



Project Summary

Development and Evaluation of Monitoring Methods for Polycyclic Aromatic Hydrocarbons in House Dust and Track-In Soil

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The analytical method for determining polycyclic aromatic hydrocarbons (PAHs) in dust and soil consists of sonication with 10 mL of hexane (C₆) for two 30-min extractions and analysis of the C₆ extract by gas chromatography/mass spectrometry (GC/MS). The analytical method for determining polychlorinated biphenyls (PCBs) in dust and soil involves sonication with 10 mL of 10 percent ether in C₆ for two 10-min extractions, silica gel column chromatography, and analysis of the target fraction by GC/MS. Quantitative recoveries of spiked perdeuterated PAH and ¹³C-labeled PCB are obtained using the above methods.

The sum of the concentrations of all target PAH in the house dust samples evaluated in this study ranged from 16 to 580 ppm. Higher concentrations were observed in entryway soil samples, and the sum of the concentrations of target PAH ranged from 68 to 4000 ppm and 58 to 5500 ppm in samples collected before (October 1992) and after (April 1993) the winter heating season, respectively. The sum of the concentrations of PAH in the pathway soil samples varied from 3.0 to 1200 ppm in samples collected before the heating season (October 1992). The sum of the concentrations of PAH ranged from 0.58 to 610 ppm and from 0.63 to 63 ppm in pathway soil and foundation soil samples collected after the heating season (April 1993), respectively. The concentrations of most 4- to 6-ring PAH, the sum of all target PAH, and the sum of PAHs that are probable human carcinogens in house dust correlated well with the corresponding levels in

entryway soil. However, there was no correlation between the PAH concentrations in house dust and in pathway soil, nor was any relationship found between house dust and foundation soil.

The PCB concentrations in house dust, entryway soil, pathway soil, and foundation soil were lower than the PAH concentrations in these samples. The sum of the concentrations of all target PCB varied from 210 to 1900 ppb in house dust, from 30 to 880 ppb in entryway soil, from 16 to 500 ppb in pathway soil, and from 18 to 210 ppb in foundation soil. Higher PCB concentrations were found in house dust samples than in entryway soil samples. Similar PCB concentrations were observed in pathway soil samples and foundation soil samples, which are lower than the PCB found in entryway soil samples. The concentrations of penta-PCB, hexa-PCB, and the sum of all target PCB in house dust correlated well with corresponding levels in entryway soil. However, this relationship was not observed for the PCB concentrations in house dust and pathway soil, nor was there any discernible relationship between the PCB concentrations in house dust and foundation soil samples.

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Introduction

Recent studies to develop suitable sampling and monitoring techniques for establishing human exposure to pesticides have suggested that relatively high levels of pesticide residues may occur in house dust. Residues tracked into the home may remain in carpets for prolonged periods due to the absence of environmental weathering effects. These residues may be picked up by the skin on contact. Once on the skin, the pesticides may be adsorbed directly or transferred to the mouth and ingested. Because young children spend a great deal of time on the floor, they are particularly susceptible to exposure to these chemicals as a result of dermal contact with house dust and the frequent hand-to-mouth contact that accompanies their normal play activities. An estimate of average daily soil and dust ingestion by young children ranges from 0.02 to 0.2 g, with a potential for up to 5 g per day for children exhibiting pica behavior who live in a dusty home or have access to exposed soil.

PAHs and PCBs represent two important groups of semivolatile organic compounds (SVOCs) that have been found in indoor and ambient air. Many PAHs are known to be carcinogens or mutagens, and adverse health effects have been linked to exposure to PAH. The presence of environmental tobacco smoke has been shown to be the most important indoor source of PAH in air. Other indoor activities that may contribute to PAH concentrations in indoor air are grilling of foods, the use of gas cooking and heating appliances, the use of fireplaces or woodstoves, the use of unvented kerosene space heaters, and the intrusion of contaminated ambient air. The levels of PCB in indoor air have been found to be higher than in outdoor air in several studies. Defective fluorescent light ballasts are suggested as one important indoor PCB source.

Higher PAH levels have been found in dust or soil samples taken near heavy traffic. Therefore, homes located downwind of heavy traffic may have higher PAH levels in house dust than those in lighter traffic areas. Very little information is available, however, about the occurrence and distribution of PAH and PCB in

house dust resulting from indoor sources or from track-in of outdoor dislodgeable soil residues. Data also suggest a possible magnification of lead (Pb) in soil near foundations. If such magnification near the foundation occurs, it may be due to the deposition of atmospheric Pb on the roof and the outside surfaces of the house, which then falls or washes down to the soil near the drip line of the roof. It is not clear whether such magnification also occurs with SVOCs, such as PAH and PCB.

Objectives

There are no established monitoring methods for PAH and PCB in house dust and track-in soil. Therefore, this study was undertaken to evaluate monitoring methods for PAH and PCB in dust and soil samples. The specific objectives of the study were

- 1) to evaluate and validate analytical methods for measuring PAH and PCB in dust and soil samples;
- 2) to obtain concentration profiles for PAH and PCB in dust and soil samples from an eight-home pilot field study conducted in Columbus, Ohio, before and after the 1992-1993 heating season;
- 3) to determine whether track-in of outdoor soil residues is an important source of PAH and PCB in house dust; and
- 4) to determine whether magnification of PAH and PCB levels occurs in the foundation soil.

This study was carried out in two phases to accomplish the above objectives:

- Phase I—Validate analytical methods for determining PAH and PCB in house dust and soil samples;
- Phase II—Conduct a small-scale pilot field study.

Procedures

Two extraction methods, Soxhlet extraction and sonication, were evaluated and validated for removing PAH and/or PCB from dust and soil sample matrices. The analytical method validated for determining PAH in house dust and soil samples consists of sonical extraction of the sample with C_6 and GC/MS analysis. The validated analytical method for determining PCB in dust and soil samples consists of

- 1) sonical extraction of the sample with 10 percent ether in C_6 ,
- 2) silica gel fractionation of the sample extract, and
- 3) GC/MS analysis of the target fraction.

A small-scale pilot field study was conducted before and after the 1992-1993 heating season by collecting and analyzing house dust and soil samples from eight homes. The first sampling session took place in June 1992 when only house dust samples were collected. The second sampling session occurred in October 1992. At each home, house dust, entryway dirt, and pathway soil samples were collected. During the third sampling session in April 1993, house dust, entryway dirt, pathway soil, and foundation soil samples were collected from each home. The dust and soil samples were prepared by the methods validated for PAH and PCB analysis.

Results

Quantitative recoveries (> 80 percent) of the spiked perdeuterated PAH were obtained when either DCM or C_6 were used as the extraction solvent with the Soxhlet technique. Both DCM and C_6 effectively remove PAH from the dust and soil samples, but the silica gel cleanup step is not required when C_6 is used. Therefore C_6 was used as the extracting solvent in the experiments to evaluate different sonication conditions. Quantitative recoveries were obtained when the samples were sonicated twice with C_6 for 30 minutes. The recoveries in this experiment ranged from 91 percent for fluorene- d_{10} to 100 percent for pyrene- d_{10} . This sonication condition was used with the spiked soil samples, and recoveries ranged from 91 percent (fluorene- d_{10}) to 98 percent (benzo(k)fluoranthene- d_{12}). The precision for measuring native PAH in triplicate samples was within 15 percent (relative standard deviation) with this sonication method. In summary, the analytical method adopted consists of extracting the sample twice by sonication with 10 mL of C_6 and analyzing the concentrated C_6 extract by GC/MS to determine the target PAH. The two 30-minute sonications with C_6 offer the best recoveries for perdeuterated PAH in spiked dust and soil samples but not for spiked ^{13}C -labeled PCB. Approximately 50 percent of each spiked ^{13}C -labeled PCB was recovered using this method. Experiments were then carried out using a more polar solvent, 10 percent ether in C_6 . In summary, the analytical method used consists of extracting the samples twice by sonication with 10 mL of 10 percent ether in C_6 for 10 minutes, fractionating the extract on a silica gel column, and analyzing the target fraction by GC/MS.

In the pilot field study, the average PAH concentrations in house dust samples were less than 1 ppm for most 2- to 3-ring PAH

and greater than 10 ppm for most 4- to 6-ring PAH. Among the measured target PAH, the most abundant PAHs found in these house dust samples were 4-ring (fluoranthene and pyrene) and 5-ring (benzofluoranthenes and benzo(a)pyrene) PAH. The least abundant PAHs found in these samples were, in general, the volatile 2-ring PAH and the reactive PAH such as acenaphthylene and cyclopenta(c,d)pyrene. Note that naphthalene concentrations were less than 1 ppm from samples collected in June 1992 and April 1993, but the concentrations were greater than 1 ppm from samples collected in October 1992. The low concentrations of acenaphthylene and cyclopenta(c,d)pyrene in house dust samples are partly due to the reactivities of these compounds. As demonstrated in previous studies, acenaphthylene and cyclopenta(c,d)pyrene can oxidize to naphthalene dicarbonylic acid anhydrides and pyrene dicarbonylic acid anhydrides, respectively. The highest PAH concentrations in dust were found in samples collected from a nonsmoker's house (H08) for all three sampling events. In this house, similar PAH concentrations were obtained from house dust samples collected before the heating season (June 1992 and October 1992). Relatively lower PAH concentrations were observed in the house dust sample collected after the heating season (April 1993). The concentrations of the well known carcinogen, benzo(a)pyrene (BaP) in this house were 54, 44, and 24 ppm in house dust samples collected during June 1992, October 1992, and April 1993, respectively. The PAH concentrations in dust samples collected from the smokers' houses (H01, H04, H05, and H06) were not always higher than those from the nonsmokers' houses. This finding suggests that the presence of environmental tobacco smoke (ETS) is not the only source for PAH in house dust. The sum of the concentrations of the seven B-2 PAH (probable human carcinogen) were 10 to 300 ppm in the dust samples collected before the heating season (June 1992 and October 1992) and 13 to 160 ppm in the samples collected after the heating season (April 1993). These levels are well above the 1 ppm level that the Washington State Model Toxics Control Act sets as standard for the B-2 PAH for residential soil at hazardous waste sites. Note that the sum of the concentrations of B-2 PAH are approximately half of the total concentrations of all 19 target PAHs (2- to 6-ring) in all but four samples collected during the three sampling sessions.

The most abundant and least abundant PAH in entryway soil are similar to those found in house dust. The concentrations of target PAH were higher in entryway soil in samples compared to house dust samples. The PAH concentrations found in entryway soil in samples collected before the heating season are within the same order of magnitude as levels in the samples collected after the heating season. The highest PAH concentrations in entryway soil samples were from House H08, which also showed the highest PAH concentrations in house dust samples. The BaP concentrations in entryway samples from House H08 were 350 and 380 ppm before and after the heating season, respectively. The sum of the concentrations for B-2 PAH were also about half of the sum of the concentrations for all 19 PAHs in most entryway soil samples. We also investigated the relationship between the measured PAH concentrations in house dust and entryway soil samples to determine whether any correlation exists between the PAH levels in these samples. A linear regression analysis was performed on each measured target PAH to determine the correlation coefficient (R^2). Stronger relationships were observed for B-2 PAH (probable human carcinogens), other nonvolatile 4- to 6-ring PAHs, and the sum of all PAHs. As expected, the volatile PAH and reactive PAH showed weaker relationships. These results suggest that the effect of track-in from the door mat is an important source of PAH in house dust.

The PAH concentrations found in pathway soil samples were lower than the levels in house dust and entryway soil samples. The least and most abundant PAH found in pathway soil samples were similar to house dust and entryway soil samples. Higher PAH concentrations were found in pathway soil samples collected before the heating season (October 1992) compared to those collected after the heating season (April 1993) for all but one household. The average concentrations from the eight houses sampled ranged from 0.059 ppm of naphthalene to 36 ppm of pyrene before the heating season, and from 0.023 ppm of naphthalene to 16 ppm of fluoranthene after the heating season. The fact the House H08 showed the highest PAH concentrations in entryway soil and house dust samples may have been caused by the pathway soil samples in this house having been taken along the driveway, the major walkway of the house. The homeowner paved the driveway ap-

proximately 2 weeks before the October 1992 sampling session.

The average PAH concentrations in the foundation soil samples ranged from 0.023 ppm of naphthalene to 3.3 ppm of fluoranthene. Levels of PAH found in the foundation soil samples were lower than the levels in the pathway samples for all but one house (H05). The PAH concentrations in the foundation soil from House H08 were not one of the highest levels of all the foundation soil samples. This can be partly explained by the fact that the foundation soil sample from House H08 was taken from the driveway. The sources of the extremely high levels of PAH in house dust, entryway soil, and pathway soil from this house (H08) are not understood clearly yet. In general, the relative concentration trend for target PAH is entryway soil > house dust > pathway > foundation soil.

The most abundant PCB found in house dust entryway soil, pathway soil, and foundation soil samples are penta-PCB, and the least abundant PCB was the most volatile mono-PCB. None of the nona-PCB and deca-PCB were found in these samples. The concentrations of penta-PCB ranged from 71 to 950 ppb in house dust samples, from 10 to 520 ppb in entryway soil samples, from 4.6 to 280 ppb in pathway soil samples, and from 7.5 to 87 ppb in foundation soil samples. The highest PCB concentrations in the house dust, entryway soil, pathway soil, and foundation soil samples are from House H03. Unlike PAH, the highest PCB concentrations were found in house dust samples followed by entryway soil samples. Similar PCB concentrations were found in pathway soil and foundation soil samples. We conducted a linear regression analysis on the measured PCB concentrations from house dust and entryway soil samples. The concentrations of penta-PCB, hexa-PCB, and total PCB show strong correlations between house dust samples and entryway soil samples. Weaker relationships were observed for mono-, di-, tri-, and tetra-PCB, which are probably due to the low concentrations for these PCBs in most of the samples. There is no correlation between the PCB concentrations in house dust and pathway soil, nor can any significant relation be established between house dust and foundation soil samples. This is probably due to differences in environmental weathering effects between pathway and foundation soil on the one hand and between entryway soil and house dust on the other.

Conclusions and Recommendations

An analytical method consisting of sonical extraction of the sample with C₆ and GC/MS analysis was validated for determining PAH in house dust and soil samples. With this method, the spiked PAHs were quantitatively recovered from dust and soil samples. The recoveries ranged from 91 (fluorene-d₁₀) to 100 (pyrene-d₁₀) percent in the dust samples and from 91 (fluorene-d₁₀) to 98 (benzo(k)fluoranthene-d₁₂) percent in the soil samples.

An analytical method for determining PCB in the dust and soil samples was validated. This method consists of

- 1) sonical extraction of the sample with 10 percent ether in C₆,
- 2) silica gel fractionation of the sample extract, and
- 3) GC/MS analysis of the target fraction.

The recoveries of spiked ¹³C-labeled PCB ranged from 91 (4-chlorobiphenyl (¹³C₆)) to 99 percent (3,3',4,4'-tetrachlorobiphenyl (¹³C₁₂)) in the dust samples and from 90 (2,2',3,3',5,5',6,6'-octachlorobiphenyl (¹³C₁₂)) to 93 percent (3,3',4,4'-tetrachlorobiphenyl (¹³C₁₂)) in the soil samples.

The sum of the target PAH concentrations in house dust ranged from 16 to 580 µg/g (ppm) in samples collected before the 1992-1993 heating season and from 25 to 310 ppm in samples collected after the heating season. PAH concentrations were higher in entryway soil samples than in the corresponding house dust samples. The sum of PAH concentrations in entryway soil samples ranged from 66 to 4000 ppm and 58 to 5500 ppm in samples collected before and after the heating season, respectively. The sum of PAH concentrations ranged from 3.0 to 1200 ppm and 0.58 to 610 ppm in pathway soil samples collected before and after the heating season, respectively. The sum of

PAH concentrations in foundation soil samples collected after the heating season ranged from 0.63 to 63 ppm.

The concentrations of those PAHs that are probable human carcinogens (designated as B-2 PAH) account for roughly half of the concentrations of the sum of all target PAHs in most dust and soil samples. With few exceptions, the general concentration trend for the PAH in the house dust samples was entryway soil > house dust > pathway soil > foundation soil. The concentrations of the 4- to 6-ring PAH, B-2 PAH, and the sum of all target PAH in entryway soil samples correlate well with the corresponding levels in house dust samples. However, there is no correlation between the PAH concentrations in house dust and in pathway soil samples. Nor does any relation exist between the PAH concentrations in house dust and in foundation soil samples. This absence of a relationship is probably due to differences in environmental weathering effects on pathway and foundation soils compared with the effects on house dust and entryway soils. The effect of track-in could be a significant factor contributing to PAH levels in house dust, and more studies are needed to investigate this factor. The presence of environmental tobacco smoke is not the only important source of PAH in house dust. Furthermore, there is no evidence that PAH magnification occurs in foundation soil samples.

The sum of the target PCB concentrations in house dust samples varied between 210 and 1900 ng/g (ppb) and, in entryway soil samples, ranged from 30 to 880 ppb. The sum of the PCB concentrations ranged from 16 to 500 ppb and from 18 to 210 ppb in pathway soil and foundation soil samples, respectively. All these samples were collected during April 1993. The PCB concentrations are lower than the PAH concentrations in all house dust, entryway soil, pathway soil and foundation soil samples. Unlike PAH, the general

concentration trend for PCB was house dust > entryway soil > pathway soil. Similar PCB concentrations were found in pathway soil and foundation soil samples. As in the case of the PAH, there is no evidence of PCB magnification occurring in foundation soil. The concentrations of penta-PCB, hexa-PCB, and total PCB house dust samples correlate well with those in entryway samples. However, there is no significant correlation for mono-, di-, tri-, and tetra-PCB concentrations in house dust and entryway soil samples, which is probably due to the low concentrations of these PCB compounds. There is also no correlation between the sum of the PCB concentrations in house dust and pathway soil samples. Furthermore, there is no relationship between the PCB concentrations in house dust and in foundation soil.

There are several important issues that remain to be addressed in order to assess exposure due to house dust and soil. In future studies, we recommend

- 1) Measuring the PAH in house dust, entryway soil, pathway soil and foundation soil in a sufficiently large sample of homes located in the same community as House H08 in this study, in order to investigate whether the high PAH concentrations observed in the house dust and soil at this house are also found in these samples.
- 2) Conducting a similar study in a city in a colder climate with a history of coal burning.
- 3) Conducting a similar study in a city in a mountain valley with a history of wood burning.
- 4) Conducting a similar study in a city with heavy traffic.
- 5) Determining the effect of track-in and dust control techniques on exposure to PAH in house dust.



