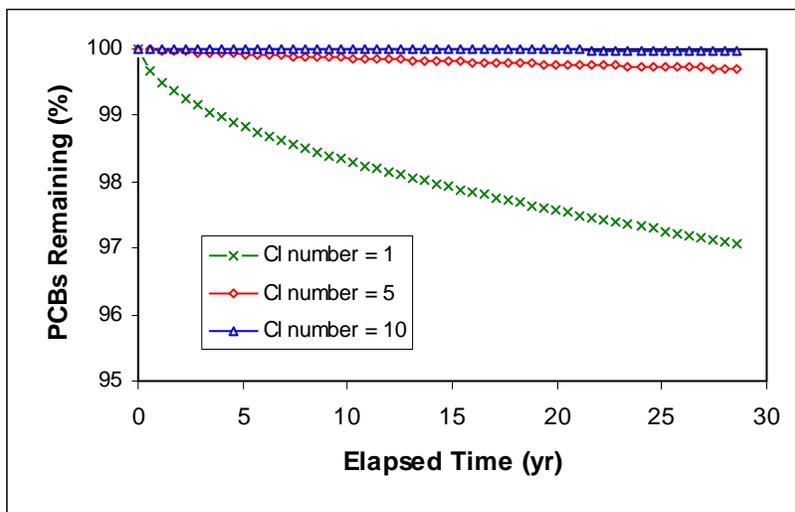

Figure A2. Percent of PCBs remaining in caulk for PCBs with chlorine numbers of 1, 5, and 10

A6. PCB Concentrations in Indoor Air Due To the Off-Gassing From Aged Caulk

Indoor air quality simulation was performed using the SLAB program in IAQX [A6], which implements a diffusion model similar to Eqs. 1 and 2 [A7]. The parameters used were:

Classroom volume	120 m^3
Ventilation rate	1 h^{-1}
Exposed area of caulk	3.5 m^2
Initial PCB content in caulk	100 mg/cm^3 ($=1\times10^8 \text{ mg/m}^3$)
Average thickness of caulk	1 cm ($=0.01 \text{ m}$)
PCB diffusivity in caulk	See Table A2
PCB's caulk/air partition coefficient	See Table A2

As shown in Figure A3, the gas-phase PCB concentrations in the classroom today are 1760, 232, and 23 ng/m^3 without consideration of indoor sinks. If we assume there is a 1-to-5 partition between indoor air and interior surfaces for PCBs, the "actual" PCB concentrations are:

PCB(Cl=1)	353	ng/m^3
PCB(Cl=5)	46	ng/m^3
PCB(Cl=10)	5	ng/m^3

These values appear to be in-line with the reported indoor air measurements.
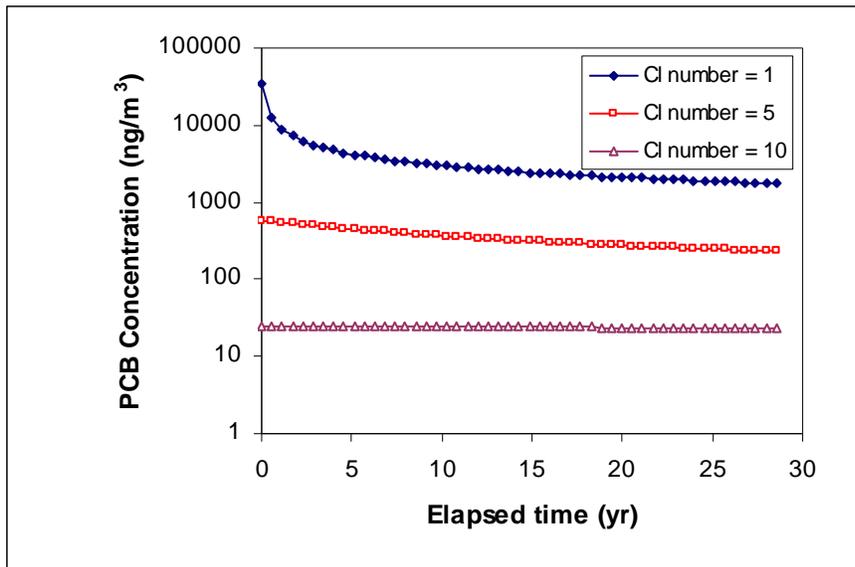

Figure A3. Predicted PCB concentrations in indoor air due to off-gassing from caulk for PCBs with chlorine numbers of 1, 5, and 10.

A7. Uncertainties

The greatest uncertainty in these simulations came from the estimation of PCB diffusivities in dry caulk. In the absence of measured values, they had to be estimated from other chemicals and building materials. It was assumed that the diffusivities of PCBs in dry caulk are similar to those in vinyl flooring and PVC carpet backing.

A8. References

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