Evaluation and Application of Methods for Estimating Children's Exposure to Persistent Organic Pollutants in Multiple Media

by

Jane C. Chuang, Christopher Lyu, Ying-Liang Chou, Patrick J. Callahan,
Marcia Nishioka, Kimberlea Andrews, Mary A. Pollard, Laura Brackney,
Charles Hines, Dave B. Davis, and Ronald Menton
Battelle
505 King Avenue
Columbus,Ohio 43201-2693

Volume I: Final Report

Contract Number 68-D4-0023
Work Assignment 3-06

Project Officer

Nancy K. Wilson
Human Exposure and Atmospheric Sciences Division
National Exposure Research Laboratory
Research Triangle Park, North Carolina 27711

National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

EPA DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under EPA Contract Number 68-D4-0023 to Battelle Memorial Institute. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

BATTELLE DISCLAIMER

Battelle does not engage in research for advertising, sales promotion, or endorsement of our clients' interests including raising investment capital or recommending investment decisions, or other publicity purposes, or for any use in litigation.

Battelle endeavors at all times to produce work of the highest quality, consistent with our contract commitments. However, because of the research and/or experimental nature of this work the client undertakes the sole responsibility for the consequences of any use, misuse, or inability to use, any information, apparatus, process or result obtained from Battelle, and Battelle, its employees, officers, or Trustees have no legal liability for the accuracy, adequacy, or efficacy thereof.

Foreword

The mission of the National Exposure Research Laboratory (NERL) is to provide scientific understanding, information and assessment tools that will quantify and reduce the uncertainty in EPA's exposure and risk assessments for environmental stressors. These stressors include chemicals, biologicals, radiation, and changes in climate, land use, and water use. The Laboratory's primary function is to measure, characterize, and predict human and ecological exposure to pollutants. Exposure assessments are integral elements in the risk assessment process used to identify populations and ecological resources at risk. The EPA relies increasingly on the results of quantitative risk assessments to support regulations, particularly of chemicals in the environment. In addition, decisions on research priorities are influenced increasingly by comparative risk assessment analysis. The utility of the risk-based approach, however, depends on accurate exposure information. Thus, the mission of NERL is to enhance the Agency's capability for evaluating exposure of both humans and ecosystems from a holistic perspective.

The National Exposure Research Laboratory focuses on four major research areas: predictive exposure modeling, exposure assessment, monitoring methods, and environmental characterization. Underlying the entire research and technical support program of the NERL is its continuing development of state-of-the-art modeling, monitoring, and quality assurance methods to assure the conduct of defensible exposure assessments with known certainty. The research program supports its traditional clients -- Regional Offices, Regulatory Program Offices, ORD Offices, and Research Committees -- and ORD's Core Research Program in the areas of health risk assessment, ecological risk assessment, and risk reduction.

Human exposure to multimedia contaminants, including persistent organic pollutants (POP) is an area of concern to EPA because of the possible mutagenicity and carcinogenicity of these compounds. These compounds originate from industrial processes and combustion and are present in a variety of microenvironments. The efforts described in this report provide an important contribution to our ability to measure and evaluate human exposure to pollutants.

Gary J. Foley
Director
National Exposure Research Laboratory

Abstract

The objectives of this work assignment were to evaluate field methods for determining children's exposure to selected persistent organic pollutants (POP), including polycyclic aromatic hydrocarbons and other semi-volatile organic compounds (SVOC), to use these methods to estimate the ranges of the potential exposures through air, dust, and food, and to estimate the ranges of total exposures for a small set of children from low-income and middle-income families.

The study was carried out in two phases to accomplish the above objectives. In Phase 1, we evaluated the sampling and analysis methods for monitoring target POP in multimedia samples and conducted a field study at nine daycare facilities. The target POP consisted of multiple compound classes: polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyl (PCB), phthalate esters (PE), phenols (Ph), organochlorine (OC) pesticides, organophosphate (OP) pesticides, and a herbicide acid (HA). The sample media included air, dust, soil, duplicate diet food, dermal wipes and urine. We applied the field methods to a field study of nine daycare facilities to monitor target POP in multiple environmental media and food. Nine daycare centers (four Head Start and five private centers) in North Carolina were recruited for the study. Samples (air, dust, soil, and food) were collected from these daycare centers and analyzed for target POP. In Phase 2, nine children were recruited as subjects from two of the nine daycare centers. The multimedia samples (air, dust, soil, food, and wipes) were collected from the daycare centers and from the subjects' homes. These samples were analyzed for target POP. In addition, urine samples were collected from the subjects. The urine samples were analyzed for selected POP and urinary POP metabolites.

This report was submitted in fulfillment of Work Assignments 2-01 and 3-06, Contract 68-D4-0023, to Battelle under the sponsorship of the United States Environmental Protection Agency. This report covers the period from January 1, 1997 to May 12, 1998, and work was completed as of May 12, 1998.

Contents

Forward iii
Abstract iv
Figures viii
Tables ix
Abbreviations xii
Acknowledgment xiii

Chapter 1 Introduction 1
Chapter 2 Conclusions 5
Chapter 3 Recommendations 9
Chapter 4 Experimental Procedures 15
Method Validation for Multimedia Samples 15
Air Samples 15
Dust and Soil Samples 17
Dermal Wipe Samples 18
Urine Samples 19
Food Samples 20
Phase 1 Field Study of Nine Daycare Centers 22
Selection of Daycare Centers 23
Field Monitoring Activities 24
Sampling Methods 28
Analytical Methods 29
Data Analysis 32
Phase 2 Field Study in Two Daycare Centers and Nine Homes 36
Selection of Homes 36
Field Monitoring Activities 37
Sampling Methods 41
Analytical Methods 42
Statistical Analysis 42
Estimates of Daily Persistent Organic Pollutants Doses 44

Contents (Continued)

Chapter 5 Results and Discussion 46
Method Validation for Multimedia Samples 46
Air Samples 46
Dust and Soil Samples 50
Dermal Wipe Samples 55
Urine Samples 55
Food Samples 57
Phase 1 Field Study 60
Recruiting of Day Care Centers 60
Field Activities 61
Concentrations of Persistent Organic Pollutants in Multimedia Samples 62
Data Analysis for Phase 1 Study 70
Summary Statistics 70
Correlation Between Sample Media 72
Correlation Between Compound Classes 74
Estimates of Daily Persistent Organic Pollutant Exposures 76
Quality Control Data for Phase 1 Study 79
Phase 2 Field Study 81
Recruiting of Subjects 81
Field Activity 82
Concentrations of Persistent Organic Pollutants in Multimedia Studies 83
Summary Statistics 91
Correlation Between Sample Media 93
Correlation Between Compound Classes 93
Daily Potential Doses of Persistent Organic Pollutants 96
Concentration Profiles of Urinary Metabolites 100
Analysis of Variance 104
Regression Models 108
Quality Control Data for Phase 2 Study 113

References 114

Contents (Continued)

Appendices

A Analytical Procedures for Duplicate Diet Food Samples A-1
B Phase I Field Study B-1
C Phase 2 Field Study C-1
D Measured Target Persistent Organic Pollutant Concentrations in Air, Dust, Soil, and Food Samples in Phase 1 Study D-1
E Summary Statics for Measured Target Persistent Organic Pollutant Concentrations in Air, Dust, and Food Samples in Phase 1 Study E-1
F Spearman and Pearson Correlation Coefficients of Persistent Organic Pollutants Between Sample Media F-1
G Spearman and Pearson Correlation Coefficients in Multimedia Samples Between Compound Classes G-1
H Estimated Children's Daily Persistent Organic Pollutants Exposure Levels in Phase 1 Daycare Centers from Inhalation, Nondietary Ingestion, and Ingestion Pathways H-1
I Summary Statistics for Estimated Children's Daily Persistent Organic Pollutant Exposure Levels in Phase 1 Daycare Centers I-1
J Summary of Recoveries Data of the Spiked Persistent Organic Pollutants in Phase 1Multimedia Samples J-1
K Results of Duplicate Air, Dust, and Food Samples K-1
L Levels of Target Persistent Organic Pollutants Found in Phase 1 Field Blanks . L-1
M Target Persistent Organic Pollutants Concentrations in Phase 2 Multimedia Samples M-1
N Summary Statistics for Phase 2 Data in Multimedia Samples N-1
O Spearman and Pearson Correlation Coefficients Between Sample Media for Persistent Organic Pollutants O-1
P Spearman and Pearson Correlation Coefficients Between Compound Classes in Multimedia Samples P-1
Q Summary of Analysis of Variance Results Q-1
R Regression Results of Urinary Metabolites Versus Environmental Sample Media and Total Daily Potential Persistent Organic Pollutant Doses R-1
S Summary of Recovery Data of the Spiked Persistent Organic Pollutants in Phase 2 Multimedia Samples S-1
T Levels of Target Persistent Organic Pollutants Found in Phase 2 Field Blanks . T-1

Figures

Figure 4.1. Locations of ten daycare centers in the Phase 1 Field Study 25

Figure 4.2. Locations of nine homes in the Phase 2 Field Study 39

Figure 4.3. Sampling schedule for the Phase 2 Field Study. 40

Figure 5.1. Distributions of average daily exposure of persistent organic pollutants from Phase 1 daycare centers 78

Figure 5.2. Average daily persistent organic pollutant exposures in Head Start centers and other centers 80

Figure 5.3. Distributions of average daily potential dose of persistent organic pollutants from homes for nine subjects 97

Figure 5.4. Distributions of average potential daily dose of persistent organic pollutants from daycare centers for nine subjects 98

Figure 5.5. Distributions of average daily potential dose of persistent organic pollutants from homes and daycare centers for nine subjects 99

Figure 5.6. Average potential daily persistent organic pollutants doses from at-home exposures in low- and middle-income subjects 101

Figure 5.7. Average potential daily persistent organic pollutants doses from at-center exposures in low- and middle-income subjects 102

Figure 5.8. Average potential daily persistent organic pollutant doses from at-home and at-center exposures in low- and middle-income subjects 103

Figure 5.9. Average concentrations of 2,4-D and 3,5,6-TCP in subjects' urine samples 105

Figure 5.10. Average concentrations of 1-naphthol, 2-naphthol, and pentachlorophenol in subjects' urine samples 106

Tables

Table 3.1. Hypotheses to be Tested in Proposed Large-scale Study 10

Table 3.2. Minimal Sample Sizes Required to Detect a Difference in Persistent Organic Pollutant Exposures Between Two Groups of Children Based on a Two Sample t-test Conducted at the Five Percent Significance Level 13

Table 3.3. Proposed Distribution of Children for the Large-Scale Study 14

Table 4.1. Summary of Daycare Centers in Phase 1 Study 26

Table 4.2. Field Monitoring Activities in Each Daycare Center 27

Table 4.3. Summary of Analytical Methods for Each Type of Samples from Phase 1 Study 30

Table 4.4. Estimated Detection Limits of Target Persistent Organic Pollutants in Multimedia Samples 33

Table 4.5 Summary of Subjects/Homes in Phase 2 Study 38

Table 5.1. Recovery of Target Persistent Organic Pollutants from Filter/XAD-2 Samples 47

Table 5.2. Recovery of Target Persistent Organic Pollutants from Filter/PUF Samples . . 48

Table 5.3. Recovery of Non-Coplanar Polychlorinated Biphenyls from Filter/XAD-2 Samples 49

Table 5.4. Recovery of 2,4-D and Pentachlorophenol from Filter/PUF Samples 51

Table 5.5. Recovery of Target Persistent Organic Pollutants from Spiked House Dust Samples 52

Table 5.6. Recovery of Target Persistent Organic Pollutants from Spiked Soil Samples 53

Tables (Continued)

Table 5.7. Recovery of Target Persistent Organic Pollutants from Spiked Dermal Wipe Samples 56

Table 5.8. Recovery of Target Analytes from Spiked Urine Samples 57

Table 5.9. Recovery of 3.5,6-TCP from Spiked Urine Samples 58

Table 5.10 Recovery of Target Persistent Organic Pollutants from Spiked Solid Food Samples 59

Table 5.11. Summary of Recruiting Daycare Centers for Phase 1 Study 61

Table 5.12. Summary of Target Persistent Organic Pollutants Determined in Multimedia Samples 63

Table 5.13. Summary of Target Persistent Organic Pollutants in Air Samples from Phase 1 Day Care Centers 64

Table 5.14. Summary of Target Persistent Organic Pollutants in Dust and Soil Samples From Phase 1 Day Care Centers 65

Table 5.15. Summary of Target Persistent Organic Pollutants in Liquid and Solid Food Samples from Phase 1 Daycare Centers 66

Table 5.16. Floor Dust Loadings from Phase 1 Day Care Centers 68

Table 5.17. Summary of Pairs of Sample Media with Significant Correlation Coefficients for Target Compound Classes 73

Table 5.18. Summary of Pairs of Compound Classes with Significant Correlation Coefficients for Each Sample Medium 75

Table 5.19. Correlation Coefficients Between Floor Dust (HVS3) and Floor Dust (Bag) 77

Tables (Continued)

Table 5.20. Summary of Recruiting Children from Daycare Centers D03 and D09 for Phase 2 Study 82

Table 5.21. Summary of Target Persistent Organic Pollutants in Air Samples from Phase 2 Study 84

Table 5.22. Summary of Target Persistent Organic Pollutants in Dust and Soil Samples From Phase 2 Study 85

Table 5.23. Summary of Target Persistent Organic Pollutants in Liquid and Solid Food Samples from Phase 2 Study 86

Table 5.24. Summary of Target Persistent Organic Pollutants in Dermal Wipe Samples From Phase 2 Study 87

Table 5.25. Floor Dust Loadings from Phase 2 Daycare Centers and Households 89

Table 5.26. Summary of Pairs of Sample Media with Significant Correlation Coefficients for Target Compound Classes 94

Table 5.27. Summary of Pairs of Compound Classes with Significant Correlation Coefficients for Each Sample Medium 95

Table 5.28. Summary of Anova on the Effect of Sampling Location: Daycare Centers Versus Homes 107

Table 5.29. Summary of Anova on the Effect of Family Income: Low-income Versus Middle-income 109

Table 5.30. Summary of Anova on the Effect of Family Income and Sampling Location: Head Start Center and Low-Income Versus Regular Center and Middle-Income 110

Table 5.31. Summary of Regression Model Results 112

Acronyms and Abbreviations

ANOVA	analysis of variance
BDL	below detection limit
DCM	dichloromethane
ECD	electron capture detection
EE	diethylether
EI	electron impact
ELISA	enzymed linked immunosorbent assay
ETS	environmental tobacco smoke
GC/MS	gas chromatography/mass spectrometry
GPC	gel permeation chromatography
HA	herbicide acid
HCl	hydrochloric acid
HP	Hewlett Packard
HVS3	High Volume Small Surface Sampler
MTBSTFA	N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide
N	sample size
NaCl	sodium chloride
N-BDL	number of samples below detection limit
NERL	National Exposure Research Laboratory
OC	organochlorine
OMB	Office of Management and Budget
OP	organophosphate
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PCP	pentachlorophenol
PE	phthalate esters
Ph	phenols
POP	persistent organic pollutants
PUF	polyurethane foam
QA	quality assurance
SIM	selected ion monitoring
SPE	solid phase extraction
SRS	analytical surrogate recovery standard
SVOC	semi-volatile organic compounds
3,5,6-TCP	3,5,6-trichloro-2-pyridinol
URG	University Research Glass
WA	Work Assignment

Acknowledgment

We thank Dr. Nancy K. Wilson of the U.S. EPA for her invaluable advice and participation during this investigation.

Chapter 1

Introduction

In 1992, the National Academy of Sciences identified polycyclic aromatic hydrocarbons (PAH) and related semi-volatile organic compounds (SVOC) as among the compound classes of highest priority for exposure research. Many of these compounds are persistent organic pollutants (POP) and are possible endocrine disrupters or may have other quasi-hormonal or reproductive effects. Many POP are sufficiently volatile or soluble to evaporate and condense, or move otherwise through environmental media, including air, water, and soil. The POP can also enter indoor microenvironments through outdoor air intrusion or through track-in and other means of transport (1,3). Additionally, there are many potential sources of POP indoors, including environmental tobacco smoke (ETS), consumer products, building materials, and home chemicals.

Young children have immature organs, immune systems, and nervous systems that make them more susceptible than adults to the potential health effects of toxic chemicals such as POP. Their major sources of exposure can be expected to be found indoors, because young children spend a lot of their time indoors (e.g., homes, daycare centers). Children can be exposed to POP by inhaling contaminated air, ingesting tainted food, ingesting nondietary substances, or absorbing pollutants through the skin from contaminated media. Exposures resulting from ingestion of dust and soil are believed to be important for young children, because they play on the floor or ground, and they tend to put many dirty food and non-food items into their mouths (4). Indoor carpets, furnishings, and dust can serve as reservoirs for POP, and thus are potential sources for human exposure to these compounds.

In previous work, methods to measure and estimate the exposures of children in low-income families to PAH were evaluated (5,6). However, such methods are incompletely developed and evaluated in field situations for estimating total exposure to POP, which include compound classes such as chlorinated organic compounds, substituted phenols, and phthalate esters. Little information is available in the literature regarding the determination of urinary metabolites of these compound classes.

Thus, small-scale POP exposure studies were carried out to obtain information for designing future large-scale POP exposure studies on children. We evaluated field methods for determining children's exposure to selected POP in multiple compound classes through multiple environmental media and conducted two field studies in selected daycare centers and in subjects' homes. We also validated an analytical method for determining 3,5,6-trichloro-2-pyridinol (3,5,6-TCP), a urinary metabolite of chlorpyrifos, to determine 3,5,6-TCP in collected urine samples, and we conducted statistical analysis of collected data.

The objectives were to evaluate field methods for determining children's exposure to selected POP, including PAH and other SVOC, to use these methods for estimating the ranges of the potential exposures through inhalation, ingestion, and dermal contact, and to estimate the ranges of total exposures for a small set of children from low-income and middle-income families.

In the first phase of this work, sampling and analysis methods for POP in multiple environmental matrices: air, dust, soil, dermal wipes, and food were evaluated and validated. Nine daycare centers located in and near Durham, North Carolina were recruited, and the informed consent forms were signed by the directors of the daycare centers prior to the start of any field sampling activities. Multimedia environmental samples (air, dust, and soil) and duplicate diet food samples were collected from these daycare centers. The target POP included multiple compound classes: PAH, phthalate esters (PE), phenols (Ph), polychlorinated biphenyls (PCB), organochlorine (OC) pesticides, organophosphate (OP) pesticides, and a herbicide acid (HA), 2,4-dichlorophenoxyacetic acid (2,4-D). In the second phase, nine children from two of

the daycare centers were recruited. These children were between the ages of two and five and spend at least 25 hr/week in daycare. Informed consent was obtained from each of the directors of the daycare centers and from the subjects' parent(s) prior to any field monitoring activities. Multimedia environmental samples were collected from the two daycare centers and the nine subjects' homes. In addition, duplicate diet food, urine, and dermal wipe samples from the nine subjects were collected both at their homes and at the daycare centers.

The specific tasks to accomplish the objectives of the two related studies were:

1. Prepare a work plan and quality assurance (QA) narrative and submit it for EPA review and approval.

2. Prepare informed consent forms, questionnaires, activity diaries, and study protocols. These were based on those developed previously under Cooperative Agreement CR822073 and modified appropriately for this study.

3. Obtain Human Subjects Committee approval (IRB approval).

4. Validate the sampling and analysis methods.

5. Find and recruit nine daycare centers for participation in the Phase 1 study.

6. Collect environmental samples from indoor and outdoor air, carpet dust, playground soil, and food at the nine daycare centers. Analyze the samples for the target POP.

7. Recruit a total of nine child subjects for the Phase 2 study from two of the Phase 1 daycare centers: four subjects from a Head Start center and five subjects from another daycare center.

8. Conduct a study of the total POP exposure of the children recruited above, having separate samples of each matrix per child from daycare and home environments.

9. Analyze the archived sample extracts of air, dust, and soil, obtained from the PAH exposure study under CR822073, for chlorpyrifos.

10. Analyze urine samples in the Phase 2 and in the PAH exposure studies for chlorpyrifos.

11. Conduct statistical analysis of the data and interpret the results.

12. Prepare this final report on the results of the studies in EPA ORD format.

Chapter 2

Conclusions

The sampling and analysis methods for persistent organic pollutants (POP) in multimedia samples were evaluated and validated. We used quartz fiber filter/XAD-2 as a sampling module for collection of POP for polycyclic aromatic hydrocarbons (PAH), phthalate esters (PE), organochlorine (OC), and organophosphate (OP) pesticides, polychlorinated biphenyls (PCB) and substituted phenols (Ph) in air, and Teflon-coated glass filter/PUF for collection of a herbicide acid (HA), 2,4-D. One analytical method — for air samples collected on filter/XAD-2 -- was validated for determining POP in all compound classes except 2,4-D. A separate analytical method was validated for the determination of 2,4-D in air samples collected on filter/PUF. The recoveries of target POP in all compound classes in air samples were, in general, greater than 70%. The overall method precision for the two methods, for all target POP except PE, was within ± 17% for the air samples. The greater variation observed in PE measurements was from the high background levels of PE. Target POP were also stable in the respective sampling modules over the 20-day storage interval.

Three analytical methods were validated to determine target POP in dust/soil. One method was for compound classes PAH, PE, OC, OP, and PCB, one for Ph, and one for HA. The POP recoveries in dust/soil were greater than 80% for most compound classes. As in the case of the air samples, greater precisions were observed in the measurement of PE in dust/soil.

An analytical method was validated to determine PAH, OC, OP, and PCB in dermal wipe samples. The overall method precision was ±30% for most target POP. Quantitative recoveries (>70%) of the spiked POP were achieved.

One analytical method was evaluated and validated for the determination of hydroxy PAH, pentachlorophenol (PCP), and 2,4-D in urine samples. The recoveries ranged from 75 to 110% and the precision was within ± 45%. A different method was used for the determination of 3,5,6-TCP in urine samples. The recoveries of 3,5,6-TCP were greater than 90%, with precision less than ± 5%.

An analytical method was developed for analyzing POP for all compound classes in foods. Quantitative recoveries (>50%) were obtained for most target POP, and precision was in general within ± 22%. The low recoveries for bisphenol-A and 2,4-D were probably due to losses through the gel permeation chromatography (GPC) or solid phase extraction (SPE) cleanup steps. The analytical method used for the food samples in this study needs to be revised to provide better accuracy and precision for compound classes such as Ph and HA.

In the Phase 1 field study, target POP concentrations in indoor air were, in general, higher than those in outdoor air. Some target compounds in the PAH, OC, and PCB classes were not detected in the air samples. Target POP concentrations in floor dust were generally higher than those in the playground soil. Most OC compounds and PCB were not found in the playground soil. Concentrations of POP in solid foods were usually higher than those in liquid foods. None of the target PCB were found in Phase 1 food samples and only a few PCB were detected in Phase 2 food samples. The most abundant POP in all sample media were phthalate esters in both Phase 1 and 2 samples.

Differences in POP concentrations in multimedia samples between Head Start daycare centers and private daycare centers were small, with the exception of PAH in playground soil. Average concentrations of PAH in the playground soil of Head Start centers were significantly higher than those at the private centers. The difference in these averages was primarily due to the extremely high levels of PAH found in the playground soil of center D01, where the PAH

levels were the highest among all Phase 1 and 2 dust and soil samples. Such high PAH levels could have come from local contamination sources. The estimated daily POP exposures from daycare centers were similar between Head Start centers and private daycare centers.

In the Phase 2 field study, POP concentration profiles in air, dust, soil, and food were generally similar to those seen in the Phase 1 samples. With few exceptions, differences in POP concentrations in these multiple sample media were small between daycare centers and homes, as well as between low-income and middle-income families. In addition, dermal wipe and urine samples were collected from each subject both at home and at the center. Differences in POP levels in wipes and urinary metabolites between these groups (home vs. daycare and low-income vs. middle-income) were also small.

The correlation of POP concentrations in different sample media was investigated separately for Phase 1 and Phase 2 data. Despite the small sample size, direct relationships between indoor air and floor dust for target POP in PAH, OC, and OP were seen in both Phase 1 and Phase 2 samples. Since collection of floor dust samples required less effort as opposed to air samples, it is feasible to collect floor dust samples for screening POP in future large-scale exposure studies. The correlation of POP in each compound class with each other compound class was also investigated separately for Phase 1 and 2 data. A direct relationship between B2 PAH (probable human carcinogens classified by U.S. EPA Integrated Risk Information System) and total PAH was observed for dust, soil, and solid food. Since B2 PAH and total PAH are in the same compound class, one expects to see a strong relationship. A strong relationship between B2 PAH and total PAH in dust and soil was also observed in our previous PAH exposure study (5,6). There were a few significant correlations between compound classes for target POP, but they were not consistent between the Phase 1 and Phase 2 data, for which the sample size was small.

The relative importance of the exposure pathways (inhalation, nondietary ingestion, dietary ingestion) from the exposures at the daycare centers in Phase 1 data was similar to those for the Phase 2 data. The differences in the distributions of exposure pathways from at-home

exposures and at-center exposures in Phase 2 data were small. The relative rank importance of the exposure pathways for the children's total daily potential doses of POP was different among the compound classes. For total daily potential doses of total target PAH, organochlorine and organophosphate pesticides, and PCB, the relative importance of exposure pathways was inhalation > dietary > nondietary; for total daily potential doses of phthalate esters, substituted phenols, and 2,4-D, it was dietary > nondietary > inhalation. Nondietary ingestion was the most important pathway for the total daily potential dose of B2 PAH.

Differences in POP concentrations in most multiple sample media between the groups of at-home versus at-center and low-income versus middle-income were not statistically significant. Significantly higher concentrations of PCB in air as well as total PAH and total phenols in foods were obtained in the samples collected at daycare centers as opposed to homes. Lower concentrations of organophosphate pesticides in outdoor air were seen in the samples from daycare centers. Low-income subjects had higher levels of phthalate esters and organochlorine pesticides and lower levels of total PAH in their wipe samples. Higher concentrations of hydroxy-PAH and 2,4-D, but lower concentrations of pentachlorophenol (PCP) and 3,5,6-TCP were found in urine samples from low-income subjects. With one exception PCP, there were no strong positive relationships between the urinary metabolites and POP in multimedia samples, as well as urinary metabolites and total daily potential doses of POP. Concentrations of PCP in the children's urine samples were significantly related to the subjects' total daily dose of PCP.

Chapter 3

Recommendations

We recommend that a large-scale field study of children's exposure to persistent organic pollutants (POP) be conducted, using the methods evaluated in this study. The results of a previous study (5,6) demonstrated that children's potential daily doses (ng/kg/day) of B2-PAH (probable human carcinogens) were higher than those of adults in each of 24 low-income households. Among those children of low-income families, inner city children appeared to have higher polycyclic aromatic hydrocarbons (PAH) exposure than rural children. Both the dietary and nondietary ingestion pathways were important for children's exposure to B2-PAH. Results from the current studies have also shown that dietary ingestion is the most important exposure pathway for phthalate esters (PE) and phenols (Ph). However, inhalation appears to be an important pathway for children's exposure to other POP, including total PAH, polychlorinated biphenyls (PCB), organochlorine (OC), and organophosphate (OP) pesticides. Children's exposures to POP from the day care centers they attend appears to be as important as exposure from their homes.

An important question is whether children in low-income families could have higher exposure to some POP than children in higher-income families. These higher exposures could derive from the location of their homes, from the location of the day care centers they attend, from the presence of environmental tobacco smoke (ETS), or from other causes. A general outline for conducting a study to explore these issues follows.

The main objective of the proposed study that we propose would be to obtain additional data on children's exposures to POP and to determine whether low-income children are at greater

POP exposure. A secondary objective is to examine the relative importance of the exposure pathways for POP in various compound classes. A third objective is to examine the effectiveness of utilizing less expensive screening tools for monitoring POP exposure. The specific hypotheses to be tested are summarized in Table 3.1.

TABLE 3.1. HYPOTHESES TO BE TESTED IN PROPOSED LARGE-SCALE STUDY

Objective	Hypothesis
Determine children's POP exposure profiles and investigate impact of SES on children's exposure to POP	Exposure to POP of low-income children is/is not higher than those of higher-income children
Investigate impact of sources by media on POP exposure	Exposure from a source(s) is/is not different in air, soil, dust, and food for different compound classes
Investigate impact of sources in homes and in day care centers on POP exposure	Exposure to POP at home is/is not equal to those at day care centers
Investigate contributions of pathways to total POP exposure	Exposure from different pathways is/is not equal and distributions are/are not equal for different compound classes
Investigate the association between screening methods versus conventional methods	Exposure measured by screening methods (ELISA and PAH monitor) does/does not correlate well with conventional methods
Investigate the association among various estimates of POP exposure	Exposure estimates from floor dust measured by HVS3 do/do not correlate well with those measured using vacuum bags. Exposure measured by multiple environmental media does/does not correlate well with biological markers. Exposures from various media do/do not correlate with each other

Sample size calculations were conducted to determine the minimum sample size required to statistically distinguish between POP exposures of children in low- and middle-income families. Sample sizes were calculated for the first hypothesis, which is the primary objective of the Battelle-proposed study. To support the sample size calculations, data on childhood POP exposures from the previous study under Cooperative Agreement CR822073 and the current study Phases 1 and 2 were first reviewed. The review assessed the distribution and variability of POP concentrations in floor dust, indoor and outdoor air, solid and liquid food, and soil for seven target POP, namely, B2 PAH, OP, PE, Ph, diazinon, chlorpyrifos, and bisphenol-A. In addition, the distribution of OH-PAH in urine was reviewed. It was found that

1. POP concentrations tend to be lognormally distributed.

2. While there are differences in the variability of POP concentrations among the six media and in urine, the standard deviations of log-transformed (ln) POP concentrations generally range from 0.50 to 2.0.

3. Differences in geometric mean POP concentrations between low-income and higher-income families as well as between daycare centers and homes generally range from 0 to 500%, between city and rural areas, they range from 0 to 150%, and between smoker and non-smoker houses, they range from 0 to 250% (B2-PAH only), depending on the compound and media.

Based on the analysis of the historical and current data the calculations were performed with the following assumptions:

1. A two-sample t-test is conducted at the 5 percent significance level on ln-transformed POP to compare the POP exposures in the following groups of children:

   - low-income families versus middle-income families,
   - at daycare centers versus at home,
   - inner city versus rural areas,
   - smokers' homes versus nonsmoker's homes.

The comparison of POP exposures in smoker versus non-smoker houses was performed only on B2 PAH, because only these two groups have data from the PAH exposure studies.

2. Sample sizes were computed that provide 80 or 90 percent power for detecting a significant difference between the two groups when the actual percent difference ranges from 10 to 200 percent. (The power represents the level of confidence desired to detect a specified difference between the two groups. An experiment designed to have 90 percent power for detecting a specified difference will be more sensitive than one designed to have 80 percent.)

3. Sample sizes were computed assuming that the standard deviation of ln-transformed POP concentrations is either 0.5, 1, 1.5, or 2.

Table 3.2 summarizes the estimated sample sizes required to detect specific differences between any two groups of children, i.e. low- and middle-income children, at-center and at-home children, inner-city and rural children, or children from smoker's and nonsmoker's homes. For example, to detect a difference between two groups of children if the standard deviation of ln-transformed POP is 1.0 and the actual percent difference between the two groups is 100 percent, roughly 34 children are needed in each group to give 80% power. If the standard deviation of ln-transformed POP is 1.5, the number of children increases to approximately 75 per group.

For all seven target POP concentrations and all six media (floor dust, indoor and outdoor air, solid and liquid food, and soil), the median percent difference in POP concentrations between the two groups of children was 60 percent, and the median standard deviation in ln-transformed POP concentrations was 1.0. As shown in Table 3.2, if the standard deviation in ln-transformed POP concentrations is 1.0 and the actual percent difference between the two groups of children is 50 percent, then a sample size of approximately 100 children per group will provide 80 percent power for detecting a statistical difference in POP exposures between any two groups of children. Under the same conditions, a sample size of approximately 130 children per group provides 90 percent confidence that a statistical difference will be detected between the two groups. To allow for missing samples and other data issues, a sample size of 120 to 160 children per group is recommended.

We could recruit 120 children each from low-income and middle-income families (targeted at 80 % power) for the large-scale study. We could also recruit children who attend daycare centers and monitor these subjects at their homes and at the centers they attend. We could recruit at Head Start centers to target low-income families, and at private centers for middle-income families. Ideally, the 120 children in each group (low-and middle-income) should be evenly distributed in each subgroup, i.e., inner city versus rural, and smokers' versus nonsmokers' homes, in order to provide the same power. The distribution of children we proposed for the large-scale study is summarized in Table 3.3.

TABLE 3.2. MINIMAL SAMPLE SIZES REQUIRED TO DETECT A DIFFERENCE IN PERSISTENT ORGANIC POLLUTANT EXPOSURES BETWEEN TWO GROUPS OF CHILDREN BASED ON A TWO SAMPLE T-TEST CONDUCTED AT THE FIVE PERCENT SIGNIFICANCE LEVEL

Power	Estimated Standard Deviation[a]	Percent Difference Between Geometric Mean POP Exposures for Two Groups of Children[b]					
		10%	25%	50%	100%	150%	200%
80%	0.5	433	80	25	11	< 10	< 10
	1	1729	316	97	34	20	15
	1.5	3889	710	216	75	43	30
	2	6913	1,262	383	132	76	53
90%	0.5	579	107	33	12	< 10	< 10
	1	2314	423	129	45	26	19
	1.5	5206	951	289	99	57	40
	2	9255	1,689	512	176	101	71

(a) Standard deviation of ln-transformed POP concentrations.

(b) Two groups of children could be low- and middle-income children, at-center and at-home children, inner city and rural, or children from smokers and nonsmokers homes.

TABLE 3.3. PROPOSED DISTRIBUTION OF CHILDREN FOR THE LARGE-SCALE STUDY

	Head Start Centers/Low-Income		**Private Centers/Middle-Income**	
	Inner City	Rural Areas	Inner City	Rural Areas
Smokers	30	30	30	30
Nonsmokers	30	30	30	30

The large-scale POP exposure study could be conducted over a period of three years. In year one, the study design, questionnaires, consent forms and protocols would be prepared; the required approvals from the Office of Management and Budget (OMB), the Human Subjects Committee at Battelle, and the U.S. EPA would be obtained. In the second year, the field sampling and analysis activities would be performed and continued through the first quarter of the third year. Data analysis would be conducted in the remainder of the third year.

The overall technical approach would be as follows:

- Establish a study design
- Establish questionnaires, consent forms, and protocols
- Obtain required approval from Office of Management and Budget (OMB) and from Human Subjects Committee at Battelle and U.S. EPA
- Recruit eligible day care centers and households
- Conduct field sampling
- Analyze collected multi-media samples
- Conduct data analysis
- Prepare final report.

Chapter 4

Experimental Procedures

Method Validation for Multimedia Samples

Air Samples

Three sets of method validation tests were carried out using the standard 4-L/min University Research Glassware (URG) air sampler. Each sampler consisted of an inlet jet equipped with an impactor for 10 μm particle collection, a filter (quartz fiber or Teflon-coated glass) and a glass cartridge packed with either XAD-2 resin or polyurethane foam (PUF) plug. These tests consisted of measurements on (1) sampling retention efficiency and storage stability of persistent organic pollutants (POP) on XAD-2 and PUF, (2) sampling retention efficiency of non-coplanar polychlorinated biphenyls (PCB) on XAD-2, and (3) sampling retention efficiency of pentachlorophenol (PCP) and 2,4-D on a combined Teflon-coated glass fiber filter/PUF cartridge. For the first set of tests, four sampling units, each consisting of three quartz fiber filter/XAD-2 sampling modules, were placed in a clean laboratory room at Battelle. Prior to sampling, six of the twelve XAD-2 traps were spiked with known amounts of the representative POP in multiple compound classes, which are: polycyclic aromatic hydrocarbons (PAH), coplanar PCB, phthalate esters (PE), phenols (Ph), organochlorine (OC) and organophosphate (OP) pesticides. The remaining six traps were not spiked with POP, nor were the filters spiked with any target POP. Spiking was performed by injecting 100 μL of the spiking solution (100 ng/compound) into the center of the XAD-2 resin bed at about 1-cm depth, followed by 5 min of air-drying. Indoor air was sampled at a flow rate of 4 L/min for 48 hours with the 12 samplers. These experiments were repeated under the same conditions except that the quartz fiber filter/XAD-2 sampling module was replaced with a quartz fiber filter/PUF sampling module.

After sampling, three of the spiked and three of the non-spiked filter/XAD-2 samples were extracted with dichloromethane (DCM) by the Soxhlet technique; filter and sorbent were combined for extraction. The filter/PUF samples were extracted with 10 % diethylether (EE) in hexane instead of DCM. Four of the remaining samples, two spiked and two non-spiked, were stored at 4 C in the dark for 10 days before extraction. The remaining two samples, one spiked and one non-spiked, were stored in the same way for 20 days before extraction. The sample extracts were concentrated to 1 mL by Kuderna-Danish evaporation and analyzed by gas chromatography/ mass spectrometry (GC/MS) for the target POP. To improve the chromatographic peak shape for PCP, the sample extracts were methylated using diazomethane and then reanalyzed by GC/MS for PCP.

For the second experiment, known amounts of 13 non-coplanar PCB (100 ng/compound), were spiked into the XAD-2 portion of two quartz filter/XAD-2 sampling modules. Air sampling, at 4 L/min for 48 hours was carried out with these two spiked modules and one non-spiked filter/XAD-2 trap. Samples were extracted with DCM immediately after sampling and analyzed by GC/MS.

In the third set of experiments, known amounts of PCP and 2,4-D (100 ng/compound) were spiked onto the filters of three Teflon-coated glass filter/PUF sampling cartridges. The filters were spiked in this experiment because prior studies have shown that 2,4-D is retained exclusively on the filter except under conditions of very high humidity. The retention characteristics of PCP with this sampling module were not known. Two non-spiked sampling modules were used as blanks. Air sampling at 4 L/min was conducted with these five samplers for 48 hours. Samples were stored for 10 days prior to extraction. Filters and PUF were extracted and analyzed separately using methods previously developed for 2,4-D, with minor modification for retention of PCP in the hexane partition step (2). This modification included removal, via Turbo-vap evaporation, of the acetonitrile from the extraction solvent prior to the hexane partition cleanup step. Analyses were carried out using a GC/electron capture detection (ECD) method.

Dust And Soil Samples

Three sets of method validation tests were conducted to determine POP in all compound classes of interest except Ph and HA, in dust and soil. These experiments consisted of (1) sonication extraction with hexane with no cleanup, (2) sonication extraction with DCM followed by silica SPE cleanup, and (3) sonication extraction with 10 % EE in hexane followed by Florisil SPE cleanup.

In the first set of experiments, nine aliquots of a house dust sample (0.5g each) and nine aliquots of a pathway soil sample (1g each) were used. Three aliquots of the dust sample were spiked with low levels of target POP (100 ng/compound); three other aliquots were spiked with higher levels of the POP (500 ng/compound); and the remaining three aliquots were non-spiked samples. The soil sample aliquots were treated the same way as the dust sample aliquots. Following spiking, the samples were air-dried in a hood for approximately 15 minutes. The spiked and non-spiked samples were extracted by sonication with 10 mL of hexane for 15 minutes and this extraction step was repeated with another 10 mL of hexane. The hexane extracts were concentrated and analyzed by GC/MS for target POP.

For the second set of experiments, DCM was used as the extraction solvent and only the low-level spiking experiments were conducted. After extraction, the sample extract was solvent exchanged into hexane and a silica SPE column was conditioned with 10% methanol in hexane, followed by 100% hexane. The sample extract was then applied to a silica SPE column. The sample extract was eluted with 8 mL of 40% hexane in DCM and followed by 8 mL of 100% DCM. Both fractions were concentrated and analyzed by GC/MS for target POP.

For the third set of experiments, the same house dust and pathway soil samples were used and low level (100 ng/compound) and high level (1000 ng/compound) spiking experiments were carried out. The extraction solvent was changed to 10% EE in hexane. After extraction, a Florisil SPE column was conditioned with 50% EE in hexane, followed by 100% hexane. The sample extract was then applied to the column and eluted with 12 mL of 15% EE in hexane. This fraction was concentrated and analyzed by GC/MS for target POP.

Additional spike recovery experiments for Ph were carried out using the methods previously developed with minor modification (7). The spiked and non-spiked dust samples were sequentially extracted with 5 % acetic acid in methanol, DCM, and 5 % acetic acid in distilled water. The resulting mixture was then partitioned with distilled water and the DCM extract was concentrated and divided into two portions. One portion was methylated with diazomethane and analyzed for PCP and the other portion was not methylated and was analyzed for other target phenols.

Dermal Wipe Samples

The dermal wipes (Johnson & Johnson Sof-Wick) were precleaned prior to use. The wipes were cut into half along the fold using clean scissors and extracted with DCM overnight. After extraction, the wipes were dried in a stainless canister with nitrogen under vacuum at 60 C for at least 12 hours. After drying the wipes were stored in a clean jar. Prior to field use, an aliquot (2 ml) of 50% isopropanol in distilled water was dispensed onto the entire surface of the wipe. The wet wipe was folded in half and placed in a clean jar ready for field use.

Six clean wipes were used in the spike recovery test. Six wipe samples were obtained from a child subject by wiping both forearms and palms during a three-day period. Four of these dermal wipe samples were spiked with known amounts of target POP including PAH, PCB, OC, and OP pesticides (20 ng/compound) and the remaining two samples were not spiked with any POP. Both spiked and non-spiked samples were extracted with 10% ethylether (EE) in hexane by the Soxhlet technique. Two of the spiked and one non-spiked sample extracts were partitioned with distilled water before concentration and the remaining spiked and non-spiked sample extracts were concentrated to 1 mL without liquid-liquid partition. The concentrated sample extracts were then subjected to the Florisil SPE column cleanup step. The Florisil column was conditioned with 50 % EE in hexane and followed by 100 % hexane. The sample extract was then applied to the column and eluted with 12 mL of 15 % EE in hexane as the first fraction and followed by 12 mL of 50 % EE in hexane as the second fraction. Both fractions were concentrated to 1 mL and analyzed by GC/MS for spiked POP. A second spike recovery

study was conducted by spiking low levels (5 ng/compound) of the target POP onto the clean wipe samples. Five spiked samples and one non-spiked samples were extracted with 15% EE in hexane. Two of the spiked and the non-spiked samples were cleaned up by a Florisil SPE column with the conditions described above. The other three spiked samples were eluted with 24 mL of 15% EE in hexane. The fractions were concentrated and analyzed for spiked POP.

Urine Samples

Two sets of method validation tests were conducted to determine 2,4-D, PCP, hydroxy PAH, and 3,5,6-TCP in urine samples. These experiments consisted of (1) analytical method validation for 2,4-D, PCP, and hydroxy-PAH and (2) analytical method validation for 3,5,6-TCP.

In the first set of experiments, eight aliquots of an adult's urine sample (50 mL each) were used. Two aliquots of the urine sample were spiked with low levels of 2,4-D, PCP, and hydroxy-PAH (20 ng/compound); two aliquots were spiked with medium levels of the target compounds (50 ng/compound), two aliquots were spiked with high levels of the target compound (500 ng/compound); and the remaining two aliquots were non-spiked samples. Each urine sample (spiked and non-spiked) was refluxed with 6 N hydrochloric acid (HCl) and DCM for one hour.

The resulting mixture was extracted with DCM by liquid-liquid partitioning. The DCM extracts were combined, concentrated, methylated by diazomethane, and solvent exchanged into hexane. The hexane extract was subsequently cleaned up by a Florisil SPE column. The SPE column was conditioned with 50 % DCM in hexane and followed by 100 % hexane. The sample extract was then applied to the column and eluted with 18 mL of 50 % DCM in hexane. The fraction was concentrated and analyzed by GC/MS for the target compounds.

In the second set of experiments, 12 aliquots of an adult's urine sample (1 mL each) were used. Nine aliquots of the urine samples were spiked with 3,5,6-TCP at three levels (1 ng, 3 ng, and 10 ng) in triplicate and the remaining three aliquots were non-spiked samples. Each urine sample (spiked and non-spiked) was fortified with the internal standard ($^{13}C^{15}N$-TCP) and acidified with 100 µl of concentrated HCl. Note that both 3,5,6-TCP and $^{13}C^{15}N$-TCP were

obtained from Dow Elanco (Indianapolis, IN). The mixture was then heated at 80°C for 2 hours. After heating, an aliquot of 10% sodium chloride (NaCl) solution was added to the mixture. The resulting extract was extracted with DCM and concentrated to approximately 1 mL. The concentrated DCM extract was solvent exchanged into toluene. The toluene extract was derivatized with 100 µl of N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) at 60°C for one hour. Standard solutions containing 3,5,6-TCP and $^{13}C^{15}N$-TCP were prepared in toluene. The standards were derivatized with MTBSTFA as described above. The samples and standard solutions were then analyzed by GC/MS.

Food Samples

The objective of the method evaluation for the food samples was to establish an analytical method which would remove the bulk of the fat from the food, but allow for adequate recovery of target POP of various compound classes. Several experiments were performed in an attempt to develop an optimal extraction and clean-up procedure to cover all compound classes of interests. This proved to be a major challenge due to the amount of fat which was contained in the samples.

Food samples were extracted with three different solvents (acetone, hexane, and DCM) in an attempt to reduce the amount of fat extracted with the analytes. The acetone removed all the water from the sample making concentration extremely difficult. The hexane and DCM extracts were placed in a freezer for a short time in an attempt to perform a gross removal of the fat. The organic solvent could not be separated from the precipitated fat, and DCM was used as extraction solvent for later experiments because of its ability to remove both polar and non-polar compounds from the food matrix. Food samples were also extracted in the presence of salts (sodium oxalate and zinc acetate) with the intent of degrading the fats.

Two chromatography columns, Sephadex and gel permeation were evaluated for the removal of the fat from the food samples. The fat and POP elution profiles of the Sephadex column were determined by residue weights and by GC/ECD analysis. The sample made of corn oil and selected POP including OC and OP pesticides was applied to a Sephadex column and

eluted with 12x1 mL DCM and aliquots of the eluates were removed for residue weight measurements of fat content. The fractions containing no residue were analyzed by GC/ECD for OC and OP pesticides. The residue weight measurements were also determined for each fraction.

Because the Sephadex column proved to be an unacceptable method for fat removal, gel permeation chromatography (GPC) was then evaluated as a means of removing the fat from the food matrix. Two GPC columns, Optima and SX-3 biobeads, were employed initially. The Optima column used a slightly lower flow rate than the biobeads column (4 mL/minute vs. 5 mL/minute), had a faster run time (30 minutes vs. 60 minutes), and had a lower loading capacity (0.5 gram vs. 1 gram). The biobeads column was chosen for evaluation tests because of its higher loading capacity. The food samples spiked with target POP including PAH, PCB, PE, Ph, OC, and OP and solvent spikes were extracted with DCM and fractionated by a biobeads column. The fat and target POP elution profiles were determined by residue weights and by GC/MS or GC/ECD analysis. The optimal GPC condition was established to separate approximately 90 % of the fat from the target POP. The optimal GPC condition consisted of a biobeads column with DCM as mobile phase operated at a flow rate of 5 mL/minute for 60 min. The dump time was set at 0 to the valley between corn oil and phthalate esters from the standard analysis, generally around 25 to 28 min. The collect time (generally 32 to 35 min.) was then set from the end of the dump time to a total fractionation time of 60 min.

After the GPC cleanup, a Florisil SPE column was used to further remove possible interference peaks from the sample extract. The eluting solvent systems were evaluated to determine the optimal elution solvent for target POP. The solvent systems evaluated were: 6% ethyl ether (EE) in hexane, 15% EE in hexane, 50% EE in hexane and 20 % acetone in hexane.

After the optimal GPC and Florisil SPE conditions were established, the spike recovery experiments for food samples were carried out. A solid food duplicate diet sample was fortified with known amounts of POP including PAH, PCB, PE, OC, and OP. Three aliquots of the spiked food samples were extracted with DCM, and fractionated through GPC using the procedures described above. The GPC fraction was concentrated to 1 mL and solvent exchanged into hexane. The hexane extract was then applied to a Florisil SPE column and eluted with 2x6

2x6 mL of 15 % EE in hexane. The collected fraction was then concentrated and analyzed by GC/MS for target POP.

The analytical method for 2,4-D developed from the previous study (2) was modified for the determination of 2,4-D and PCP in Phase 1 food samples. The procedures were described in the later section of Phase 1 analytical methods. The PCP could not be recovered by this method. Acceptable recoveries of 2,4-D were obtained but multiple SPE columns were required for each sample because the SPE columns became plugged. Therefore, one additional evaluation test was carried out for the determination of PCP and 2,4-D in food samples. The solid food sample was spiked with known amounts of 2,4-D and PCP, extracted with DCM, and fractionated by GPC. The GPC fraction was methylated with diazomethane, concentrated, and solvent exchanged to hexane for Florisil SPE column clean-up. The eluting solvent used was 50% DCM in hexane. Adequate recoveries of PCP and 2,4-D were obtained from this experiment. Thus, the Phase 2 food sample was extracted with DCM and fractionated by GPC. The GPC fraction was split into two portions. Portion I was cleaned by Florisil SPE and analyzed for target PAH, PCB, OC, OP, PE, and Ph. Portion II was methylated, cleaned by Florisil SPE, and analyzed for 2,4-D and PCP. The analytical procedures for the food samples are described in Appendix A.

Phase 1 Field Study of Nine Daycare Centers

The Phase 1 field study was conducted in nine daycare centers which are located in urban and rural areas, primarily in Durham County, North Carolina. Four of the daycare centers are in the Head Start program, which serves mostly low-income clients, and five are not. Approvals were obtained from the Human Subjects Committees at Battelle before field activities began.

This section summarizes the procedures used for selection of nine daycare centers; the study consent forms, the questionnaires, and building characteristics observation survey; the sampling procedures used to collect air, dust, soil, and food; and the analytical methods used to determine POP in the collected samples. The recruiting material, consent form, pre-monitoring questionnaire, post-monitoring questionnaire, and house/building characteristics observation survey used in the Phase 1 study are presented in Appendix B.

Selection of Daycare Centers

We used ***Select Phone***, a national telephone database on CD-ROM developed by ProCD Inc., to prepare the target list for recruiting the daycare centers which are not in the Head Start program. The database contains 100 million U.S. business and residential listings on six CD-ROM discs. We used the SIC code (child care providers) and geographic locations (Durham, Chapel Hill, and Raleigh, North Carolina) to select the eligible daycare centers. Battelle survey staff called every daycare center on the target list to confirm the addresses and phone numbers, the names of daycare center directors, and obtain some general information about the centers (age groups of the children, number of children enrolled in the daycare center, and business hours).

A total of 202 advance letters were mailed to the directors of eligible child daycare centers in the Durham, Chapel Hill, and Raleigh areas. The letter provided the background information about the study and informed the center directors that they would be contacted by our study staff. We began calling the center directors one week after the mailing of advance letters. Most daycare center directors had to obtain approval from their board of directors or the daycare owner in order to participate in the study. It took at least one to two weeks to get a final response from a daycare center. We obtained participation consent from 18 daycare centers in the Durham/Chapel Hill areas and 6 in the Raleigh area.

For daycare centers in the Head Start program, we used the ***Select Phone*** database (using name search) to identify all Head Start daycare centers in the same geographical areas (Durham, Chapel Hill, and Raleigh, North Carolina). Head Start program is a federally funded child care program which provides free child care services to low income families. To be eligible for the program services, a family's income must meet the federal income guidelines and other criteria. About 90% of the children in a Head Start center are from low income families.

The same procedures were used to recruit the Head Start centers. Advance letters were mailed to the Head Start directors. About one week after the mailing of advance letters, survey staff called the Head Start directors to obtain participation consent. Initially, the Head Start centers' directors were concerned about the potential negative effects from the study and were reluctant to participate in the study. Many phone calls were made to different levels of

people in charge of the program to persuade them to participate in the study. Final selection of the centers was based on the numbers of children enrolled, the location of the centers, and the type of centers (private/Head Start). Nine daycare centers (five private and four Head Start) were selected for the Phase 1 study; one Head Start backup center and five backups for private centers were also assigned.

Field Monitoring Activities

The Phase 1 field sampling activities were performed in March 1997. Initially nine daycare centers were planned for the study. Figure 4.1 displays the locations of the participating daycare centers for the Phase 1 study. We had to use one of the backup centers (D10), because the outdoor sampling of one daycare (D05) was disrupted. A piece of plastic had blocked the cooling fan of the sampling module and the sampling pump overheated. Additional 24-hr outdoor air sampling was conducted for D05. The other multimedia samples were collected from daycare D05 as planned. A summary of the daycare centers participating in the Phase I study is given in Table 4.1. The field monitoring activities for each daycare center are summarized in Table 4.2.

The pre-monitoring questionnaire and the post-monitoring questionnaire used were modified from previous EPA work. The pre-monitoring questionnaire contains the information about the use of chemicals, and children's daily activities at the center. The post-monitoring questionnaire collects information about the participant's feed back about the study activities. A field data log book was also used for each daycare center to record critical information during the sampling period and pictures were taken to document the progress of the study.

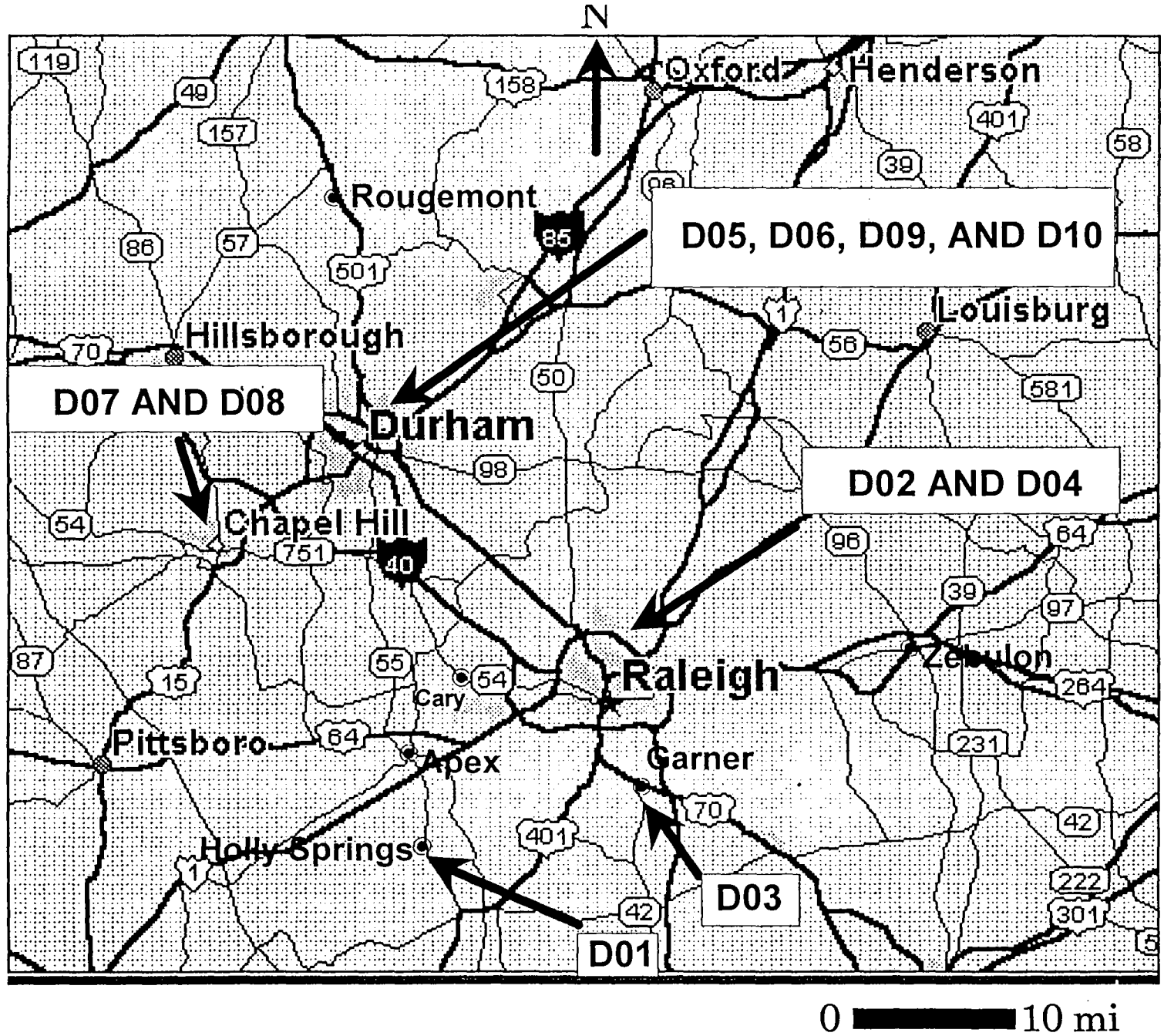


Figure 4.1. Locations of ten daycare centers in the Phase 1 Field Study.

TABLE 4.1. SUMMARY OF DAYCARE CENTERS IN PHASE I STUDY

Daycare Center Code	Number of Children	Age Group	Type
D01	118	3-4 years old	Head Start
D02	120	4-5 years old	Head Start
D03	106	4-5 years old	Head Start
D04	60	6 weeks to 12 years old	Private
D05	112	6 weeks to 12 years old	Private
D06	374	3-4 years old	Head Start
D07	65	6 weeks to 5 years old	Private
D08	200	2 months to 12 years old	Private
D09	86	6 weeks to 5 years old	Private
D10	99	2-6 years old	Private

TABLE 4.2. FIELD MONITORING ACTIVITIES IN EACH DAYCARE CENTER

Monitoring Day	Activity
DAY - 1	1. Pick up signed consent form 2. Collect copies of food menus 3. Collect used vacuum bag, if available 4. Conduct pre-monitoring interview 5. Give instructions on food sample collection 6. Remind the participant: next appointment time, no vacuum inside the classroom 7. Complete the building observation survey 8. Set up indoor air monitor, mark the location on the sketch 9. Set up outdoor air monitor, mark the location on the sketch 10. Take indoor/outdoor temperature (at the location of the air monitor) 11. Take pictures of sampling activities
DAY - 2	1. Check the air flow of the air monitors 2. Record indoor/outdoor temperature
DAY - 3	1. Unload indoor air samplers, remove air monitors 2. Record indoor/outdoor temperature 3. Collect dust samples, vacuum the classroom 4. Unload outdoor air samplers, remove air monitors 5. Collect 1 soil sample (selected classroom children's play areas), mark the location on the sketch 6. Conduct post-monitoring interview 7. Collect food samples, examine the samples 8. Present the certificate of appreciation to the participant 9. Confirm the mailing information of the check ($50) with the participant 10. Take pictures of sampling activities

Sampling Methods

Indoor and outdoor air were sampled simultaneously during a 48-hour period at each daycare center. A 4 L/min URG sampler was used. Each sampler consisted of an inlet jet equipped with an impactor for <10 μm particle collection, a filter (quartz fiber or Teflon-coated glass) and a glass cartridge packed with either XAD-2 or a PUF plug. The indoor samplers were placed in a Styrofoam sampling box equipped with a cooling fan. The sampling box was placed in a playpen in the classroom to be sampled. A stroller net was used to cover the top of the playpen to keep children from playing with the sampling module. A real-time PAH monitor was also placed in the playpen to monitor particle-bound PAH indoors (8,9). The outdoor sampling modules were placed in a dog house, purchased new for this use, outside the daycare center. After 48-hour sampling, the sample module was sealed at both ends, wrapped with aluminum foil, and placed in a cooler ready for transporting back to the laboratory for analysis. The initial (Day-1) and final (Day-3) flow rate of each sampler was recorded; sampler flow rate was also checked and recorded at the mid-point (Day-2) of the sampling period.

The floor dust samples were collected using the High Volume Small Surface Sampler (HVS3) in designated areas in the classroom where the children's highest play activities occur. The HVS3 unit was operated following an ASTM Standard Method and the manufacturer's manual (10,11). The vacuum bag samples from the same classrooms in seven daycare centers were also collected. The bag samples were not obtained from the remaining three daycare centers because they were not available. The dust samples were collected and transferred to clean jars, and placed in a cooler for shipping.

The playground soil samples were collected from each daycare center. According to the procedures used in the previous EPA studies (5), the playground soil was scraped from the top 0.5-cm of soil. A minimum area of 0.093 m^2 (1 ft^2) was scraped with a stainless steel spatula, and the soil was placed in a clean jar.

The duplicate diet food samples were collected from each daycare center. A training session and a food collection protocol were provided to the daycare center staff before the field sampling activities began. At each daycare center, two servings of all food served for the

children was collected during the 2-day monitoring period. One was placed in a glass container and one was placed in a plastic container.

In addition to the field samples, field blanks in all sample media were collected as quality control samples. The field blank for air samples was a filter/XAD-2, or filter/PUF, that was processed through field handling and shipping together with the field samples without sampling air. The field blanks for dust, soil, and food samples were the empty containers that were used for the respective samples that were processed through field handling and shipping.

Analytical Methods

The analytical methods used to analyze the samples (air, dust, soil, and food) collected in Phase 1 are summarized in Table 4.3.

The filter/XAD-2 samples and field blanks were spiked with known amounts of surrogate recovery standards (SRS), and extracted with dichloromethane (DCM) by the soxhlet technique. The SRS included pyrene-d_{10}, chrysene-d_{12}, DDE-^{13}C, DDT-^{13}C, 2,2',4,5,5-pentachloro-biphenyl-^{13}C, and fenchlorfos. The DCM extract was concentrated by Kuderna Danish (K-D) evaporation and divided into two portions. Portion I was analyzed by GC/MS operated in the electron impact (EI), selected ion monitoring (SIM) mode for target PAH, PCB, PE, Ph, OC, and OP. Three GC/MS analyses were performed for each sample extract, one for PAH and PE, one for PCB, and one for OC and OP. Portion II was methylated and analyzed by GC/MS for pentachlorophenol (PCP).

The filter/PUF samples were analyzed for 2,4-D. The results of the method evaluation tests showed that 2,4-D was retained in the filter, and thus only the filter samples were analyzed for 2,4-D. The analytical method used for 2,4-D analysis was developed and validated in a previous study (2). The filter sample was extracted with a phosphate buffer solution in a sonication bath, and the extract was processed through a C18 SPE column. The target fraction was concentrated, methylated, and analyzed by GC and ECD for 2,4-D.

TABLE 4.3. SUMMARY OF ANALYTICAL METHODS FOR EACH TYPE OF SAMPLES FROM PHASE 1 STUDY

Media	Analytical Method	Analyte Class
Indoor/Ambient Air	Soxhlet extraction with DCM, GC/MS analysis	PAH, PCB, PE, Ph, OC, OP
	Sonication with phosphate buffer and C18 SPE cleanup, methylation, GC/ECD analysis	HA
Dust/Soil	Sonication with 10 % EE in hexane, Florisil SPE cleanup, GC/MS analysis	PAH, PCB, PE, OC,OP
	Sonication with phosphate buffer, C18 SPE cleanup, methylation, GC/ECD or GC/MS analysis	HA
	Sonication with 5 % acetic acid in methanol, DCM, and 5 % acetic acid in water, methylation, GC/MS analysis	Ph
Food	Hobart chopper, Brinkman Homogenization DCM extraction, GPC, and Florisil SPE cleanup, GC/MS analysis	PAH, PCB, PE, Ph, OC, OP
	Hobart chopper, Brinkman Homogenization phosphate buffer extraction, liquid-liquid partitionation, C18 SPE cleanup, GC/MS analysis	HA

The dust samples were separated into coarse and fine (<150 μm) fraction and only the fine fractions of the dust samples were subjected to subsequent analysis. The soil samples were not separated into fine and coarse fractions. An aliquot of each dust and soil sample was spiked with known amounts of SRS, and extracted twice each with 10 mL of 10% EE in hexane in a sonication bath for 20 minutes. The sample extract was combined and concentrated to 1 mL. A Florisil SPE column was conditioned with 50% EE in hexane, followed by 100% hexane. The concentrated sample extract was then applied to the column and eluted with 12 mL of 15% EE in hexane. This fraction was concentrated and analyzed by GC/MS for target PAH, PCB, PE, OC, and OP.

A second aliquot of each dust and soil sample was used for analysis of phenols. The dust/soil samples were sequently extracted with 5% acetic acid in methanol, DCM, and 5% acetic acid in distilled water. The mixture was washed with distilled water and the DCM extract was concentrated. One portion of the DCM extract was methylated and analyzed for PCP and the other portion was not methylated and was analyzed for other target phenols.

A third aliquot of each dust and soil sample was used for analysis of 2,4-D acid. The analytical method used was developed from the previous EPA study (2). In brief, the dust/soil sample was extracted with phosphate buffer, with cleanup by C18 SPE column, and analysis by either GC/ECD (soil) or GC/MS (dust).

The solid and liquid food samples collected in glass containers from all daycare centers were extracted separately and analyzed for target POP. Only one solid and one liquid food sample collected in plastic containers from daycare D09 were prepared for target POP analysis. The analytical procedures used for food samples are described in Appendix A. In brief, an aliquot of the homogenized food sample was spiked with known amounts of an analytical surrogate recovery standard (SRS), extracted with DCM, fractionated by GPC, and subjected to final cleanup by Fluorisil SPE. The target fraction was concentrated, and analyzed for target PAH, PCB, PE, OC, and OP.

A second aliquot of the food sample was prepared for the determination of 2,4-D using the method for 2,4-D in dust/soil described earlier with minor modification. The food sample was spiked with known amounts of SRS (3,4-D) and extracted with phosphate buffer. The sample extract was partitioned with hexane to remove fat. The mixture had to be centrifuged to separate into two layers because of the emulsion problems. The aqueous layer was then acidified and applied to a C18 SPE column. The SPE column was soon plugged up by the sample extract. Typically, 4 to 5 SPE columns were used for one sample extract. The target fractions from the SPE columns of the same sample were combined, concentrated, methylated, and analyzed by GC/MS for 2,4-D.

The sample extracts and standard solutions were analyzed by 70 eV electron impact (EI) GC/MS. A Hewlett-Packard (HP) GC/MS was operated in the SIM mode. Data acquisition and

processing were performed with an Chem Station data system. The GC column was a DB-5 fused silica capillary column (60 m x 0.32 mm; 0.25 μm film thickness). Helium was used as the GC carrier gas. Following injection, the GC column was held at 70°C for 2 min and then was temperature-programmed to 150°C at 15°C/min and then to 290°C at 6°C/min. The MS was operated in the SIM mode. Peaks monitored were the molecular ion peaks and their associated characteristic fragment ion peaks. Identification of the target analytes was based on their GC retention times relative to those of corresponding internal standards and relative abundance of the monitored ions. Quantification of target analytes was based on comparisons of the integrated ion current responses of the target ions to those of the corresponding internal standards using average response factors of the target analytes generated from standard calibrations.

The detection limits of target POP were estimated according to the analytes' signal to noise ratios from the lowest levels of standard calibrations. The estimated detection limits of target POP expressed in units corresponding to each sample medium are summarized in Table 4.4.

Data Analysis

The types of samples collected in the Phase 1 study were indoor air, outdoor air, carpet dust, playground soil, liquid food, and solid food samples. Target POP included multiple compound classes: PAH, phthalate esters (PE), phenols (Ph), polychlorinated biphenyl (PCB), organochlorine (OC) pesticides, organophosphate (OP) pesticides and a herbicide acid (HA). A total of 57 individual target compounds and seven sums of target compounds in the respective compound classes were included in the analysis. The sums of target compounds in their respective compound class were calculated in a way that treated below detection limit (BDL) values as zeros and added up the non-BDL values.

Summary statistics (sample sizes, number of samples below detection limit, mean, standard deviation, minimum and maximum) of the target POP and the sums of the target POP of

TABLE 4.4. ESTIMATED DETECTION LIMITS OF TARGET PERSISTENT ORGANIC POLLUTANTS IN MULTIMEDIA SAMPLES

Analyte Class	Estimated Detection Limit				
	Air ng/m^3	Dust/Soil ppm	Food ppb	Dermal Wipe ng/wipe	Urine ng/mL
PAH	0.01-0.04	0.001	0.04	0.5	NA
PCB	0.04	0.001	0.04	0.5	NA
PE	0.04	0.001	0.04	0.5	NA
Ph	0.1	0.001	0.1	NA	0.03
OC	0.1	0.001	0.04	0.5	NA
OP	0.1	0.001	0.04	0.5	NA
2,4-D	0.1	0.001	0.2-0.5	NA	0.03
OH-PAH	NA[a]	NA	NA	NA	0.02-0.03
3,5,6-TCP	NA	NA	NA	NA	1.0

(a) NA denotes not applied.

the seven compound classes were determined. Pearson correlation coefficients were calculated based on natural log transformed data. Note that half of the detection limit was used for the measurement that was BDL when calculating means, standard deviations, and the Pearson correlation coefficient. Average of old and new carpet samples for the floor dust HVS3 measurement from D09 was used in the correlation analysis.

The estimates of POP exposure through multiple pathways, inhalation, nondietary ingestion, and dietary ingestion were determined. The estimates of POP exposure through inhalation were based on the time-weighted concentration, indoor and outdoor POP levels, the amount of time spent indoors and outdoors, and the portion of 24-hr day that the child spent at the daycare center. The time spent indoors and outdoors was based on the schedule provided by each daycare center. The total operation time of each daycare center varied from 6 to 12 hours. For the calculation, we assumed that the child spent the entire period at the daycare center. The maximum exposure estimates from inhalation pathway was based on the following equation:

$$E_{inh} = \frac{C_i * t_i + C_o * t_o}{t_i + t_o} * \frac{V * F}{1000}$$

where

E_{inh}	=	estimates of daily POP exposure through inhalation at the daycare center, μg/day
C_i	=	indoor POP concentration at the daycare center, ng/m^3
C_o	=	outdoor POP concentration at the daycare center, ng/m^3
t_i	=	child's time spent indoors at the daycare center, min
t_o	=	child's time spent outdoors at the daycare center, min
V	=	the estimated child ventilation rate, 15 m^3/day
F	=	fraction of the 24-hr day child spent at the daycare center.

The maximum POP exposure estimates from nondietary ingestion pathway were based on HVS3 carpet dust and playground soil POP levels, the amount of time spent indoors and outdoors, and the portion of the 24-hr day that child spent at the daycare center. The equation is described as follows:

$$E_n = \frac{t_i * D_i + t_o * P_o}{t_i + t_o} * M * F$$

where

E_n	=	estimates of daily POP exposure through nondietary ingestion at the daycare center, μg/day
D_i	=	POP concentration in the floor dust, μg/g
P_o	=	POP concentration in the playground soil, μg/g
t_i	=	child's time spent indoors at the daycare center, min
t_o	=	child's time spent outdoors at the daycare center, min
M	=	child's estimated daily dust/soil intake, 0.1 g
F	=	fraction of the 24-hr day child spent at the daycare center.

The maximum exposure estimates from dietary ingestion pathway were based on the POP levels in solid and liquid food samples, and the amounts of the liquid and solid food samples collected. The following equation is used for the calculation:

$$E_d = \frac{S_i * M_s + L_i * M_e}{2}$$

where

E_d	=	estimates of daily POP exposure through dietary ingestion at the daycare center, μg/day
S_i	=	POP concentration in the solid food samples, μg/kg

L_l = POP concentration in the liquid food sample, μg/kg

M_s = the total amount of the solid food samples collected during 48-hr, kg/2 days

M_e = the total amount of the liquid food samples collected during 48-hr, kg/2 days.

We assumed a ventilation rate of 15 m^3/day for children (12,13) and the dust/soil ingestion rate is 0.1 g/day for children (14,15).

Phase 2 Field Study in Two Daycare Centers and Nine Homes

The Phase 2 study was conducted in two daycare centers (D03 and D09) and in nine homes. Nine children were recruited from the two daycare centers; four from D03 and five from D09. Multi-media samples were collected at daycare centers and at subjects' homes during a 48-hours sampling period. Dermal wipe and urine samples were also collected from each subject at daycare centers and at the homes. Informed consents were obtained from both the directors of the Daycare centers and the parents of the subjects before any field activities were occurred.

This section summarizes the procedures used for selection of nine subjects, the sampling protocols, and the analytical procedures. The recruiting materials, consent forms, pre-monitoring questionnaire, post-monitoring questionnaire, house/building characteristics observation survey and child activity diary used in the Phase 2 study are presented in Appendix C.

Selection of Homes

After reviewing the POP data obtained from the Phase 1 study, and consulting with the EPA project officer, it was decided to select daycare D03 (Head Start) and D09 (private) for the Phase 2 study. The directors from both daycare centers agreed to participate in the Phase 2 study. A study information package was developed for recruiting children from these two daycare centers. Included in the package were a cover letter, a participation summary sheet, and a brief home survey. Forty packages were delivered to these two daycare centers and were distributed by the center directors to the selected classrooms (children aged two to five). During

the first two weeks, only two responses were received, far fewer than the 9 subjects needed for the study. A more aggressive recruiting campaign was carried out after the approval of each center's director. New and simplified study flyers were developed and sent to the selected classrooms. Battelle staff members also spent time at the daycare centers during the time when parents pick up their children and discussed with parents the potential involvement in the study. With this aggressive recruiting approach, eleven parents responded to our recruiting flyers. One child from each home was involved in the study. Among these subjects, five attend daycare D03 and six attend daycare D09. All these children spend at least 25 hours per week in the daycare centers. Therefore nine selected homes and two backup homes were scheduled for Phase 2 field sampling activities. The backup home in the D03 group was used to replace an originally selected home, because we were unable to contact the participant the day before field sampling activities began.

Field Monitoring Activities

The Phase 2 field sampling activities were performed in June 1997. Table 4.5 summarizes the information on the two daycare centers and nine homes in the Phase 2 study. Figure 4.2 shows the locations of these nine homes and two daycare centers. The sampling activities were completed during a period of two weeks. Figure 4.3 displays the sampling schedule for the Phase 2 study. In the first week, the field sampling activities were conducted in D03 and in the four homes of the subjects who attend D03. The four subjects were divided into two groups based on the classrooms they attend. Subjects HA3 and HB3 are in the same classroom (group 1) and subjects HC3 and HD3 are in another classroom (group 2). As shown in Figure 4.3, group 1 homes were monitored during the first 48-hr period and followed by group 2 homes. Because all the children's parents work during the day, the appointment time for setting up monitoring activities was usually after 6:30 pm. Two field teams were involved in the Phase 2 study . The field monitoring activities for each home are similar to the Phase 1 study (Table 4.2) except that additional biological samples (dermal wipe and urine) were collected. The field monitoring activities of the daycare centers were modified slightly from the Phase 1 study. The

TABLE 4.5 SUMMARY OF SUBJECTS/HOMES IN PHASE 2 STUDY

Subject Code	Daycare Center Classroom No.	Adult Smoker in Home	Subject's Sex, Age	Subject's Race	Low-Income Family
HA3	D03 Classroom #2	None	Girl, 4	Hispanic	Yes
HB3	D03 Classroom #2	None	Boy, 4	Black	Yes
HC3	D03 Classroom #1	1[a]	Boy, 4	Black	Yes
HD3	D03 Classroom #1	None	Girl, 4	Black	Yes
HE9	D09 Classroom #2	None	Boy, 2-1/2	White	No
HF9	D09 Classroom #2	None	Girl, 3-1/2	White	No
HG9	D09 Classroom #1	None	Boy, 5	White	No
HH9	D09 Classroom #1	None	Boy, 4	White	No
HI9	D09 Classroom #1	None	Girl, 5	White	No

(a) One parent of this subject is a light smoker, approximately 3-4 cigarettes were smoked inside the house with the window open.

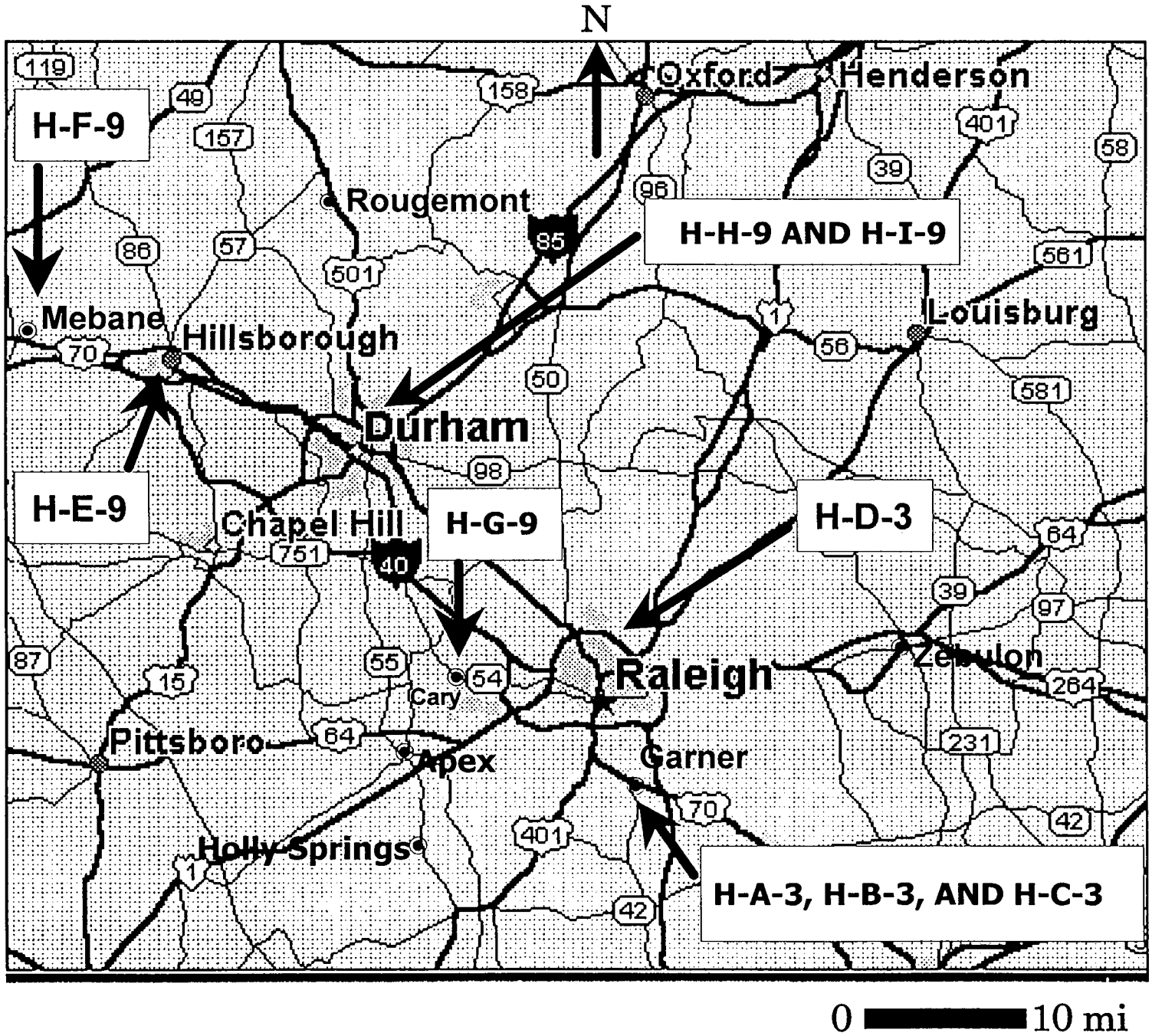


Figure 4.2. Location of nine homes in the Phase 2 Field Study.

WEEK 1

Daycare Center: D03

Day 1 Day 2 Day 3 Day 4 Day 5

Home Group 1: HA3 and HB3

Day 1 Day 2 Day 3

Home Group 2: HC3 and HD3

Day 1 Day 2 Day 3

WEEK 2

Daycare Center: D09

Day 1 Day 2 Day 3 Day 4 Day 5

Home Group 1: HE9 and HF9

Day 1 Day 2 Day 3

Home Group 2: HG9, HH9, and HI9

Day 1 Day 2 Day 3

Figure 4.3. Sampling Schedule for the Phase 2 Field Study.

three-day activities (Phase 1) were modified to five days to cover the two groups of subjects. Note that only one indoor air sampler and one outdoor air sampler were used in D03 because of the availability of the air samplers. The two classrooms were located across a hallway from each other. The indoor air samplers were placed in classroom #2, and two consecutive 48-hr samples were taken. Two 48-hr outdoor air samples were also taken during the same time period. Two floor dust samples were collected from both classrooms and only one playground soil sample was taken. Two sets of the food samples for both subject groups were collected from D03. The dermal wipes and urine samples were also collected from each subject at D03. In the second week, similar field monitoring activities were carried out in daycare D09 and in five subjects' homes. Similarly, these five subjects were divided into two groups: HE9 and HF9 in Group 1 and HG9, HH9, and HI9 in Group 2.

Sampling Methods

The sampling methods used in the Phase 2 study for air, dust, soil, and food samples were the same as those used in the Phase 1 study. To reduce the noise levels generated from the air samplers, insulation materials were added to the sampling box and longer vent tubes were added to the samplers. Dermal hand wipe and urine samples were collected in the Phase 2 study. Training sessions for the collections of hand wipe and urine samples were conducted for the participating daycare centers' staff members and participating parents. The sample collection protocols (Appendix C) were also provided. For each subject, two wipe samples were collected at the daycare center before the subject ate lunch and two wipe samples were collected at the subject's home before the subjects ate dinner on each of the two days during the 48-hr sampling period. For each subject, four urine samples, one each morning (the first void), and one each evening (2-3 hours after dinner or before going to bed), were collected at the subject's home. Two urine samples, one each afternoon (after lunch) were collected at the daycare center. The collected wipe and urine samples were stored in clean chilled coolers at daycare centers or at homes, then in a freezer after sample retrieval until they were sent to the laboratory for analysis. At least one field blank in each sample medium was collected as a quality control sample.

Analytical Methods

The analytical methods used for air, dust, soil, and food samples collected in the Phase 2 study were the same as those used in the Phase 1 study, except for the food samples used for the 2,4-D analysis. The GPC fraction of the food sample was split into two portions. One portion was methylated and cleaned up by Florisil SPE for the determination of 2,4-D and PCP, and the other portion was only cleaned up by Florisil SPE for the determination of other target POP. The detailed analytical procedures for the analysis of the food samples are described in Appendix A.

The dermal wipe samples of each subject collected at home were combined, for extraction, as were those collected at the daycare center. Known amounts of SRS were added to each combined wipe sample and extracted with 10 % EE in hexane by the Soxhlet technique. The extract was dried with sodium sulfate anhydride and concentrated to 1 mL. A Florisil SPE column was conditioned with 50 % EE in hexane followed by 100 % hexane. The sample extract was then applied to the column and eluted with 24 mL of 15 % EE in hexane. The collected fraction was concentrated and analyzed by GC/MS for target POP.

Urine samples from each subject collected at the daycare center were combined, as were those collected at home. One aliquot (30 mL) of each composite sample was used for determining 2,4-D, PCP, and hydroxy-PAH, and another aliquot (1 mL) was used for determining 3,5,6-TCP. The analytical procedures used were the same as those described in the method validation section. Another aliquot (5 mL) of each composite sample was sent to Smith Kline Beecham Clinical Laboratories (St. Louis, MO) for determination of creatinine.

Statistical Analysis

Statistical analyses were conducted on the following types of samples collected in Phase 2 field studies:

- 48-hr integrated indoor and outdoor air samples

- House dust samples collected by HVS3
- Playground soil samples
- 48-hr duplicate diet food samples
- Composite dermal wipe samples
- Composite grab urine samples.

Summary statistics (sample size, number of below detection limit, mean, standard deviation, minimum, and maximum) were determined for each of the above sample types. Four additional types of statistical analyses were performed: Spearman correlation analyses, Pearson correlation analyses, analysis of variance (ANOVA), and regression models. While summary statistics and Spearman correlation coefficients were performed on the raw data, the Pearson correlation analyses, ANOVA, and regression analyses were carried out on natural log-transformed data. For POP concentrations less than the detection limit, half of the detection limit was used.

Summary statistics were generated for measured POP data by compound, sample medium, and family income. In addition, summary statistics were generated on the calculated data of estimated daily dose by compound, exposure pathway, and family income.

Spearman and Pearson correlation coefficients were calculated on Phase 2 data to examine the relationships between POP concentrations for different sample media and the relationship of target POP concentration in each compound class within the sample medium.

An analysis of variance (ANOVA) model was employed to examine the effects of sampling location (home vs. daycare center) and family income (low-income vs. middle-income) on POP concentrations for each sample medium. The neutral log-transformed data in Phase 2 multimedia samples (air, dust, soil, food, wipe, and urine) were used for ANOVA. Urine data calculated in two units, ng/mL and μmole/mole, were fitted separately to the ANOVA models.

Regression models were employed to examine the relationships between urinary metabolites and concentrations of corresponding POP in multimedia samples, as well as between the urinary metabolites and estimated total daily POP dose levels. For each measurement unit

(ng/mL and μmole/mole), two different types of regression models were fitted to the data of measured urinary metabolites. The first type of model included factors for sampling location (at daycare center versus at home) and POP concentrations in multimedia samples. The POP data in playground soil were not included in the model, because POP concentrations in soil were low, and initial analyses showed that soil was not a significant factor for urinary metabolite concentrations. The second type of model included factors for sampling location and total estimated daily POP doses. The total estimated daily POP doses were computed as the sums of the estimated daily potential POP doses from inhalation, nondietary ingestion, and dietary ingestion that resulted from the exposures at homes and at daycare centers. Separate models were fitted to selected hydroxy PAH, PCP, 2,4-D, and 3,5,6-TCP data in subjects' urine samples. All regression models were fitted to the log-transformed data.

Estimates of Daily Potential Persistent Organic Pollutant Doses

The exposure values (ng/day) for inhalation and ingestion (dietary and nondietary) can be converted to units of potential dose by assuming 100% absorption in the lung and stomach, and normalizing for body mass. Various factors can be found in the literature to account for physical, chemical, and/or physiological processes. For maximum estimates, this conversion gives upper limits on POP available for delivery to target organs (lung or stomach). The potential daily dose of PAH in ng/kg/day was estimated using the following equations:

$$D_{inh} = \frac{C_i * t_i + C_o * t_o}{t_i + t_o} * \frac{V}{W} * F$$

$$D_n = \frac{t_i * D_i + t_o * P_o}{t_i + t_o} * \frac{M * 1000}{W} * F$$

$$D_d = \frac{C_f * M_f * 1000}{W} * F$$

where

D_{inh}	=	estimated dose through inhalation at home or at daycare center, ng/kg/day
D_n	=	estimated dose through nondietary exposure at home or at daycare center, ng/kg/day
D_d	=	estimated dose through dietary exposure at home or at daycare center, ng/kg/day
W	=	the measured body weight of the subject, kg
C_i	=	indoor POP concentration at home or at daycare center, ng/m^3
C_o	=	outdoor POP concentration at home or at daycare center, min
t_i	=	subject's time spent indoors at home or at daycare center, min
t_o	=	subject's time spent outdoors at home or at daycare center, min
V	=	the estimated subject's ventilation rate, 15 m^3/day
D_i	=	PAH concentration in the floor dust at home or at daycare center, μg/g
P_o	=	PAH concentration in the pathway soil at home or at daycare center, μg/g
M	=	subject's estimated daily dust/soil intake, 0.1 g
C_f	=	POP concentration in the daily food samples at home or at daycare center, μg/kg
M_f	=	the daily mass of food intake at home or at daycare center, kg/day
F	=	Fraction of the time the subject spends at home or at daycare center.

We assumed a ventilation rate of 15 m^3/day for child subjects (12,13) and that the dust/soil ingestion rate is 0.1 g/day for the child (14,15). The body weight of each subject was measured during the Phase 2 field study.

Chapter 5

Results and Discussion

Method Validation for Multimedia Samples

Air Samples

The recovery data for spiked persistent organic pollutants (POP) from the first experiment are listed in Tables 5.1 and 5.2. The results show that for the filter/XAD-2 sampling modules, quantitative recoveries were obtained for target POP except for phthalate esters (PE), under all storage conditions tested. This finding also demonstrated, by extension, that the XAD-2 sorbent can retain the target POP under the 48-hr sampling conditions used. Greater than 100 percent recoveries of PE are partly due to the difference between spiked and native air levels of these compounds, with the amount spiked being approximately 5 times lower than that collected on the non-spiked sampling modules. In addition, sample handling and processing also contribute to background levels of PE. As seen in Table 5.2, quantitative recoveries of most POP were also obtained from filter/PUF samples under the storage and sampling conditions tested here. Low recovery of acenaphthene-d_{10} from PUF was anticipated, as this sorbent cannot retain 3-ring PAH due to their relatively high volatility (16). The low recovery of bisphenol-A was probably due to incomplete extraction from the PUF; the extraction solvent for PUF (10% EE in hexane) has a much lower solvent strength (0.04) than DCM (0.42). There was no evidence of loss or degradation of the POP over the 20-day storage interval.

The retention efficiencies for the 13 non-coplanar PCB congeners on XAD-2 are listed in Table 5.3. As seen there, recoveries were quantitative: 90-120%.

TABLE 5.1. RECOVERY OF TARGET PERSISTENT ORGANIC POLLUTANTS FROM FILTER/XAD-2 SAMPLES

Target Compound	Recovery, % [a]		
	Day-0	Day-10	Day-20
PAH			
Acenaphthene-d_{10}	91 ± 9	94 ± 2	107
Pyrene-d_{10}	85 ± 6	83 ± 3	92
Chrysene-d_{12}	82 ± 1	81 ± 1	91
Benzo[k]fluoranthene-d_{12}	86 ± 6	90 ± 3	110
OC Pesticide			
Lindane	106 ± 18	129 ± 1	120
Aldrin	82 ± 1	90 ± 5	107
p,p'-DDE	89 ± 0	85 ± 2	100
Dieldrin	100 ± 5	98 ± 3	103
Endrin	93 ± 2	112 ± 1	137
p,p'-DDT	94 ± 5	120 ± 4	118
OP Pesticide			
Diazinon	82 ± 12	125 ± 3	113
Chlorpyrifos	81 ± 8	112 ± 3	134
PCB (Coplanar)			
3,3', 4,4'-tetrachlorobiphenyl (77)	89 ± 5	79 ± 1	85
3,3' 4,4'5-pentachlorobiphenyl (126)	83 ± 3	81 ± 1	90
2,2'4,4'6,6'-hexachlorobiphenyl (155)	85 ± 1	84 ± 0	101
PE (Phthalate Ester)			
Di-n-butylphthalate	96 ± 49	83 ± 0	113
Benzylbutylphthalate	159 ± 90	83 ± 29	440
Ph (Phenols)			
Bisphenol-A	77 ± 13	83 ± 12	111
Pentachlorophenol	85 ± 7	89 ± 3	83

(a) Day-0, Day-10, and Day-20 represented 0-, 10-, and 20-day storage intervals after sampling. Data are from triplicate Day-0 samples, duplicate Day-10 samples, and one Day-20 sample.

TABLE 5.2. RECOVERY OF TARGET PERSISTENT ORGANIC POLLUTANTS FROM FILTER/PUF SAMPLES

Target Compound	Recovery, % [a]		
	Day-0	Day-10	Day-20
PAH			
Acenaphthene-d_{10}	5 ± 1	5 ± 1	5
Pyrene-d_{10}	101 ± 0	99 ± 3	79
Chrysene-d_{12}	91 ± 1	102 ± 2	90
Benzo[k]fluoranthene-d_{12}	88 ± 4	107 ± 1	76
OC Pesticide			
Lindane	99 ± 10	110 ± 4	104
Aldrin	70 ± 27	89 ± 14	82
p,p'-DDE	101 ± 2	98 ± 2	96
Dieldrin	101 ± 2	92 ± 2	88
Endrin	131 ± 7	121 ± 3	120
p,p'-DDT	140 ± 7	112 ± 3	114
OP Pesticide			
Diazinon	102 ± 7	119 ± 4	78
Chlorpyrifos	115 ± 5	116 ± 4	87
PCB (Coplanar)			
3,3', 4,4'-tetrachlorobiphenyl (77)	97 ± 1	85 ± 2	81
3,3' 4,4'5-pentachlorobiphenyl (126)	83 ± 6	90 ± 1	88
2,2'4,4'6,6'-hexachlorobiphenyl (155)	97 ± 3	100 ± 2	97
PE (Phthalate Ester)			
Di-n-butylphthalate	38 ± 13	129 ± 17	94
Benzylbutylphthalate			
Ph (Phenols)			
Bisphenol-A	38 ± 6	53 ± 1	36
Pentachlorophenol	93 ± 1	98 ± 0	69

(a) Day-0, Day-10, and Day-20 represented 0-, 10-, and 20-day storage intervals after sampling. Data are from triplicate Day-0 samples, duplicate Day-10 samples, and one Day-20 sample.

TABLE 5.3. RECOVERY OF NON-COPLANAR POLYCHLORINATED BIPHENYLS FROM FILTER/XAD-2 SAMPLES

Compound [a]	Recovery, % [b]
2,4,4'-Trichlorobiphenyl (28)	96 ± 0
2,2',5,5'-Tetrachlorobiphenyl (52)	95 ± 1
2,2',3,5'-Tetrachlorobiphenyl (44)	100 ± 2
2,3',4',5-Tetrachlorobiphenyl (70)	108 ± 1
2,2'3,5',6-Pentachlorobiphenyl (95)	92 ± 1
2,2',4,5,5'-Pentachlorobiphenyl (101)	112 ± 2
2,2'3,4,5'-Pentachlorobiphenyl (87)	119 ± 1
2,3,3',4',6-Pentachlorobiphenyl (110)	114 ± 2
2,3',4,4',5-Pentachlorobiphenyl (118)	111 ± 2
2,3,3'4,4'-Pentachlorobiphenyl (105)	108 ± 2
2,2'4,4',5,5'-Hexachlorobiphenyl (153)	110 ± 1
2,2'3,4,4'5'-Hexachlorobiphenyl (138)	103 ± 2
2,2'3,4,4',5,5'-Heptachlorobiphenyl (180)	119 ± 0

(a) The number in the paretheses are the PCB congener's numbers.
(b) Data are from duplicate Day-0 samples.

Table 5.4 summarizes the results of experiments for retention and recovery of 2,4-D and PCP from Teflon-coated glass filters and PUF. As shown there, the extraction and cleanup methods can be applied equally well to PCP and 2,4-D, and 3,4-D serves adequately as an analytical surrogate recovery standard (SRS) for each analyte in assessing analytical losses. Relative to the analytical method, 2,4-D recovery from the filter following air sampling appeared to be quantitative (83 vs 80%) despite the 3,4-D recovery being slightly lower than expected (66 vs 73%). No 2,4-D was detected in the PUF extract. In contrast, PCP appears to have moved from filter to PUF during the 48-hr sampling interval, with negligible amounts found on the filter after sampling. On the basis of the 3,4-D recovery, we surmised that the PCP was probably completely recovered on the PUF, with the loss being due to analytical losses, rather than sampling losses. However, on the basis of a single set of samples for method validation, it seems more prudent to approach PCP sampling as collection on XAD-2 and extraction with DCM prior to analysis.

According to the results from the above method validation tests, we then used a quartz fiber filter/XAD-2 as a sampling module for collection of target POP including PAH, OC, OP, PCB, PE and Phenols in air. We used a Teflon-coated glass fiber filter/PUF to collect 2,4-D.

Dust and Soil Samples

The recovery data for spiked POP in house dust and soil samples are presented in Table 5.5 and 5.6, respectively. Because the analytical methods for determining phenols and 2,4-D were validated from previous studies (2,7), we therefore excluded phenols and 2,4-D acid from these experiments to simplify the sample matrix effect. Quantitative recoveries of most target POP from house dust were obtained when hexane and 10% EE in hexane were used as the extraction solvent. Recoveries of chlorpyrifos and phthalate esters were difficult to assess in the low-level spike experiments because of the high levels of these compounds were present in the nonspiked house dust. Levels of chlorpyrifos and benzylbutyl phthalate in the nonspiked dust were approximately 20 times and over 100 times higher, respectively, than the spike level. For the high-level spike experiments, quantitative recoveries of chlorpyrifos were obtained.

TABLE 5.4. RECOVERY OF 2,4-D AND PENTACHLOROPHENOL FROM FILTER/PUF SAMPLES

Compound	Recovery, %	
	Filter	PUF
Method Spike[a]		
PCP	74 ± 4	70 ± 2
2,4-D	83 ± 14	80 ± 1
3,4-D	73 ± 5	82 ± 2
Day-10 Air Samples[b]		
PCP	2 ± 1	49 ± 3
2,4-D	80 ± 5	0 ± 0
3,4-D	66 ± 3	51 ± 5

(a) Known amounts of PCP, 2,4-D, and 3,4-D were spiked onto filters and PUF plugs for method spike samples. Data were from triplicate filter and PUF samples.

(b) Known amounts of PCP and 2,4-D were spiked onto filter samples but not PUF plugs prior air sampling, and known amounts of 3,4-D were spiked onto both filter and PUF samples before sample extraction. Data were from triplicate filter and PUF samples.

TABLE 5.5. RECOVERY OF TARGET PERSOSTEMT ORGANIC POLLUTANTS FROM SPIKED HOUSE DUST SAMPLES

Target Compound	Recovery, % [a]				
	Hexane (H) none	Hexane (L) none	10% EE in Hexane (H) Floirsil-SPE	10% EE in Hexane (L) Floirsil-SPE	DCM (L) Silica-SPE
PAH					
Acenaphthene-d_{10}	97 ± 29	107 ± 11	86 ± 1	89 ± 2	NA[c]
Pyrene-d_{10}	90 ± 30	96 ± 7	85 ± 1	91 ± 2	NA
Chrysene-d_{12}	85 ± 24	97 ± 7	81 ± 2	98 ± 2	NA
Benzo[k]fluoranthene-d_{12}	94 ± 11	103 ± 6	110 ± 24	111 ± 1	NA
OC Pesticide					
Lindane	118 ± 28	114 ± 8	100 ± 1	105 ± 2	NA
Aldrin	105 ± 34	105 ± 7	93 ± 1	101 ± 2	NA
p,p'-DDE	95 ± 29	100 ± 12	87 ± 0.1	95 ± 2	NA
Dieldrin	140 ± 10	125 ± 23	96 ± 1	130 ± 3	NA
Endrin	115 ± 20	115 ± 16	92 ± 2	114 ± 4	NA
p,p'-DDT	136 ± 25	91 ± 4	101 ± 1	107 ± 5	NA
OP Pesticide					
Diazinon	100 ± 29	93 ± 20	88 ± 2	86 ± 10	NA
Chlorpyrifos	24 ± 4	ND[b]	91 ± 1	273 ± 68	NA
PCB (Coplanar)					
3,3', 4,4'-tetrachlorobiphenyl (77)	95 ± 37	77 ± 7	84 ± 1	94 ± 2	NA
3,3' 4,4'5-pentachlorobiphenyl (126)	84 ± 18	101 ± 8	83 ± 1	91 ± 2	NA
2,2'4,4'6,6'-hexachlorobiphenyl (155)	86 ± 19	91 ± 6	81 ± 0.3	90 ± 4	NA
PE (Phthalate Ester)					
Di-n-butylphthalate	90 ± 40	150 ± 27	ND	66 ± 16	NA
Benzylbutylphthalate	ND[b]	ND[b]	ND	188 ± 162	NA

(a) Data were from triplicate spiked and non-spiked dust samples; H denotes high-level spike (500ng/compound or 1000 ng/compund) and L denotes low-level spike (100 ng/compound).
(b) ND denotes negative recovery data were obtained because of high levels of these compounds present in the dust sample.
(c) NA denotes that the sample extracts were not analyzed because a precipitate formed during the concentration step after Silica SPE cleanup.

TABLE 5.6. RECOVERY OF TARGET PERSISTENT ORGANIC POLLUTANTS FROM SPIKED SOIL SAMPLES

Target Compound	Recovery, % [a]			
	Hexane (H) none	Hexane (L) none	10% EE in Hexane (L) Floirsil-SPE	DCM (L) Silica-SPE
PAH				
Acenaphthene-d_{10}	103 ± 1	110 ± 15	85 ± 2	54 ± 3
Pyrene-d_{10}	110 ± 8	113 ± 6	94 ± 5	58 ± 3
Chrysene-d_{12}	110 ± 2	103 ± 5	95 ± 7	71 ± 3
Benzo[k]fluoranthene-d_{12}	105 ± 2	97 ± 7	98 ± 5	111 ± 10
OC Pesticide				
Lindane	78 ± 3	77 ± 9	94 ± 2	94 ± 4
Aldrin	103 ± 1	100 ± 15	94 ± 2	82 ± 5
p,p'-DDE	110 ± 8	127 ± 22	95 ± 2	64 ± 3
Dieldrin	108 ± 3	116 ± 19	109 ± 4	88 ± 3
Endrin	112 ± 2	103 ± 21	102 ± 5	123 ± 12
p,p'-DDT	103 ± 6	69 ± 7	107 ± 3	108 ± 8
OP Pesticide				
Diazinon	59 ± 4	19 ± 1	86 ± 6	77 ± 2[b]
Chlorpyrifos	91 ± 17	34 ± 4	81 ± 8	97 ± 3
PCB (Coplanar)				
3,3', 4,4'-tetrachlorobiphenyl (77)	113 ± 2	113 ± 5	94 ± 4	61 ± 4
3,3' 4,4'5-pentachlorobiphenyl (126)	112 ± 5	109 ± 8	94 ± 5	68 ± 3
2,2'4,4'6,6'-hexachlorobiphenyl (155)	110 ± 5	110 ± 8	94 ± 5	76 ± 4
PE (Phthalate Ester)				
Di-n-butylphthalate	107 ± 5	76 ± 13	111 ± 37	68 ± 5
Benzylbutylphthalate	108 ± 6	97 ± 7	99 ± 6	92 ± 7

(a) Data were from triplicate spiked and non-spiked soil samples; H denotes high-level spike (500 ng/compound or 1000 ng/compound) and L denotes low-level spike (100 ng/compound).

(b) Data were the sum of the recovery data of hexane/DCM and DCM fractions.

For the same reason mentioned above, the recovery data of PE cannot be obtained because native PE levels were still much higher than the high-level spike (1000 ng/compound). The fractions of the dust samples generated from DCM extraction were not analyzed by GC/MS, because a yellow participate formed during the concentration step after the silica SPE cleanup step. In general, satisfactory recoveries for spiked POP were obtained from house dust when 10% EE in hexane was used as the extraction solvent, followed by a Florisil SPE clean up step.

Quantitative recoveries were obtained for most POP from pathway soil for all the experiments. At the lower spike level (100 ng/compound), the recovery of chlorpyrifos was 34% when hexane was used and the recovery improved to greater than 81% when the more polar solvent 10% EE in hexane was used. Satisfactory recoveries (68 to 111%) of PE from the soil sample were obtained. This is mainly because the native levels of PE in the soil sample were in the same range as the spike level. Quantitative recoveries (>80%) of all target POP were observed when 10% EE in hexane was used as the extraction solvent, followed by Florisil-SPE clean-up step.

From the results of the above experiments, we decided to use the analytical method validated here to determine all target POP except phenols and 2,4-D for both Phase 1 and 2 dust/soil samples. This method consists of (1) sonication of the sample with 10% EE in hexane; (2) clean-up of the extract using an SPE cartridge; and (3) analysis of the fraction by GC/MS.

An analytical method was developed from the previous study to determine all target phenols except PCP in dust and soil (7). The spiked dust samples were analyzed for target phenols using the above analytical method with miner modifications (as described in Chapter 4 experimental section). Quantitative recoveries were obtained from the triplicate spiked samples. The recovery data were: 107±3 % for nonylphenols, 93±3 % for PCP, and 104±8 % for bisphenol-A. Therefore, this modified analytical method was used to determine target phenols in the Phase 1 and 2 samples. The analytical method developed for the 2,4-D analysis in dust and soil matrix in a previous study (2) was used in the Phase 1 and 2 samples, thus no method validation experiments were carried out for the 2,4-D analysis in dust and soil.

Dermal Wipe Samples

The spike recovery data for the dermal wipe samples are summarized in Table 5.7. As shown in Table 5.7, quantitative recoveries were obtained for most of the spike compounds. It should be noted that the higher level spike experiments were conducted on real hand wipe samples and the low-level spike experiments were conducted on clean wipes. The recovery data of phenanthrene, and two phthalate esters could not be obtained because the background levels of these compounds were much higher than the spiked level (20 ng/compound). For the same reason, the recoveries of lindane could not be obtained in the low-level spike experiments. An interference peak was eluted closely to aldrin, and the two peaks were not completely resolved from each other in the low-level spiked sample; this could cause the recoveries greater than 100%. There is no difference in recoveries of the spiked POP between the two methods evaluated with and without the liquid-liquid partitioning step as described in section 4. Therefore, the analytical method used in the low-level spike experiments and the Phase 2 dermal wipe samples did not include the liquid-liquid partitioning step. Note that target PAH and OP pesticides were present in both fractions (15 % EE in hexane and 50 % EE in hexane) in the high-level spike experiments. The recovery data shown in Table 5.7 are the sums of the data in both fractions. Another eluting condition, 24 mL of 15 % EE in hexane was conducted in the low-level spike experiments. As shown in this table, satisfactory recoveries were obtained in both eluting conditions in the low level spike experiments. Therefore the method used in the Phase 2 dermal wipe samples consisted of Soxhlet extraction the wipe sample with 10 % EE in hexane, Florisil SPE cleanup with 24 mL of 15 % EE in hexane, and GC/MS analysis.

Urine Samples

Table 5.8 summarizes the spike recovery data of the spiked urine samples, and shows that acceptable recoveries were obtained. The recoveries ranged from 75±10 % for 1-hydroxypyrene to 99±13 % for 2,4-D in high-level spike experiments (10 ppb); from 76±34% for 1-hydroxypyrene to 110±1% for 6-hydroxyindeno[1,2,3-c,d]pyrene in medium-level spike

TABLE 5.7. RECOVERY OF TARGET PERSISTENT ORGANIC POLLUTANTS FROM SPIKED DERMAL WIPE SAMPLES

Target Compound	Recovery, %[a]		
	High Level (20 ng/Compound)	Low Level (5 ng/compound)	
	A	A	B
PAH			
Acenaphthene	95 ± 14	114 ± 8	99 ± 11
Phenanthrene	ND[b]	ND[b]	ND[b]
Pyrene	105 ± 7	105 ± 21	94 ± 14
Benzo[a]pyrene	78 ± 7	86 ± 22	98 ± 8
OC Pesticides			
Lindane	88 ± 8	ND	ND
Aldrin	74 ± 8	130 ± 51	134 ± 22
p, p'-DDE	72 ± 8	102 ± 5	96 ± 7
Dieldrin	93 ± 10	86 ± 8	85 ± 6
Endrin	112 ± 8	103 ± 30	128 ± 8
p,p'-DDT	107 ± 6	117 ± 41	134 ± 32
OP Pesticides			
Diazinon	88 ± 10	103 ± 24	91 ± 9.6
Chlorpyrifos	102 ± 8	98 ± 25	94 ± 23
PCB	114 ± 9	106 ± 9	101 ± 7
3,3',4,4'-tetrachlorobiphenyl (77)	95 ± 10	99 ± 1	104 ± 23
2,2'5,5'-tetrachlorobiphenyl (52)	106 ± 12	122 ± 4	113 ± 11
3,3',4,4',5-pentachlorobiphenyl (126)	89 ± 10	96 ± 6	107 ± 8
2,2',3,5',6-pentachlorobiphenyl (95)	ND	ND	ND
	ND	ND	ND
PE (phthalate ester)			
Di-n-butylphthalate			
Benzylbutylphthalate			

(a) A denotes that the Florisil SPE column was eluted with 12 mL of 15% EE in hexane and 12 mL of 50% EE in hexane, and B denotes that the Florisil SPE column was eluted with 24 mL of 15% EE in hexane.

(b) ND denotes negative recovery data were obtained because of high levels of these compounds were present in the non-spiked wipe samples.

TABLE 5.8 RECOVERY OF TARGET ANALYTES FROM SPIKED URINE SAMPLES

Target Compound	Recovery, %[a]		
	High Level (10 ppb)	Medium Level (1 ppb)	Low Level (0.4 ppb)
3,4-D	99 ± 13	116 ± 4	102 ± 24
Pentachlorophenol	75 ± 10	85 ± 7	90 ± 3
1-Hydroxypyrene	91 ± 9	76 ± 34	79 ± 12
6-Hydroxyindeno[1,2,3-c,d]pyrene	88 ± 2	110 ± 1	125 ± 7

(a) Data were from duplicate spiked sampled.

experiments (1 ppb); and from 79 ±12% for 1-hydroxypyrene to 125 ±7% for 6-hydroxy[1,2,3-c,d]pyrene in low-level spike experiment (0.4 ppb). This analytical method consisted of hydrolysis with 6N HCl, methylating with diazomethane, fractioning with Florisil SPE column, and analyzing by GC/MS were used in the Phase 2 urine samples.

Table 5.9 summarizes the spike recovery data of 3,5,6-TCP in the spiked urine samples. Quantitative recoveries (>90%) were obtained from the spiked urine samples at all three spiked levels (1 ppb, 3 ppb, and 10 ppb). Thus, this analytical method was used for Phase 2 urine samples to determine 3,5,6-TCP in urine samples. The analytical method consisted of hydrolysis the urine sample with concentrated HCl, extracting the mixture with DCM, solvent exchanging DCM to toluene, derivatizing the toluene extract with MTBSTFA, and analyzing the extract by GC/MS.

Food Samples

The optimal analytical methods developed from the method evaluation experiments for the determination of POP in PAH, PCB, PE, Ph, OC, OP, and 2,4-D in duplicate diet food samples are described in Appendix A. In brief, the food sample was extracted with DCM, passed

TABLE 5.9. RECOVERY OF 3,5,6-TCP FROM SPIKED URINE SAMPLES

Spike Level	Recovery of 3,5,6-TCP[a], %
10 ppb	94 ± 3.5
3 ppb	94 ± 4.2
1 ppb	93 ± 2.0

(a) Data were from triplicate spiked samples.

through GPC, applied to a Florisil SPE column, and analyzed for GC/MS for all target analytes but 2,4-D and PCP. A portion of the GPC fraction was methylated, and fractionated by Florisil SPE from 2,4-D and PCP analysis. Note that the evaluation experiments were conducted on the solid samples only. We expected that the sample matrix of the liquid food is simpler than the solid food. Thus, the analytical method developed for the solid food was modified slightly on the extraction step for the liquid food (Appendix A). Table 5.10 summarizes the recoveries data of target POP in the spiked solid food samples. In general, acceptable recoveries of the spiked POP were obtained and slightly better recoveries for most target POP were observed in the second set of samples. This is partly because we replaced the TurboVap concentration with Kuderna Danish concentration, to minimize the losses of analytes in the concentration steps. Note that recoveries of DDT were greater than 100% in all the spiked food samples. Further tests were conducted by spiking known amounts of DDT into food sample matrix, and the results showed that the GC responses of DDT in the food sample matrix were about twice of those in clean solvent without the food matrix. This is probably due to the food sample matrix having deactivated the surfaces of GC injector or column, which caused the responses of DDT to increase. Recoveries greater than 100% were also observed for nonylphenols and PE. This is mainly because of the high background levels of the non-spiked food samples. The low recovery of bisphenol-A was partly due to the loss through Florisil SPE cleanup step. Several problems were encountered when we prepared the food samples. The DCM extract needed to be filtered prior to applying to GPC; very often the filter was plugged because of the sample matrix, and

TABLE 5.10 RECOVERY OF TARGET PERSISTENT ORGANIC POLLUTANTS FROM SPIKED SOLID FOOD SAMPLES

Target Compound	Recovery, %[a]		
	I	II	III
PAH			
Acenaphthene	61 ± 3	88 ± 6	NA
Pyrene-d_{10}	54 ± 3	85 ± 3	NA
Chrysene-d_{10}	46 ± 2	109 ± 15	NA
Benzo[k]fluoranthene-d_{12}	45 ± 1	106 ± 5	NA
OC Pesticide			
Heptachlor	100 ± 2	105 ± 5	NA
Lindane	72 ± 4	89 ± 7	NA
Aldrin	76 ± 9	90 ± 4	NA
p,p'-DDE	84 ± 5	87 ± 3	NA
Dieldrin	93 ± 13	96 ± 4	NA
Endrin	122 ± 19	83[d]	NA
p,p'-DDT	153 ± 20	193 ± 26	
OP Pesticide			
Diazinon	58 ± 2	83 ± 3	NA
Chlorpyrifos	58 ± 2	101 ± 5	NA
PCB			
2,2'4-trichlorobiphenyl	63 ± 4	76 ± 13	NA
2,2'5,5'-tetrachlorobiphenyl	62 ± 2	76 ± 10	NA
2,3,4,4'5-pentachlorobiphenyl	54 ± 2	73 ± 12	NA
2,2'3,5,6-pentachlorobiphenyl	52 ± 2	85 ± 19	NA
2,2'4,4',5,5'-hexachlorobiphenyl	56 ± 4	82 ± 13	NA
PE (Phthalate Ester)			
Di-n-butylphthalate	83 ± 1	ND	NA
Benzylbutylphthalate	90 ± 4	ND	NA
Ph (Phenols)			
Nonylphenol	ND[b]	ND	NA
Bisphenol-A	29 ± 3	64 ± 3	NA
Pentachlorophenol	NA[c]	NA	85 ± 2
HA (Herbicide Acid)			
2,4-D	NA	NA	63 ± 3

(a) Data were from triplicate spiked solid food samples; I denotes 25 g of high-fat food samples, II denotes 25 g of medium fat food samples, and III denotes 10 g of medium fat food samples.
(b) ND denotes not determined; the recoveries were greater than 200%.
(c) NA denotes the target analytes were not analyzed in these samples.
(d) Only one measurement reported, interference peaks were observed in the other two duplicate samples.

more than one filter was used to complete the filtration. This step could also contribute to the loss of the spiked analytes. In order to include PE into the GPC fraction, the fat was not completely removed from the sample extract after GPC. Approximately 90% of the fat was removed after GPC, and even after Florisil SPE cleanup, the sample matrix was still very complex. Due to the time and cost constraints, we did not continue further evaluation experiments, and used this method (Appendix A) for the Phase 1 and 2 samples.

Better analytical methods could be developed by dividing the compound classes into three groups; the first group would contain the stable POP including PAH, PE, PCB, and some OC (i.e., chlordanes and heptachlor). We recommend use of the method developed for PAH to determine these analytes (5, 6). The method consists of KOH digestion, liquid-liquid partitioning, column cleanup and GC/MS. The second group would contain less stable POP including OP, Ph, and some OC. We recommend use of the analytical method described here (Appendix A) with minor modifications to determine these compounds. The cut-off point for the GPC fraction would be changed to completely remove the fat and some PE. Since PE would not be the compound of interest, complete removal of the fat may simplify the sample matrix. The third group would include 2,4-D and PCP. The analytical method described here could be modified to improve the recoveries of these compounds. The modifications could include the use of acidic organic solvent for extracting solid food sample and then acidifying the liquid food sample prior to organic solvent extraction. The cleanup steps could include GPC and Florisil SPE.

Phase 1 Field Study

Recruiting of Daycare Centers

The results of recruiting daycare centers for the Phase 1 study are summarized in Table 5.11. The overall response rate (private daycare and Head Start centers) was about 14%. The most common reasons for those daycare centers/directors who refused to participate in the study were: (1) not interested in the study; (2) short of staff, would not have time to do the

TABLE 5.11. SUMMARY OF RECRUITING DAYCARE CENTERS FOR PHASE 1 STUDY

Type	Location	Agreed to Participate	Did not Agree to Participate	Bad[a] Data	Total
Private Daycare Centers	Durham/Chapel Hill	18	97	3	118
	Raleigh	6	73	0	79
Head Start Centers	Raleigh	1	0	0	1
	Durham	1	0	0	1
	Holly Springs	1	0	0	1
	Cedar Grove	1	0	0	1
	Garner	1	0	0	1
	Total	29	170	3	202

(a) Bad data denotes disconnected telephone number.

study; and (3) not approved by the owner or board of directors, company policy, concerns about study findings that may damage the image of the daycare center or even cause problems for their license. The $50 payment for participation was an effective incentive for many participants. Nevertheless, the recruiting methods we used were effective and cost-efficient. All recruiting activities were completed in about four weeks. Our goal was to recruit 9 daycare centers; we qualified 29. We can apply the same methods for a future larger study in multiple geographical areas.

Field Activities

The Phase 1 sampling activities were conducted in ten daycare centers (9 scheduled centers and 1 backup center) during a period of three weeks in March 1997. In general, we received good cooperation from each daycare center. There was no problem with the collection

of food samples by the staff of each daycare center. The teachers from two daycare centers (D01 and D05) complained about the noise of the indoor air samplers. A backup daycare center (D10) was sampled during the third week of the Phase 1 field study because the outdoor samplers used in D05 were overheated. Multi-media samples were collected from these daycare centers as planned (Table 4.2). It took approximately one hour to complete the pre-monitoring questionnaire. The most difficult question for the daycare director to answer was the use of chemicals. For many daycare centers, the maintenance work was done by an outside contractor or a different division of the same organization. Many phone calls were made to trace the information about the use of chemicals in these daycare centers. For future large scale studies, the pre-monitoring questionnaire could be simplified to collect only key information that is essential to the study. There was no problem in conducting the post-monitoring questionnaires; it took approximately 15 minutes to complete the interview.

Concentrations of Persistent Organic Pollutants in Multimedia Samples

Table 5.12 summarizes the target POP in multiple compound classes determined in the Phase 1 multimedia samples. The sums of the concentrations of target POP in each compound class in air, dust/soil, and food are summarized in Table 5.13 through 5.15, respectively. These tables show the sums of all target analytes in each compound class. Also reported is the sum of selected target 4- to 6-ring PAH ranked as probable human carcinogens (B2) in the U.S. EPA Integrated Risk Information System and designated as B2 PAH. For ease of discussion in this chapter, the sums of target POP in each compound class were referred as the respective compound class. The data reported in these tables were corrected for the corresponding field blanks. Note that the reported data were not corrected for the recoveries of the spiked SRS except for 2,4-D. The reported 2,4-D data were corrected for the recoveries of SRS (3,4-D). The individual target POP data in indoor air, outdoor air, HVS3 floor dust, vacuum bag floor dust, playground soil, liquid food and solid food samples are summarized in Table D-1 through D-7, respectively, in Appendix D.

TABLE 5.12. A SUMMARY OF TARGET PERSISTENT ORGANIC POLLUTANTS DETERMINED IN MULTIMEDIA SAMPLES

Compound Class	Target Analyte
PAH	Naphthalene
	Biphenyl
	Acenaphthylene
	Acenaphthene
	Fluorene
	Phenanthrene
	Anthracene
	Fluoranthene
	Pyrene
	Cyclopenta[c,d]pyrene
	Benz[a]anthracene*
	Chrysene*
	Benzo[b]fluoranthene*
	Benzo[k]fluoranthene*
	Benzo[e]pyrene
	Benzo[a]pyrene*
	Indeno[1,2,3-c]pyrene*
	Dibenz[a,h]anthracene*
	Benzo[g,h,i]perylene
	Coronene
PE	Dibutylphthalate
	Benzylbutylphthalate
OP	Diazinon
	Chlorpyrifos
OC	Lindane
	Heptachlor
	Aldrin
	gamma-Chlordane
	alpha-Chlordane
	p,p'-DDE
	Dieldrin
	Endrin
	p.p'-DDT
PCB	2-Chlorobiphenyl
	4-Chlorobiphenyl
	2,6-Dichlorobiphenyl
	4,4'-Dichlorobiphenyl
	2,4,4'-Trichlorobiphenyl
	2,2'5,5'-Tetrachlorobiphenyl
	2,2'3,5'-Tetrachlorobiphenyl
	2,3',4',5-Tetrachlorobiphenyl
	3,3',4,4'-Tetrachlorobiphenyl
	2,2',3,5',6-Pentachlorobiphenyl
	2,2',4,5,5'-Pentachlorobiphenyl
	2,2',3,4,5'-Pentachlorobiphenyl
	2,3,3',4',6-Pentachlorobiphenyl
	2,3',4,4',5-Pentachlorobiphenyl
	2,3,3',4,4'-Pentachlorobiphenyl
	3,3',4,4',5-Pentachlorobiphenyl
	2,2',4,4',5,5'-Hexachlorobiphenyl
	2,2',3,4,4',5'-Hexachlorobiphenyl
	3,3',4,4',5,5'-Hexachlorobiphenyl
	2,2',3,4,4',5,5'-Heptachlorobiphenyl
Ph	Pentachlorophenol
	Nonylphenol
	Bisphenol-A
HA	2,4-D

* Denotes that the target PAH are ranked as possible human carcinogen (B2) by U.S. EPA's Integrated Risk Information System.

TABLE 5.13. SUMMARY OF TARGET PERSISTENT ORGANIC POLLUTANTS IN AIR SAMPLES FROM PHASE 1 DAY CARE CENTERS

Compound Class	Concentration, ng/m^3									
	D01	D02	D03	D04	D05	D06	D07	D08	D09	D10
Indoor Air										
PAH	497	262	690	120	180	171	116	171	204	241
B2 PAH	0.617	0.771	0.557	0.627	0.703	0.605	0.615	0.686	0.442	0.246
PE	985	359	477	229	273	230	121	448	127	144
OP	38.1	47.7	13.7	10.8	76.1	16.7	9.01	20.0	8.23	12.3
OC	81.9	36.1	59.3	358	23.7	18.7	16.5	74.4	18.0	42.1
PCB	7.32	5.71	22.9	8.72	10.8	246	18.6	11.4	54.8	258
Ph	273	236	529	211	223	153	52.8	221	86.5	81.6
HA	<0.1	0.225	<0.1	0.216	<0.1	<0.1	0.113	0.242	0.474	0.228
Outdoor Air										
PAH	75.8	127	88.5	71.8	35.1	317	82.2	120	70.2	139
B2 PAH	0.317	0.423	0.248	0.517	0.153	0.705	0.313	0.288	0.196	0.331
PE	128	876	436	74	104	227	73.3	793	199	106
OP	3.18	30.0	3.60	26.2	3.07	11.9	0.755	6.35	5.46	8.47
OC	15.5	13.4	8.56	10.3	11.1	7.00	13.2	11.0	4.26	7.50
PCB	15.5	11.2	7.71	9.42	7.88	9.34	6.44	7.75	8.20	8.05
Ph	81.3	113	76.3	39.5	42.4	103	107	101	31.6	41.4
HA	<0.1	0.217	<0.1	<0.1	0.382	0.322	0.401	0.544	0.318	0.195

TABLE 5.14. SUMMARY OF TARGET PERSISTENT ORGANIC POLLUTANTS IN DUST AND SOIL SAMPLES FROM PHASE 1 DAY CARE CENTERS

Compound Class	Concentration,[a] ppm										
	D01	D02	D03	D04	D05	D06	D07	D08	D09-1	D09-2	D10
Floor Dust											
PAH	2.82	9.98	3.07	1.08	0.588	0.600	0.436	1.22	0.388	8.20	9.42
B2 PAH	0.993	4.50	1.25	0.507	0.281	0.303	0.172	0.583	0.130	4.40	5.29
PE	61.2	38.4	61.2	105	89.7	57.9	22.9	221	50.6	139	100
OP	0.799	1.35	0.623	0.433	1.19	0.975	0.205	1.55	0.096	0.742	0.840
OC	1.66	1.23	1.20	3.62	1.08	0.597	1.06	1.43	1.58	1.25	0.761
PCB	0.143	0.697	0.586	0.354	0.072	2.76	0.138	0.166	0.139	24.8	28.2
Ph	9.14	14.7	5.35	7.52	10.7	15.2	5.51	16.2	9.77	16.5	8.33
HA	0.118	0.052	0.020	0.264	0.050	0.235	0.024	0.315	0.139	0.160	0.618
Playground Soil											
PAH	13.1	1.04	0.574	0.101	0.061	0.167	0.060	0.255	0.197	NA[b]	0.127
B2 PAH	5.59	0.397	0.211	0.024	0.012	0.052	0.017	0.075	0.055	NA	0.042
PE	0.247	0.290	0.250	0.231	1.24	1.22	0.245	0.278	0.312	NA	0.242
OP	0.012	0.010	0.006	0.040	0.011	0.011	0.004	0.004	0.004	NA	0.008
OC	0.006	0.005	0.005	0.070	0.022	0.022	0.024	0.007	0.036	NA	0.014
PCB	0.004	0.001	0.007	0.004	0.001	0.001	0.09	0.008	0.007	NA	0.006
Ph	0.522	0.187	0.204	0.305	0.255	0.255	0.237	0.276	0.255	NA	0.136
HA	<0.001	0.003	<0.001	<0.001	<0.001	<0.001	<0.001	0.005	<0.001	NA	<0.001

(a) D09-1 denotes the floor dust sample was collected from the classroom where the air sample was taken and equipped with a new carpet (2 months old). D09-2 denotes the floor sample taken from another classroom equipped with an old crpet (2 years old).

(b) NA denotes not applied, only one playground soil samples was collected from D09.

TABLE 5.15. SUMMARY OF TARGET PERSISTENT ORGANIC POLLUTANTS IN LIQUID AND SOLID FOOD SAMPLES FROM PHASE 1 DAYCARE CENTERS

Compound Class	Concentration, ppb									
	D01	D02	D03	D04	D05	D06	D07	D08	D09	D10
Liquid Food										
PAH	0.86	3.12	2.76	0.81	0.53	0.60	0.57	0.53	3.31	0.68
B2 PAH	<0.04	<0.04	<0.04	0.05	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
PE	64.4	32.3	22.5	25.0	26.8	86.5	49.0	16.6	86.4	34.1
OP	<0.04	0.26	<0.04	<0.04	<0.04	0.23	0.180	<0.04	0.12	0.08
OC	2.00	1.31	1.28	1.20	<0.04	<0.04	0.24	0.090	0.82	0.31
PCB	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Ph	3.45	10.1	<0.1	7.77	7.50	7.97	10.3	7.12	8.43	6.43
HA	0.29	0.22	0.64	0.58	0.39	0.20	2.36	1.59	2.08	1.71
Solid Food										
PAH	1.87	2.56	2.70	6.19	3.15	4.32	6.00	4.01	3.31	9.15
B2 PAH	0.05	0.08	0.48	1.01	0.08	0.68	0.88	0.62	0.47	0.42
PE	191	188	199	194	342	279	387	154	253	234
OP	0.56	0.66	0.55	0.37	2.70	15.17	1.60	0.63	0.49	1.19
OC	0.40	2.26	0.34	4.32	5.46	0.25	1.15	0.48	2.81	3.04
PCB	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Ph	28.6	30.2	68.6	55.8	55.3	50.4	49.1	36.6	44.2	57.9
HA	0.28	0.30	3.14	2.47	1.30	1.45	1.48	0.42	0.26	2.44

The concentrations of PAH found in indoor air were higher than those in the corresponding outdoor air. The B2 PAH concentrations in air only represent a small portion of the total PAH concentrations. These PAH concentration profiles are in agreement with those from previous studies (5,6). Higher indoor concentrations were also observed for target POP in other compound classes including PE, OC, OP, PCB, and Ph. Similar indoor and outdoor concentrations were measured for 2,4-D. In general, concentrations of target POP in all compound classes were of the same order of magnitude among all day dare centers. The most abundant air concentrations were found for target POP in the compound classes of phthalate esters (PE), PAH, and phenols (Ph), followed by PCB, OC, OP, and 2,4-D.

Concentrations of individual target POP in each compound class (Appendix D) showed that few target PAH including cyclopenta[c,d]pyrene, dibenzo[a,h]anthracene, and coronene were not detected in the air samples. The individual target POP in PE, OP, and Ph were found in most air samples. However, many target POP in OC were not detected in the air samples. Only four of nine compounds, namely lindane, heptachlor, gamma-chlordane, and alpha-chlordane, were found in all air samples. Similarly, a few of the target individual PCB congeners were not detected in the air samples. The herbicide acid 2,4-D was found in 13 of 20 air samples. Note that there were two outdoor air samples from D05. The D05-1 sample was collected under the condition where the air pumps were overheated, and the D05-2 sample was a 24-hr sample and collected the day after D05-1 was taken. The overheating resulted from blockage of the fan of the outdoor sampling box by a piece of plastic bag. One of the air pumps for filter/PUF was stopped, and the other one for filter/XAD-2 was still functioning (D05-1) when the field technician checked the samplers on Day-3 of the monitoring period. The concentrations of phenols in D05-1 sample were significantly higher than in D05-2 sample. This is probably due to sampling artifacts from the heated plastic bubble wrap.

The dust samples were separated into coarse and fine fractions and only the fine fractions (<150 μm) were analyzed for target POP. The floor dust loadings of the daycare centers are summarized in Table 5.16. Levels of the floor dust ranged from 1.06 to 35.8 g/m^2 for the fine dust loadings. The highest and lowest floor dust loading was observed in daycare center #8

TABLE 5.16. FLOOR DUST LOADINGS FROM PHASE 1 DAY CARE CENTERS

Day Care Center[a] Code	Age of Carpet, years	Dust Loading, g/m^2		
		Total	Fine Fraction (<150 μm)	Percent of Fine Fraction, %
D01	13	16.8	13.6	81
D02	4	6.96	3.84	55
D03	DK[b]	22.2	18.5	83
D04	5	16.8	11.3	67
D05	1	9.54	7.67	80
D06	1	15.9	15.1	95
D07	3	18.8	15.0	79
D08	1	36.7	35.8	92
D09-1	0.17	3.83	1.98	52
D09-2	2	2.31	1.06	46
D10	5	14.7	13.7	93

(a) D09-1 denotes the floor dust sample was collected from the classroom where the air sample was taken, and the carpet was about 2 months old (0.17 years old). D09-2 denotes the floor dust sample was collected from another classroom and the carpet was 2 years old.

(b) DK denotes don't know.

(D08) and #9 (D09), respectively. The fine dust loadings accounted for 46 to 95% of the total dust loadings.

The target POP concentrations in dust and soil (ppm) were calculated by subtracting the amounts of target analytes in the field blank from those in the sample and dividing by the amounts of dust analyzed. The reported concentrations were based on the dried weights, which are corrected for moisture content. The data reported in Table 5.14 were the floor dust samples collected with HVS3. Higher concentrations of target POP in all compound classes were observed in the floor dust samples as opposed to the playground soil samples. With one exception, PAH concentrations in the playground soil sample from D01 were higher than that in the floor dust sample. The highest PAH concentrations in Phase 1 dust and soil samples were found in the playground soil sample from D01. The concentrations of B2 PAH and total target PAH in this soil sample were 5.59 and 13.1 ppm, respectively. It is possible that there were local contamination sources of PAH that affected this playground soil sample. Concentrations of total target PAH and B2 PAH in the floor dust samples ranged from 0.388 to 9.98 ppm and from 0.130 to 5.29 ppm, respectively. Concentrations of B2 PAH accounted for approximately 50% of the total PAH concentrations. This finding is in agreement with the house dust samples analyzed in the previous study (1, 5-7).

With few exceptions, concentrations of OC, OP, Ph and PCB were of the same order of magnitude among the ten daycare centers. Note that higher PCB concentrations were found in D09-2 and D10. For daycare center #9 (D09), two floor dust samples were taken from two classrooms. The sample D09-1 was from a classroom with a new carpet (2 months old) and D09-2 was from another classroom with an older carpet (2 years old). Higher concentrations of the target POP in all compound classes were observed in D09-1 as opposed to D09-2. Note that the dust loadings of these two classrooms were about the same (Table 5.16). Upon further examination of the relationship between ages of the carpet (Table 5.16) and the POP concentrations, there was no clear trend to be seen. Phthalate esters (PE) were the most abundant contaminants found in the dust and soil samples. Concentrations of PE ranged from 22.9 to 221 ppm in the floor dust samples and from 0.231 to 1.24 ppm in the playground soil samples.

Among all the compound classes monitored, the least abundant contaminant in dust/soil was herbicide acid, 2,4-D. Concentrations of 2,4-D in the dust samples were less than 1 ppm and not detected in most soil samples. Concentrations of individual target POP in each compound class (Appendix D) indicated that mono- and di-chlorobiphenyls were not detected in the dust samples, and only a few PCB congeners were detected in the playground soil samples. The individual target POP in PAH, PE, OP, and Ph were found in most dust and soil samples. Target OC including aldrin, DDE, dieldrin, endrin, and DDT were detected in all dust samples but not in most soil samples. The other OC such as lindane, heptachlor, and cholordanes were found in all dust samples and most soil samples.

The data for the liquid and solid food samples are expressed in units of ng of POP, and in g of food sample (ppb). These POP concentrations were obtained by subtracting the amounts (ng) of POP in the field blank from the amount of (ng) of POP in the sample, and then dividing by the amount (g) of food used. Note that PCB were not found in any solid and liquid food samples. The B2 PAH and OP were only detected in few liquid food samples. The most abundant contaminants found in liquid and solid food were PE. The concentrations of PE ranged from 16.6 to 86.4 ppb in liquid food samples and from 188 to 387 ppb in solid food samples. The concentrations of phenols were above 10 ppb. The concentrations of target POP in other compound classes were mostly less than 5 ppb. Note that higher concentrations of phthalate esters were detected in both solid and liquid food samples collected with plastic containers as opposed to those collected with glass containers. Similar concentrations of other target POP were found in food samples collected by both types of containers. Thus, in Phase 2 study we used the glass containers for collecting liquid and solid food samples.

Data Analysis for Phase I Study

Summary Statistics

Summary statistics by compound class and by sample media for each target POP and the sums of target POP in each compound class are presented in Table E-1 thorough E-7 in

Appendix E. Each table contains sample size (N), number of samples below detection limit (N-BDL), mean, standard deviation, minimum, and maximum values of multimedia samples. For the target analytes below detection limit, half of the detection limit was used for the calculation of summary statistics. Note that the target POP data in liquid and solid food samples collected in plastic containers are not included in the summary statistics.

Tables E-1 and E-2 show that the average indoor air POP concentrations are higher than the average outdoor air POP concentrations across all compound classes, except for the herbicide acid (2,4-D) and a few target compounds. Some of the target analytes in PAH, OC pesticides, and PCB were not detected in the air samples.

Tables E-3 and E-4 summarize the POP data in HVS3 floor dust and vacuum bag floor dust samples, respectively. The 2,4-D analysis was not performed in the vacuum bag samples. The average POP levels were higher in the vacuum bag floor dust samples as opposed to the HVS3 floor dust samples for all compounds classes except PCB. Summary statistics for playground soil samples are presented in Table E-5. Note that most target analytes in OC pesticides and in PCB were not found in the playground soil samples. Summary statistics for liquid and solid food samples are presented in Table E-6 and E-7, respectively. The target PCB were not found in any liquid and solid food samples. In general, average POP levels were higher in the solid food samples than that in the liquid food samples across all compound classes.

Summary statistics for target POP by two groups of centers (Head Start versus private) are presented in Table E-8 through E-14. Average indoor and outdoor concentrations of PAH and PE in Head Start centers were higher than those in the private centers. The reversed trend was observed for HA. Similar average concentrations of OP, OC, PCB, and Ph in air were found in two groups of centers. Differences between the two groups of centers in POP in air were not significant, and were probably related to their locations. Comparable concentrations of target POP in floor dust collected by HVS3 in all compound classes but PCB were found in both groups of centers. Higher average PCB concentrations in floor dust were found in the private centers as opposed to Head Start centers. This is mainly from the high PCB levels found in centers D09 and D10. A significant difference in the playground soil concentrations of PAH was seen between the two groups of centers. This is because the unusually high levels of PAH found

in D01 resulted in significantly higher average concentrations of PAH in the Head Start centers. In fact, the highest PAH levels among all Phase 1 dust/soil samples were in the D01 playground soil sample. Comparable average PAH concentrations in playground soil were obtained in PAH data from both groups of centers if D01 was excluded. There could be a local contamination sources, which affected playground soil in D01. Levels of target POP in other compound classes were similar between the two groups of centers. Although the average food concentrations of POP showed differences between the two groups of centers, these differences were not significant, given the small sample size and the great day-to-day variability in the foods served and the cooking methods.

Correlation Between Sample Media

It is of interest to know whether the levels of POP in one sample medium (e.g., dust) are related to their levels in other sample media. The correlation between the measured target POP concentrations in different sample media was investigated. Note that initially, the vacuum bag floor dust samples were not included, and only the HVS3 floor dust samples were used for the correlation analysis between sample media. Spearman correlation coefficients (r) and Pearson correlation coefficients (r) for the sums of target POP in each compound class in one sample medium (e.g., floor dust) with those levels in another sample medium (e.g., playground soil) are summarized in Appendix F. Note that the Spearman correlation coefficients were obtained by ranking of the raw data and the Pearson correlation coefficients were calculated by the log-transformed data.

Table 5.17 summarizes the pairs of sample media that had significant relationships at least at 0.05 or lower confidence levels. Note that the results of Spearman correlation coefficients and Pearson correlation coefficients were not identical but similar to each other. This is mainly because Spearman correlation coefficients use the rankings of concentrations and Pearson correlation coefficients use the log-transformed concentrations. The direct relationships were observed between indoor air and floor dust, for target POP in PAH, OC, OP, and PCB. The correlation between indoor air and playground soil was seen in total PAH, and PCB. A direct

TABLE 5.17. SUMMARY OF PAIRS OF SAMPLE MEDIA WITH SIGNIFICANT CORRELATION COEFFICIENTS FOR TARGET COMPOUND CLASSES

Compound Class[a]	Pair of Media with Significant Correlation Coefficient[b]	
	Spearman Method[c]	Pearson Method[d]
B2 PAH	—	(IA, LF)**
Total PAH	(IA, FD) (IA, PS)** (IA, SF) (PS, FD) (LF, FD) (SF, PS)	(IA, PS) (LF, FD) (SF, PS)
OC	(IA, FD)	(IA, FD)**
OP	(IA, FD)**	(IA, FD)
PE	(IA, SF))	
PCB	(IA, PS)	(IA, FD)**
PH	—	(IA, LF)
HA	—	—

(a) PE = phthalate esters, PH = phenols, OC = OC pesticide, OP = OP pesticide, and HA = herbicide acid.
(b) IA = indoor air, OA = outdoor air, F = floor dust, LF = liquid food, SF = solid food, and PS = playground soil. All pairs are at least significant at the 0.05 level, while pairs with 0.01 significant level are marked with **, and pairs with negative correlations are underlined.
(c) Spearman's correlation method in raw data.
(d) Pearson's correlation method in log-transformed data.

correlation between floor dust and pathway soil was significant at 0.05 level for total PAH. There were significant but negative relationships observed between solid food samples and indoor air samples for total PAH and PE. The reason for the negative relationship is not known.

Correlation Between Compound Classes

It is of interest to know whether the levels of POP in one compound class are related to another compound class within each sample medium. Spearman and Pearson correlation coefficients between compound classes within each sample medium are presented in Appendix G. Table 5.18 summarizes the pairs of compound classes had correlation coefficients significant, at least, at 0.05 or lower confidence levels. As shown in the Table 5.18, there were quite a few significant relationships between compound classes for target POP. The direct relationship between total target PAH and B2 PAH was expected since they all are in the same compound classes. This relationship was observed in the Phase 1 dust/soil samples as well as dust/soil samples from previous studies (1, 5-7). The significant correlation between B2 PAH and total PAH was also found in outdoor air and solid food samples. There was no correlation between B2 PAH and total PAH in indoor air samples. This was probably due to contamination sources for the abundant 2- to 3-ring PAH which were different from those for B2 PAH in indoor microenvironments, and produced high levels of 2- to 3-ring PAH in the indoor air.

Significant correlations between B2 PAH and other compound classes including OP, PCB, and PE were observed in air and in dust samples. The negative relationship between B2 PAH and PCB was probably due to the unusually high indoor PCB concentrations in D06. The direct relationships between total PAH and two other compound classes PE and Ph were found in indoor air samples. In general, several pairs of compound classes were correlated with each other in indoor air and floor dust samples. Fewer pairs of compound classes with direct relationships were observed in outdoor air, playground soil, and food samples. It is possible to monitor one compound class as a marker for other compound class for indoor samples (air, dust) for future large-scale studies. Since this was a small data set, more data are needed to examine this hypothesis.

TABLE 5.18. SUMMARY OF PAIRS OF COMPOUND CLASSES WITH SIGNIFICANT CORRELATION COEFFICIENTS FOR EACH SAMPLE MEDIUM

Sample Medium	Pair of Compound Classes with Significant Correlation Coefficient[a]	
	Spearman Method[b]	Pearson Method[c]
Indoor Air	(B2-PAH, OP) (B2-PAH, PCB)** (PE, TARGET PAH) (PH, TARGET PAH) (OP, PE) (PH, PE)** (PH,OP)	(B2-PAH, PCB)** (PE, TARGET PAH) (PH, TARGET PAH) (PH, PE)**
Outdoor Air	(B2-PAH, OP)	(B2-PAH, TARGET PAH)**
Floor Dust (HVS 3)	(B2-PAH, TARGET PAH)** (B2-PAH, PCB) (PCB, TARGET PAH) (HA, PE) (PH, OP)	(B2-PAH, TARGET PAH)** (B2-PAH, PCB) (HA, PE) (PH, OP)
Floor Dust (bag)	(B2-PAH, TARGET PAH)** (B2-PAH, PE)** (PE, TARGET PAH)	(B2-PAH, TARGET PAH)** (B2-PAH, PE)** (PE, TARGET PAH)**
Playground Soil	(B2-PAH, TARGET PAH)** (B2-PAH, OC) (OC, TARGET PAH)	(B2-PAH, TARGET PAH)** (B2-PAH, OC)** (OC, TARGET PAH) (PH, OP)
Liquid Food	(OC, TARGET PAH)**	(OC, TARGET PAH)
Solid Food	(B2-PAH, TARGET PAH) (HA, PH)**	(B2-PAH, TARGET PAH) (HA, PH)**

(a) PE = phthalate esters, PH = phenols, OC = OC pesticide, OP = OP pesticide, and HA = herbicide acid. All pairs are at least significant at the 0.05 level, while pairs with 0.01 significant level are marked with **, and pairs with negative correlations are underlined.
(b) Spearman's correlation method in raw data.
(c) Pearson's correlation method in log-transformed data.

Correlation coefficients were also determined for target POP found in the HVS3 floor dust and vacuum bag floor dust samples. Table 5.19 shows correlation matrices for each compound class in these two types of samples. Table 5.19 shows the Pearson correlation coefficients on both raw data and log-transformed data as well as Spearman correlation coefficients on the raw data. The results were similar among the three correlation coefficients for each target compound class. Direct relationships were observed for compound classes B2 PAH, PAH, and PCB between these two types of samples. It is possible to use floor dust samples as an indicator for other sample media and to use less expensive screening methods for determining POP in the dust samples. The vacuum bag floor dust samples instead of HVS3 floor dust samples could also be used in the screening step in future large-scale exposure studies.

Estimates of Daily Persistent Organic Pollutant Exposure

The potential daily POP exposure of child subject from each daycare center was estimated for the inhalation (air), nondietary (dust/soil), and dietary (food) pathways as described in Chapter 4. The POP exposures were expressed in ng/day, for the time that a child spends in daycare, which is slightly less than half of the 24-hr period for the average child in this study (but which may be most of the child's waking hours). The estimated daily POP exposures through the three pathways are summarized in Appendix H. Summary statistics for the estimated daily children's POP exposures from Phase 1 daycare centers are presented in Appendix I. Note that the estimated daily POP dose (ng/kg/day) normalized by each child's body weight was calculated only for the Phase 2 data but not for the Phase 1 data, since the children were monitored individually only in Phase 2.

Figure 5.1 displays the average distribution of the estimated daily POP exposure through the three pathways at Phase 1 daycare centers. The results showed that most important pathway for children's POP exposure at daycare centers was dietary ingestion except for compound class PCB. Since none of the target PCB were found in the food samples, dietary ingestion was the least important pathway for PCB exposure for children in these daycare centers. For total PAH exposure, the inhalation pathway was almost as important as the dietary pathway. This is

TABLE 5.19. CORRELATION COEFFICIENTS BETWEEN FLOOR DUST (HVS3) AND FLOOR DUST (BAG)

Compound Class	Pearson Correlation Coefficient of Raw Data	Pearson Correlation Coefficient of Log-Transformed Data	Spearman Correlation Coefficient of Raw Data
B2 PAH	0.704	0.738*	0.821*
Target PAH	0.598	0.731*	0.893**
Phthalate Esters	0.444	0.602	0.643
OP Pesticides	0.0765	0.273	0.357
OC Pesticides	-0.403	-0.406	-0.429
Target PCB	0.764*	0.679*	0.536
Phenols	0.386	0.439	0.357

* ---significant at 0.05 level.
**---significant at 0.01 level.

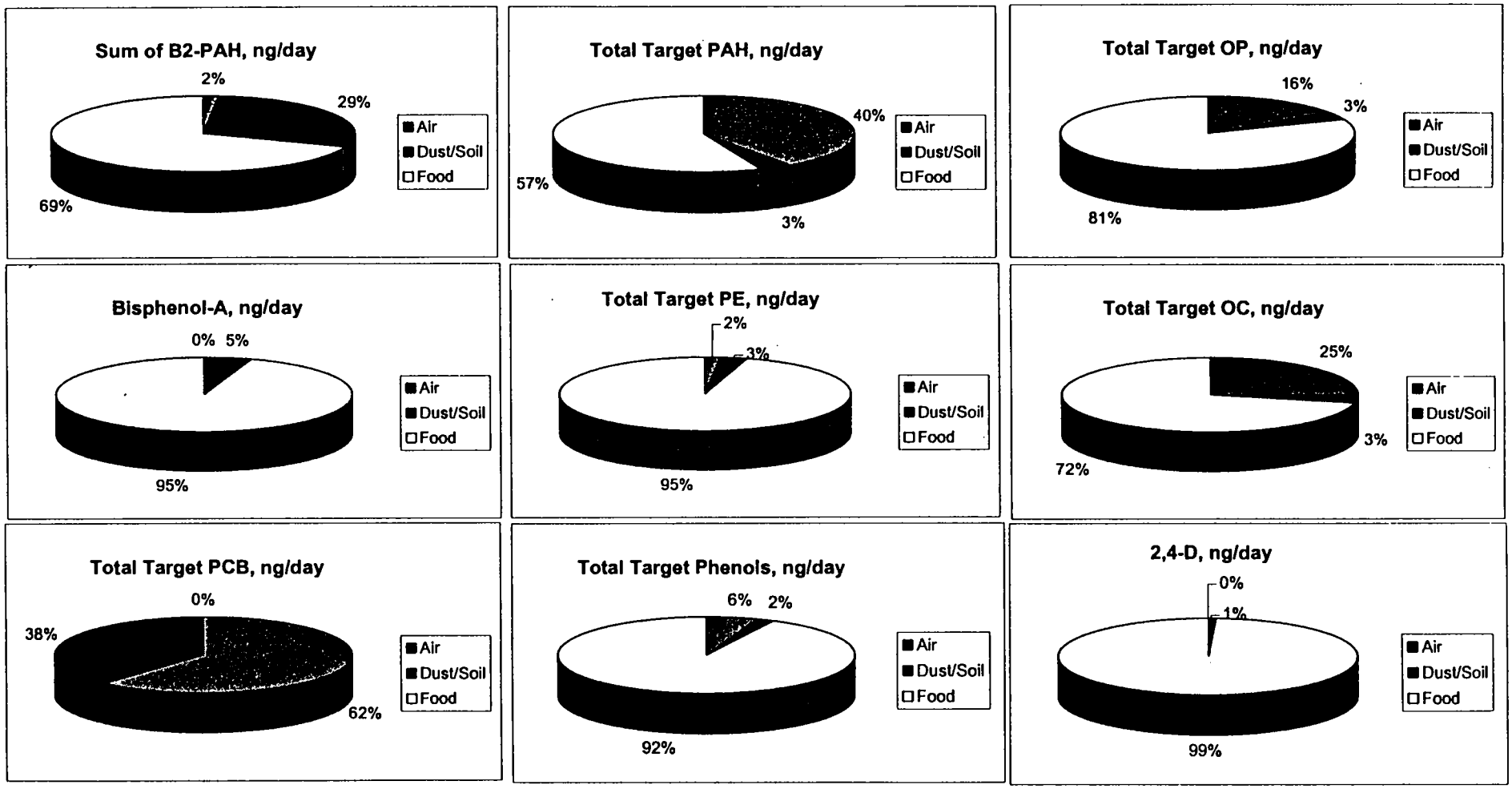


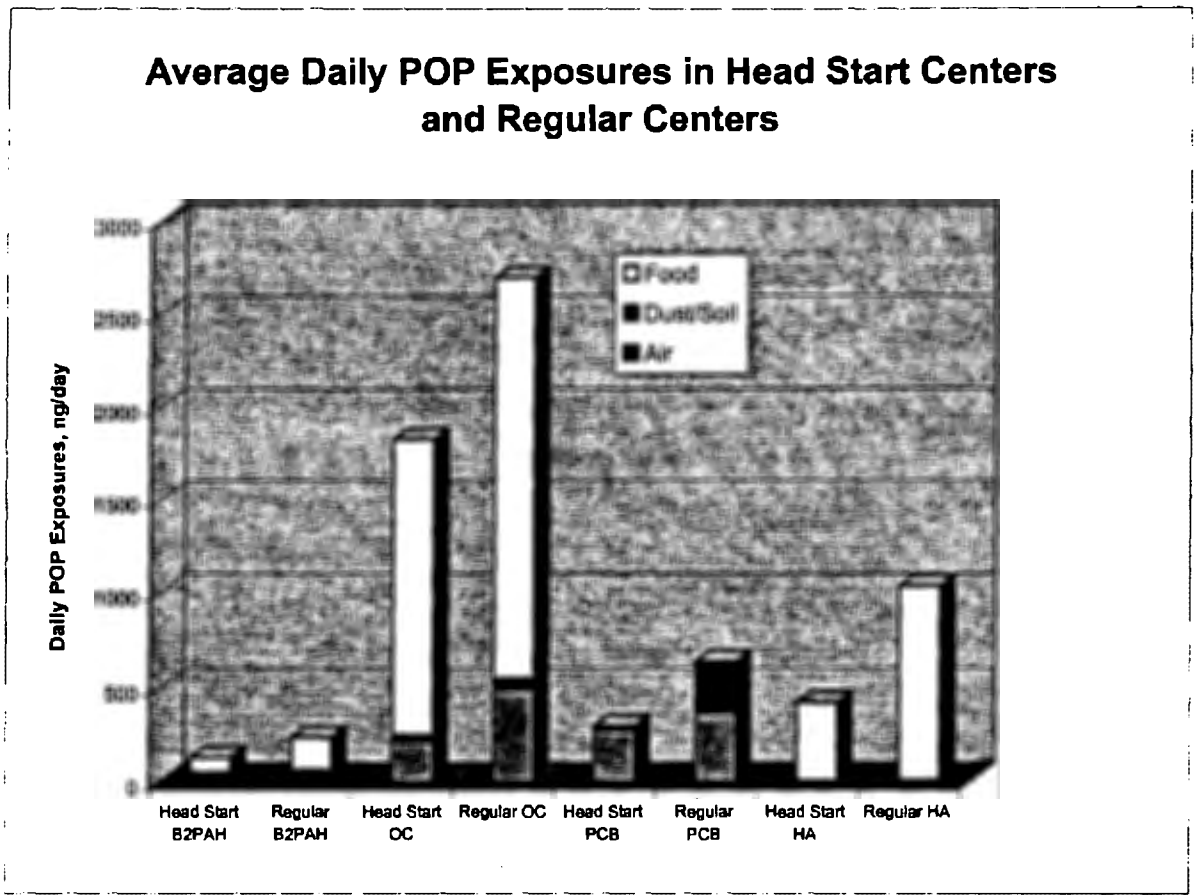
Figure 5.1. Distributions of average daily exposure of persistent organic pollutants from Phase 1 daycare centers.

probably because of the high levels of 2- to 3-ring PAH found in air samples. For B2 PAH, PE, and HA, the estimated daily exposure through nondietary ingestion pathway was greater than that through inhalation pathway. The reverse relative trend was observed for total PAH, OP and OC pesticides, PCB, and phenols.

As shown in Appendix I, the averages of daily POP exposures in PAH, PE, O, and Ph through air in Head Start centers were slightly higher than that in the private centers. The reverse trend of the inhalation pathway was seen in the average daily POP exposures in OP, OC, PCB, and HA. With one exception, differences between the two groups of centers in the average daily POP exposures through nondietary and dietary ingestion were small for all target compound classes. The average daily PCB exposures through nondietary ingestion were higher at the private centers, by a factor of 11. This difference was from the higher PCB levels in the dust and soil samples from private center D09 and D10. Figure 5.2 displays the average daily potential POP exposures for these two groups of centers through inhalation (air), nondietary ingestion (dust/soil), and dietary ingestion (food) pathways in Phase 1 study. Note that levels of average daily Ph and PE exposures shown in Figure 5.1 need to be multiplied by 10 and 20, respectively, to obtain the actual average levels. Differences in daily POP exposures through all three pathways between Head Start centers and private centers, in general, were small. Higher average daily B2 PAH, OC, PCB, and HA exposure levels were observed in the private centers. Higher average OP, and total PAH exposure levels were seen in the Head Start centers.

Quality Control Data for Phase I Study

Accuracy was assessed by means of spike recoveries of analytical surrogate recovery standards (SRS). Known amounts of perdeuterated and/or ^{13}C-labelled POP were spiked into each air, dust, soil, and food samples prior to sample preparation. The recovery data of the spiked POP for each type of sample are presented in Appendix J. In general, acceptable recoveries (>70%) for the spiked POP were obtained in most of the samples. The recoveries of DDT-^{13}C were greater than 100% in the food samples. As discussed earlier in this Chapter, this was mainly because the GC responses of DDT-^{13}C were



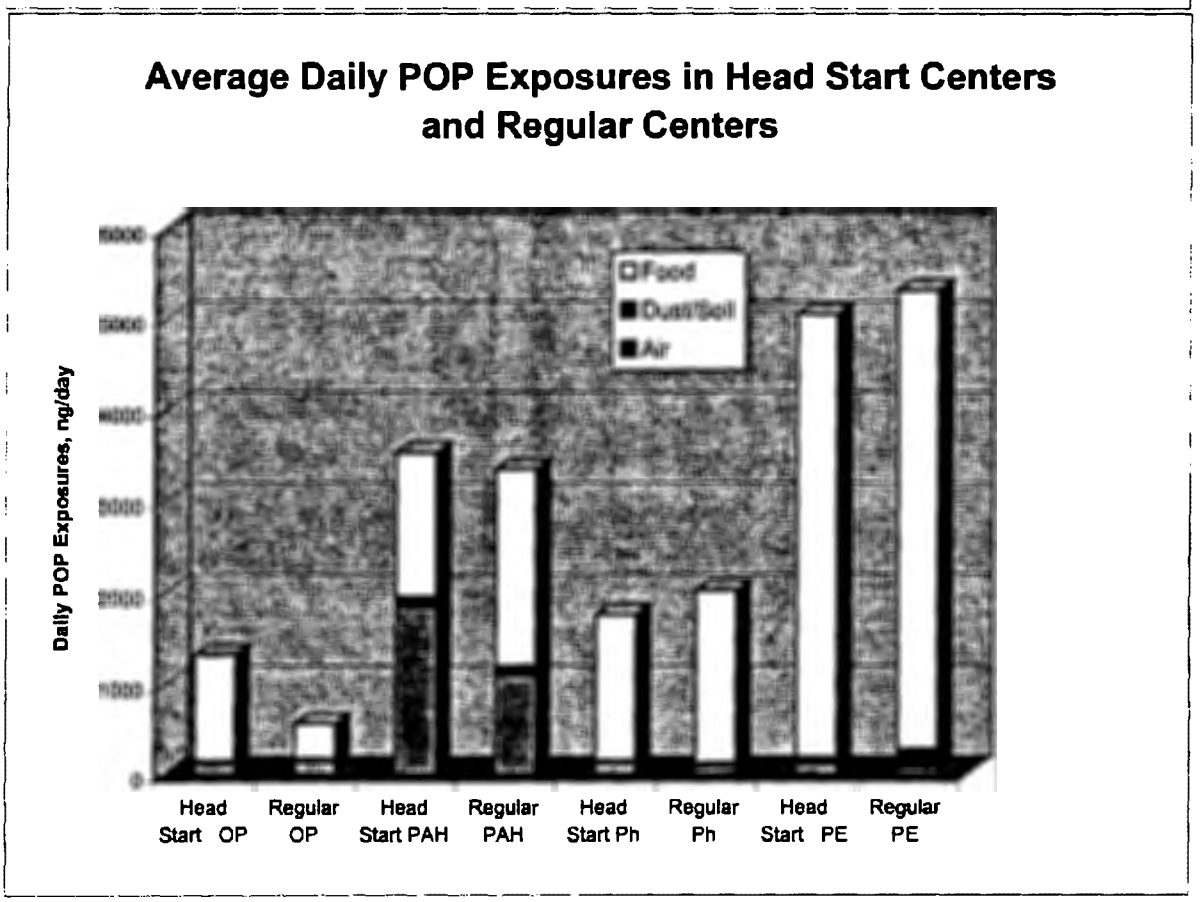


Figure 5.2. Average daily persistent organic pollutant exposures in Head Start centers and other centers.

better than that in the standard solutions. Note that the recoveries of DDT-^{13}C reported in Appendix J were corrected for this factor.

The overall method precision was expressed as percent of relative standard deviation (%RSD) in duplicate field samples. The precision data of target POP are presented in Appendix K. Note that the duplicate air sample was not collected for 2,4-D (HA) analysis. Only duplicate dust samples but not soil samples were processed because the dust sample matrices are more complicated than the soil samples. The overall method precision was within ±10% for the air and dust samples. The precision for the food sample matrices were within ±20% for all compound classes but 2,4-D. As mentioned in earlier method evaluation section, several problems occurred when analyzing food samples, such as plugged columns, which could have contributed to the larger variations observed in the duplicate samples.

The results of target POP found in the field blanks are presented in Appendix L. None of the PCB and OC pesticides were found in the field blanks. The highest levels of target POP found in the blanks for all sample media were the two phthalate esters (PE). This is because phthalate esters are common environmental contaminants. Much higher levels of PE were found in most samples. All data reported here were corrected for the respective field blanks. In general, the field blank data demonstrated that there was no significant contamination due to sample handling and preparation.

Phase 2 Field Study

Recruiting of Subjects

The results of recruiting children from the two daycare centers (D03 and D09) for the Phase 2 study are summarized in Table 5.20. The overall response rate was about 17%. We recruited 11 families, 5 low-income families and 6 middle-income families, in less than four weeks. Based on 17% response rate, we estimated that we can recruit 6 families per daycare center. If we used all 29 daycare centers recruited for the study, we could have recruited

174 households for the study. Thus, it is feasible to apply the recruiting method used in this study for a future large-scale study.

TABLE 5.20. SUMMARY OF RECRUITING CHILDREN FROM DAYCARE CENTERS D03 AND D09 FOR PHASE 2 STUDY

	D03	D09	OVERALL
Target Children	30	36	66
Agreed to Participate	5	6	11
Response Rate	17%	17%	17%

Field Activity

The Phase 2 sampling activities were conducted in two daycare centers and nine homes during a two-week period in June 1997. In general, we received good cooperation from participating daycare centers and families. The indoor air samplers were modified to reduce noise levels because of the complaints received in the Phase 1 study. We did not receive any complaints about the noise levels of the indoor air samplers for the Phase 2 study.

In general, there were no major problems in collecting multimedia samples in Phase 2 study. The outdoor air sampling at home D (HD3) was interrupted for four hours due to power outage. Therefore, the sampling time was extended for an additional four hours. In daycare center D09, 24-hour instead of 48-hour duplicate-diet food samples were collected because the daycare center had special activities and did not provide lunch during the second day of field monitoring. The children brought their own lunch on that day. Two of nine participating parents from the low-income families complained that duplicate-diet food collection is too much burden for them.

Two types of child activity diaries were employed in Phase 2 study, one for daycare activities and one for home activities. Most parents thought that the diaries are well organized

and easy to follow. Two adult participants complained that the instructions for self-administrated food frequency questions were not clear enough for them to understand. One common difficult question for most participants was the use of household chemicals, as we observed in Phase 1 study.

Concentrations of Persistent Organic Pollutants in Multimedia Samples

The target analytes determined in Phase 2 samples were the same as Phase 1 samples (Table 5.12) except that 2- and 4-chlorobiphenyl were excluded. The sums of levels of target POP in each compound class in air, dust/soil, food, and wipe samples are summarized in Tables 5.21 through 5.24, respectively. The reported data were corrected for the corresponding field blanks but not corrected for the spiked SRS recoveries except for 2,4-D. The reported concentrations of 2,4-D were corrected for the SRS (3,4-D) recoveries and for the background levels. The individual target POP data are presented in Appendix M.

Target POP data in indoor and outdoor air samples are presented in Tables M-1 and M-2 in Appendix M. Concentrations of target POP in indoor air samples were, in general, higher than those in the corresponding outdoor air samples. Levels of target POP in the two 48-hr indoor and outdoor air samples from each daycare center were similar. The POP concentrations observed in the day-to-day variations were, in general, smaller than those observed in the site-to-site variations (between daycare centers, and among daycare centers and homes). As seen in Phase 1 air samples, with few exceptions the highest air concentrations were of PE, PAH, and phenols, followed by OC, OP, and HA. The HA, 2,4-D was detected in few indoor and outdoor air samples. As shown in Appendix M, some of the target OC were not detected in the air samples. No p,p'-DDT was found in outdoor air samples. Some target PCB were not found in the air samples. The phthalate ester concentrations in the Phase 2 field blanks were five to ten times higher than those in the Phase 1 field blank. After blank correction, the phthalate esters were below the detection limit in the outdoor air sample from household HI9. Since phthalate esters are common environmental contaminants, the Phase 2 field blank could be contaminated with phthalate esters. Consequently, the reported values of PE (corrected for the field blank)

TABLE 5.21. SUMMARY OF TARGET PERSISTENT ORGANIC POLLUTANTS IN AIR SAMPLES FROM PHASE 2 STUDY

Compound Class	Concentrations, ng/m³[a]												
	D03-1	D03-2	D09-1	D09-2	HA3	HB3	HC3	HD3	HE9	HF9	HG9	HH9	HI9
Indoor Air													
PAH	1240	1090	206	218	400	205	585	215	429	1300	513	276	446
B2 PAH	0.666	0.570	0.553	0.653	0.964	0.550	1.00	0.650	0.496	0.589	0.657	0.642	0.656
PE	914	857	373	383	572	312	511	404	333	272	602	243	627
OP	36.1	28.1	3.09	4.77	161	16.8	6.71	36.0	3.70	147	38.1	1150	5.99
OC	61.7	50.5	7.37	8.69	60.2	28.1	17.0	6.94	10.4	20.5	186	120	19.4
PCB	42.2	33.6	29.0	38.8	17.0	11.9	11.4	4.58	8.28	4.31	13.2	64.7	15.6
Ph	227	173	240	402	194	355	310	3.43	108	107	418	206	4.71
HA	<0.1	<0.1	0.073	<0.1	<0.1	<0.01	<0.1	0.311	<0.1	<0.1	0.313	<0.1	<0.1
Outdoor Air													
PAH	65.0	75.6	98.2	61.0	40.6	63.6	48.8	115	34.0	137	112	176	93.3
B2 PAH	0.666	0.499	0.567	0.483	0.766	0.412	0.514	0.543	0.409	0.522	0.500	0.468	0.417
PE	151	179	277	220	86.1	53.2	524	125	73.0	270	81.7	203	<0.04
OP	1.77	1.36	0.792	1.17	1.92	1.57	2.09	1.48	4.54	2.70	2.06	1.84	2.36
OC	3.06	1.98	1.99	1.29	2.20	1.39	1.74	0.701	0.964	0.801	5.56	1.95	1.26
PCB	4.66	3.61	5.15	7.95	3.73	1.32	2.82	1.35	0.951	2.084	1.12	2.48	0.662
Ph	1.85	0.984	10.3	9.95	1.33	3.37	7.64	2.88	5.31	7.29	1.41	2.80	3.01
HA	<0.1	<0.1	0.170	<0.1	0.069	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

(a) The first letter of the sample code denotes the location of the collected sample, D = daycare centers, H = households; the last two letter/number denotes the unique code of the daycare center or household.

TABLE 5.22. SUMMARY OF TARGET PERSISTENT ORGANIC POLLUTANTS IN DUST AND SOIL SAMPLES FROM PHASE 2 STUDY

Compound Class	Concentrations, ppm[a]												
	D03-1	D03-2	D09-1	D09-2	HA3	HB3	HC3	HD3	HE9	HF9	HG9	HH9	HI9
Floor Dust													
PAH	6.07	4.66	0.778	0.452	0.556	0.540	1.19	0.737	0.591	11.1	1.64	1.40	1.21
B2 PAH	2.56	1.93	0.320	0.196	0.222	0.213	0.514	0.327	0.261	5.32	0.733	0.590	0.520
PE	0.080	7.81	8.34	6.12	6.70	6.49	1.11	10.9	3.07	16.4	4.79	5.11	9.13
OP	0.098	0.337	0.057	0.071	0.420	0.109	0.034	0.255	0.058	0.956	1.38	6.45	0.113
OC	0.608	0.977	0.035	0.043	1.14	0.196	0.078	0.327	0.053	0.349	1.14	0.632	0.194
PCB	0.148	0.613	0.182	0.134	0.085	0.105	0.027	0.056	0.036	0.256	0.271	0.099	0.310
Ph	5.24	14.4	55.9	49.1	7.71	10.6	4.02	8.29	11.4	9.96	6.88	11.6	9.31
HA	0.051	0.069	0.269	0.188	7.29	1.44	0.027	0.029	1.64	0.083	0.169	0.113	0.350
Playarea Soil													
PAH	0.093	-[b]	0.023	-	0.138	0.006	0.033	0.535	0.014	0.236	0.026	0.033	0.031
B2 PAH	0.042	-	0.010	-	0.036	0.003	0.014	0.236	0.007	0.065	0.012	0.015	0.014
PE	0.008	-	0.161	-	0.160	<0.001	0.263	0.137	0.081	0.112	0.216	0.092	0.114
OP	0.002	-	<0.001	-	<0.001	<0.001	<0.001	<0.001	<0.001	0.009	0.002	0.001	0.002
OC	0.004	-	0.007	-	0.238	0.007	0.007	0.008	0.004	0.006	0.012	0.006	0.007
PCB	0.001	-	0.003	-	0.017	<0.001	<0.001	0.008	<0.001	<0.001	<0.001	<0.001	<0.001
Ph	0.077	-	0.061	-	0.167	0.094	0.086	0.070	0.041	0.062	0.094	0.038	0.092
HA	<0.001	-	<0.001	-	0.151	0.032	<0.001	0.022	<0.001	0.020	0.024	0.017	0.020

(a) The first letter of the sample code denotes the location of the collected sample, D = daycare centers, H = households; the last two letter/number denotes the unique code of the daycare center or household.
(b) Only one soil sample was taken from each daycare center.

TABLE 5.23. SUMMARY OF TARGET PERSISTENT ORGANIC POLLUTANTS IN LIQUID AND SOLID FOOD SAMPLES FROM PHASE 2 STUDY

Compound Class	Concentrations, ppb[a]												
	D03-1	D03-2	D09-1	D09-2	HA3	HB3	HC3	HD3	HE9	HF9	HG9	HH9	HI9
Liquid Food													
PAH	2.18	1.04	0.469	0.263	0.212	0.285	0.061	0.146	0.160	0.248	0.962	0.146	0.501
B2 PAH	0.450	<0.04	0.114	<0.04	<0.04	0.219	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
PE	8.40	4.25	30.3	7.57	5.97	9.14	8.97	24.2	5.70	9.58	63.1	35.2	14.1
OP	<0.04	<0.04	0.317	<0.04	0.234	0.198	<0.04	0.432	<0.04	<0.04	<0.04	<0.04	<0.04
OC	0.221	0.626	0.744	0.495	0.642	<0.04	<0.04	0.470	0.243	0.210	<0.04	0.564	0.289
PCB	<0.04	0.196	<0.04	0.175	<0.04	<0.04	0.072	<0.04	0.134	0.094	<0.04	<0.04	<0.04
Ph	0.139	4.68	4.51	2.39	<0.1	<0.1	<0.1	<0.1	0.280	<0.1	2.59	3.28	1.37
HA	2.01	0.917	1.80	1.64	0.353	0.705	3.19	3.02	1.50	0.954	0.675	1.67	1.03
Solid Food													
PAH	4.92	6.36	3.63	1.59	7.10	5.60	2.13	2.68	3.41	3.68	5.09	1.98	2.94
B2 PAH	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
PE	25.7	126	103	14.1	461	176	20.5	52.5	101	17.9	96.5	17.0	145
OP	0.473	0.270	1.65	0.214	0.660	0.261	0.085	1.37	0.172	0.981	0.408	1.12	2.31
OC	0.088	0.350	<0.04	0.138	0.621	0.060	0.666	<0.04	<0.04	0.197	0.818	0.621	2.08
PCB	<0.04	<0.04	<0.04	0.220	0.380	<0.04	<0.04	0.268	0.411	0.136	0.161	<0.04	0.398
Ph	35.2	10.8	23.0	12.9	67.7	26.1	15.0	12.8	34.6	21.3	80.4	26.2	21.4
HA	<0.5	<0.5	1.45	0.920	2.20	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

(a) The first letter of the sample code denotes the location of the collected sample, D = daycare centers, H = households; the last two letter/number denotes the unique code of the daycare center or household.

TABLE 5.24. SUMMARY OF TARGET PERSISTENT ORGANIC POLLUTANTS IN DERMAL WIPE SAMPLES FROM PHASE 2 STUDY

Compound Class	Concentrations, ng/wipe[a]								
	A3	B3	C3	D3	E9	F9	G9	H9	I9
Daycare Center									
PAH	5.61	21.6	6.93	4.47	22.8	12.7	15.5	10.5	15.4
B2 PAH	<0.5	6.29	0.60	1.16	1.13	0.51	<0.5	<0.5	0.49
PE	<0.5	1080	1350	552	344	<0.5	227	<0.5	69.6
OP	<0.5	3.12	2.35	14.6	<0.5	<0.5	<0.5	2.69	<0.5
OC	1.28	5.11	1.28	2.24	<0.5	<0.5	<0.5	<0.5	<0.5
PCB	1.61	1.49	0.79	<0.5	1.41	0.92	<0.5	0.67	<0.5
Home									
PAH	0.65	12.6	5.62	1.89	14.0	29.3	4.00	14.3	13.0
B2 PAH	0.63	0.57	2.47	0.50	<0.5	3.32	<0.5	0.55	<0.5
PE	496	59.1	1060	868	<0.5	219	63.4	113	446
OP	13.7	0.90	6.43	4.10	<0.5	10.1	1.10	23.9	<0.5
OC	0.80	<0.5	10.5	<0.5	<0.5	1.27	3.55	0.62	<0.5
PCB	<0.5	0.61	0.53	1.57	<0.5	0.54	<0.5	<0.5	1.52

(a) The number in the subject code denotes the daycare center that the subject attends; 3 = D03, Head Start and 9 = D09, regular daycare center.

could be underestimated. For future studies, more field blanks are needed to establish the background levels if phthalate esters are the target analytes.

Extremely high level of chlorpyrifos (1150 ng/m^3) was observed in household HH9 indoors. The questionnaire data showed that indoor insecticides/pesticides application is performed once every three months by a commercial contractor. Only days before the field monitoring period, indoor application was conducted. Such a high indoor chlorpyrifos level could result from the indoor application. However, the commercial contractor claimed that chlorpyrifos was not in the material used.

The floor dust loadings of the Phase 2 samples are summarized in Table 5.25. Levels of the fine dust loadings ranged from 1.92 to 8.38 g/m^2 in the two daycare centers and from 0.28 to 20.2 g/m^2 in the nine households. The fine dust loadings accounted for 28 to 75% of the total dust loadings in these samples. The dust loadings of the private daycare D09 were slightly lower than that of the Head Start daycare D03. Higher dust loadings were observed in the four low-income homes (HA3, HB3, HC3, and HD3) as compared to those from the five middle-income homes. A similar relationship between the dust loadings and household income was observed in previous studies (1.5,6). The highest (20.2 g/m^2) and the lowest (0.34 g/m^2) fine dust loadings were observed in HA3 (low-income) and HH9 (middle-income), respectively.

The reported POP concentrations (ppm) in dust and soil samples were corrected for the background levels and for the moisture content. The target POP data of floor dust and playground soil samples are given in Tables M-3 and M-4 in Appendix M. Concentrations of target POP in all compound classes in the floor dust samples were higher than those found in the corresponding soil samples. Most target POP in PAH, PE, and Ph were detected in the dust and soil samples. The target POP in OP, OC, PCB, and HA were found in most dust samples but not soil samples.

Levels of B2 PAH in the floor dust samples ranged from 0.196 to 2.56 ppm in the daycare centers and from 0.213 to 5.32 ppm in the households. Concentrations of B2 PAH in the soil samples were less than 0.1 ppm in the daycare centers and less than 0.3 ppm in the households. Levels of B2 PAH found in most dust and soil samples accounted for approximately half of the total PAH concentrations in these samples. This finding was in agreement with the

TABLE 5.25. FLOOR DUST LOADINGS FROM PHASE 2 DAYCARE CENTERS AND HOUSEHOLDS

Sample Code[a]	Age of Carpet, year	Dust Loading, g/m^2		
		Total	Fine Fraction (<150 μm)	Percent of Fine Fraction, %
D03-1	DK[b]	11.1	8.38	75
D03-2	DK	11.9	8.05	68
D09-1	0.2	3.50	1.92	55
D09-2	0.2	7.71	5.13	67
HA3	7	27.3	20.2	74
HB3	DK	4.14	1.64	40
HC3	2	4.10	2.06	50
HD3	1	27.2	18.4	68
HE9	3	3.05	1.32	43
HF9	8	1.00	0.28	28
HG9	5	1.51	0.72	48
HH9	11	0.63	0.34	54
HI9	7	0.65	0.39	60

(a) The first letter of the sample code denotes the location of the collected sample, D = Daycare center, H = Household; the last two letter/number denotes the unique code of the daycare center of household.

(b) DK denotes don't know.

results of the Phase 1 samples and those from the previous studies. Concentrations of the sums of PE ranged from 0.080 to 16.4 ppm in the dust samples and from <0.001 to 0.216 ppm in the soil samples. Concentrations of sums of target phenols in the dust and soil samples were from 4.02 to 55.9 ppm and from 0.038 to 0.167 ppm, respectively.

Levels of target POP in OP, OC, PCB, and HA were either not detected or present at low levels (<0.1ppm) in the soil samples. With few exceptions, concentrations of target POP in OP, OC, and PCB were generally less than 1 ppm in the dust samples. Note that the highest concentration (6.45 ppm) of OP, mainly from chlorpyrifos (6.44 ppm) was found in the dust sample from HH9 where the highest indoor air concentration of this compound was observed.

Target POP data of the solid and liquid food samples are presented in Tables M-5 and M-6 in Appendix M. Target PAH found in the liquid and solid food samples were mostly 2- to 4-ring PAH. The B2 PAH were detected in none of the solid food samples and only in two of the liquid food samples. The levels of total target PAH ranged from 0.061 to 2.18 ppb in liquid food samples and from 1.59 to 7.10 ppb in solid food samples. Higher concentrations of PE were observed and ranged from 4.25 to 63.1 ppb in liquid food samples and from 14.1 to 461 ppb in solid food samples. Levels of Ph in the solid food ranged from 10.8 to 80.4 ppb and were less than 5 ppb in liquid food samples. Levels of OP, OC, and PCB found in most liquid and solid food samples were less than 1 ppb. The concentrations of total target PAH in the liquid food samples were, in general, lower than those in the solid food samples. These relative concentration profiles were also observed in target POP in PE, OP, and Ph. Concentrations of target POP in OC and PCB in the solid food samples were not always higher than those in the liquid food samples.

The HA, 2,4-D, was detected in all the liquid food samples and only in three solid food samples. Concentrations of 2,4-D ranged from 0.353 to 2.01 ppb in the liquid food samples and from 0.92 to 2.20 ppb in the solid food samples. Note that the recoveries of PCP and 2,4-D in the spiked solid food samples were only 33% and 20%, respectively. As noted earlier in Table 5.10, better recoveries of PCP (85%) and 2,4-D (63%) were obtained using the same analytical method in the method validation phase. The low recoveries of the spiked Phase 2 food samples could be attributed to differences in the sample matrix and the sample size (50 g versus

10 g). In addition, the recoveries of the spiked SRS 3,4-D were from 20 to 90% in the solid food samples and from 17 to 44% in the liquid food samples. The reported PCP values were not corrected for the PCP recovery obtained from the matrix spiked sample, since this recovery was based on only one matrix spike sample, and there were no SRS available for PCP. Thus, the reported values for PCP could be underestimated. However, the reported 2,4-D values were corrected for the SRS (3,4-D) recoveries. The analytical method for the determination of these compounds in food sample matrix needs to be modified for better overall method precision and accuracy.

Target POP data of dermal wipe samples from each child subject collected at daycare centers and at home are presented in Tables M-7 and M-8 in Appendix M. Concentrations of target POP in PAH, OC, OP, and PCB were in the same order of magnitude among the daycare wipe samples and the home wipe samples. The concentration ranges of PE were greater than those observed in the above compound classes, and ranged from <0.5 to 1350 ng/wipe in daycare-wipe samples and from <0.5 to 1060 ng/wipe in home-wipe samples. Note that high levels (1190 ng/wipe) of PE were found in the field blank wipe sample. The reported values were corrected for the background levels. For the household (HH9) having the highest chlorpyrifos levels in indoor air and house dust, the highest concentration (23.9 ng/wipe) of this compound was also found in the subject's composite wipe sample collected at home. The level of chlorpyrifos was 2.69 ng/wipe in the composite wipe sample collected from the same subject at the daycare center.

Summary Statistics

Summary statistics by compound class, by sample media, by sampling location, and by family income for target POP are presented in Appendix N. Each table contains sample size, number of samples below detection limit, mean, standard deviation, minimum, and maximum values. Table N-1 through N-10 summarize the POP data in the multimedia samples collected at subjects' homes. Table N-11 through N-20 summarize the POP data in the multimedia samples

collected at daycare centers that subjects attend. Tables N-21 through N-30 summarize the data by groups of low- and middle-income families.

Average indoor and outdoor concentrations of OP in samples collected at homes were higher than those collected at daycare centers. The high indoor average of OP is partly from the high level of chlorpyrifos in the indoor air of HH9. Differences in average concentrations of POP in other compound classes in indoor and outdoor air between these two groups of samples (home vs. daycare) were small. Comparable concentrations of POP in all compound classes but OP were obtained in these two groups of floor dust samples. Average concentration of OP in the floor dust samples collected at homes was higher than in those collected at daycare centers, but lower average concentration of Ph was seen in the dust samples from homes. Concentrations of POP in playground soil samples were similar between these two groups of samples for all compound classes except OC. Higher OC concentrations were seen in the playground soil samples collected at homes. Comparable POP concentrations in liquid and solid food were observed in these two groups of samples. Average levels of chlorpyrifos in dermal wipe samples collected at homes were more than twice those in the wipes collected at daycare centers. Concentrations of other POP in dermal wipes were similar in these two groups of samples.

Average indoor concentration of OP (mainly chlorpyrifos) in middle-income homes was higher than that in the low-income homes. As mentioned before, this is from the high chlorpyrifos in HH9. Differences between the two groups of samples (low-income vs. middle-income) in average POP concentrations in other compound classes in air were not significant. For floor dust samples, higher average concentrations of PAH, OP, and PCB were seen in the middle-income families while higher concentrations of Ph and HA were seen in the low-income families. In general, average POP concentrations in playground soil were low and the differences in the concentrations in soil between low- and middle-income families were small. There were differences in concentrations of POP in food between the two groups of families. Average levels of PE in dermal wipe of the low-income subjects were higher than those of middle-income subjects. This trend was seen in wipe samples collected at homes as well as at daycare centers. Similar levels of other POP in wipe sample were observed in these two groups of subjects.

Correlation Between Sample Media

Correlation coefficients of measured target POP in different sample media were calculated by Spearman and Pearson methods. The results of Spearman and Pearson correlation coefficients are summarized in Table O-1 through Table O-11, as well as in Tables O-12 through O-22, respectively, in Appendix O. Table 5.26 summarizes the pairs of sample media showed significant correlations, at least, at 0.05 or lower confidence levels.

Direct relationships were observed between indoor air and floor dust for target POP in PAH, OC, and OP. This relationship was also seen in the Phase 1 data. A significant correlation between indoor air and outdoor air was also observed in B2 PAH, OC, and PCB. Significant correlations were seen between indoor air and solid food for OC and between outdoor air and solid food for HA. There were few significant but negative relationships between liquid food and other sample media such as floor dust and pathway soil.

Correlation Between Compound Classes

The results of Spearman and Pearson correlations between compound classes within each sample medium are presented in Tables P-1 through P-6, and in Tables P-7 through P-12, respectively, in Appendix P. Table 5.27 summarizes the pairs of compound classes that had correlation coefficients significant, at least, at 0.05 levels.

The positive correlation between B2 PAH and total PAH was seen in floor dust, solid food, and playground soil. This relationship was also observed in the Phase 1 samples. Several pairs of compound classes were correlated with each other in playground soil, which was not seen in the phase 1 samples. This is probably related to the locations of the collected samples. For example, direct relationships were also seen between OC and OP in indoor air, as well as those in floor dust. Because of the variability of types of food, and methods of cooking, we do not expect a lot of direct relationships between compound classes in the food samples. Only one pair of compound classes with direct relationships was observed in liquid and in solid food. This could be due to the sources of the foods, and the cooking methods used.

TABLE 5.26. SUMMARY OF PAIRS OF SAMPLE MEDIA WITH SIGNIFICANT CORRELATION COEFFICIENTS FOR TARGET COMPOUND CLASSES

Compound Class[a]	Pair of Media with Significant Correlation Coefficient[b]	
	Spearman Method[c]	Log-Transformed Data[d]
B2 PAH	(PS, OA)	(IA, OA)
Target PAH	(IA, FD)** (OA ,FD)	(IA, FD)**
OC	(IA, OA) (IA, FD)** (IA, SF)	(IA, OA)** (IA, FD)** (IA, SF)
OP	(IA, FD)**	(IA, FD)**
PE	<u>(OA, SF)</u>	
PCB	(IA, OA)	(IA, OA)
PH	<u>(PS, FD)</u> (LF, FD)	(LF, FD)
HA	(OA, SF)** <u>(LF, FD)</u> <u>(LF, PS)</u>	(OA, SF)** <u>(FD, LF)</u>** (SF, FD) <u>(LF, PS)</u>
BEN	(IA, PS) <u>(OA, SF)</u>** (LF, FD)	
CHL	(IA, FD)**	(IA, FD)**
BIS		(SF, PS)

(a) PE = phthalate esters, PH = phenols, OC = OC pesticide, OP = OP pesticide, HA = herbicide acid (2,4-D), BEN = benzylbutylphthalate, CHL = chlorpyrifos, and BIS = bisphenol-A.

(b) IA = indoor air; OA = outdoor air, FD = floor dust, LF = liquid food, SF = solid food, and PS = playground soil. All pairs are at least significant at the 0.05 level, while pairs with 0.01 significant level are marked with **, and pairs with negative correlations are underlined.

(c) Spearman's correlation method in raw data.

(d) Pearson's correlation method in log-transformed data.

TABLE 5.27. SUMMARY OF PAIRS OF COMPOUND CLASSES WITH SIGNIFICANT CORRELATION COEFFICIENTS FOR EACH SAMPLE MEDIUM

Sample Medium	Pair of Compound Classes with Significant Correlation Coefficient[a]	
	Spearman Method[b]	Log-Transformed Data[c]
Indoor Air	(B2-PAH, PE) (OC, OP)**	(OC, OP)
Outdoor Air	(B2-PAH, PCB) (B2-PAH, HA) (PCB, PE)** (PCB, OP)	(B2-PAH, PCB) (PCB, PE) (PCB, OP) (HA, OP)
Floor Dust (HVS 3)	(B2-PAH, TARGET PAH)** (B2-PAH, HA) (OC, OP)**	(B2-PAH, TARGET PAH)** (OC, OP)**
Liquid Food	(PCB, PE)	(PCB, PE)
Solid Food	(TARGET PAH, PE)**	(TARGET PAH, PE)**
Playground Soil	(B2-PAH, TARGET PAH)** (OC, PE) (PCB, OC) (OC, PH) (OC, HA) (PH, HA)	(B2-PAH, TARGET PAH)** (PCB, OC)** (OC, PH) (OC, HA)

(a) PE = phthalate esters, PH = phenols, OC = OC pesticide, OP = OP pesticide, and HA = herbicide acid (2,4-D). All pairs are at least significant at the 0.05 level, while pairs with 0.01 significant level are marked with **, and pairs with negative correlations are underlined.

(b) Spearman's correlation method in raw data.

(c) Pearson's correlation method in log-transformed data.

Daily Potential Doses of Persistent Organic Pollutants

The potential daily potential doses of POP were calculated for the inhalation (air), nondietary ingestion (dust/soil), and dietary ingestion (food) pathways for nine subjects. The daily POP potential doses were calculated from at-home and at-center exposures separately, as well as from combined at-home and at-center exposures. The calculated daily potential doses of POP from at-home exposure, at-center exposure, and combined total exposure, are presented in Tables M-11 through M-13, respectively, in Appendix M. Summary statistics of the daily POP potential doses are given in Appendix N. It should be noted that these potential doses reported here are maximum external doses based on the measured concentrations and exposures as calculated previously.

Figures 5.3 through 5.5 show the distributions of average daily POP potential doses through the three pathways from exposures at homes, at centers, and at both locations. Similar distributions of average POP potential doses in the three pathways were seen among exposures at homes, and at centers for compound classes of total PAH, PE, PCB, Ph, and HA. Dietary ingestion was the most important pathway for PE, Ph, and HA whereas inhalation was the most important pathway for total PAH, and PCB. Different distributions of average POP potential doses of OC, OP, and B2 PAH were observed between at-home and at-center exposures. Inhalation was the most important pathway for average daily potential doses of OC and OP from at-home exposures, but dietary ingestion was the most important pathway from at-center exposures. Nondietary ingestion (at-home exposure) and dietary ingestion (at-center exposure) were important pathways for average daily potential dose of B2 PAH.

The distributions of subjects' total daily potential doses of POP from both at-home and at-center exposures differ among compound classes. The relative importance of exposure pathways was inhalation > dietary > nondietary ingestion for average total daily potential doses of total PAH, OP, OC, and PCB. For total daily potential doses of PE, Ph, and HA, the relative importance of exposure pathways was dietary > nondietary ingestion > inhalation. The nondietary ingestion was the most important pathway for total daily potential dose of B2 PAH, and followed by dietary ingestion and air.

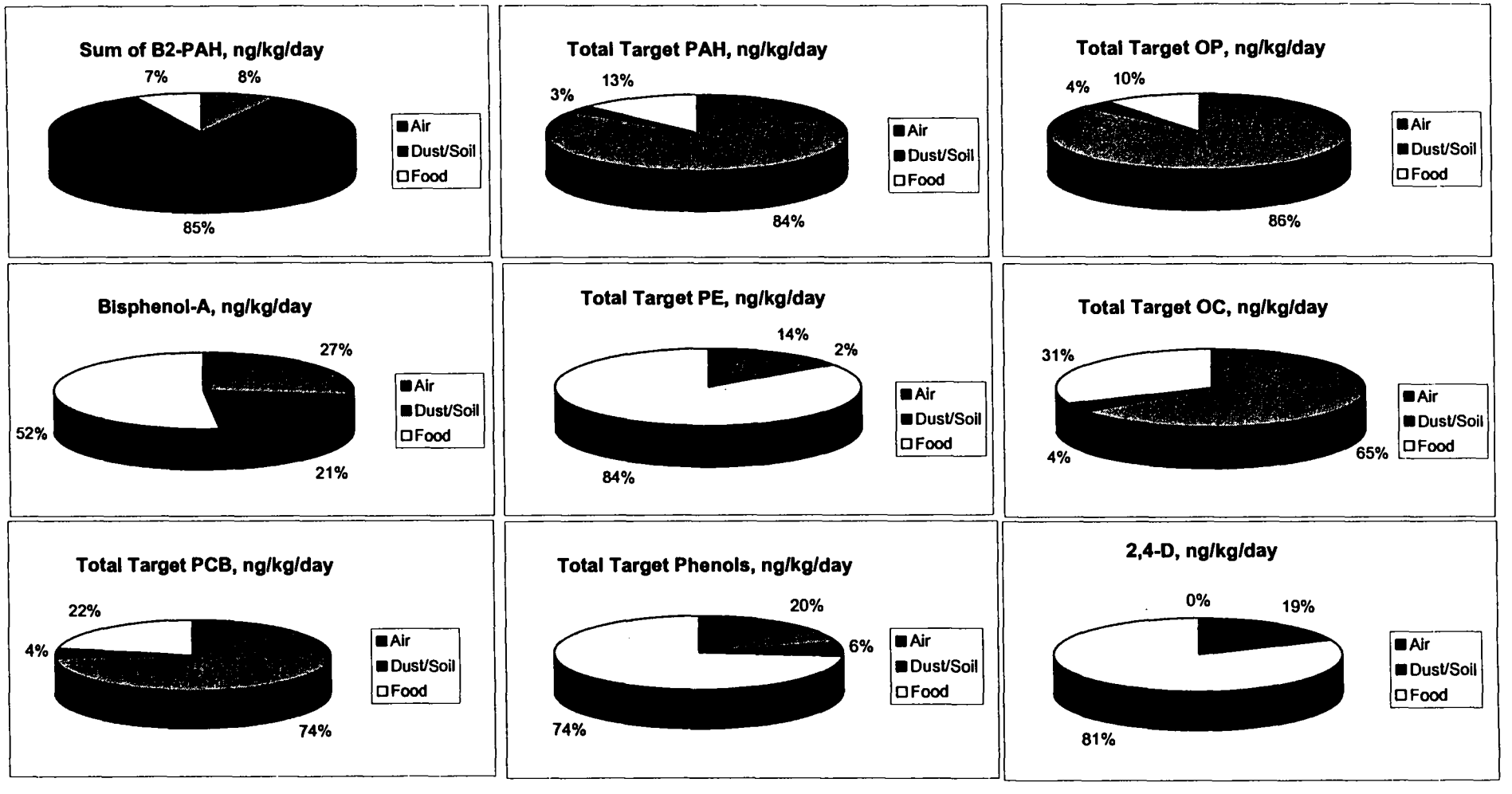


Figure 5.3. Distribution of average daily potential dose of persistent organic pollutants from homes for nine subjects.

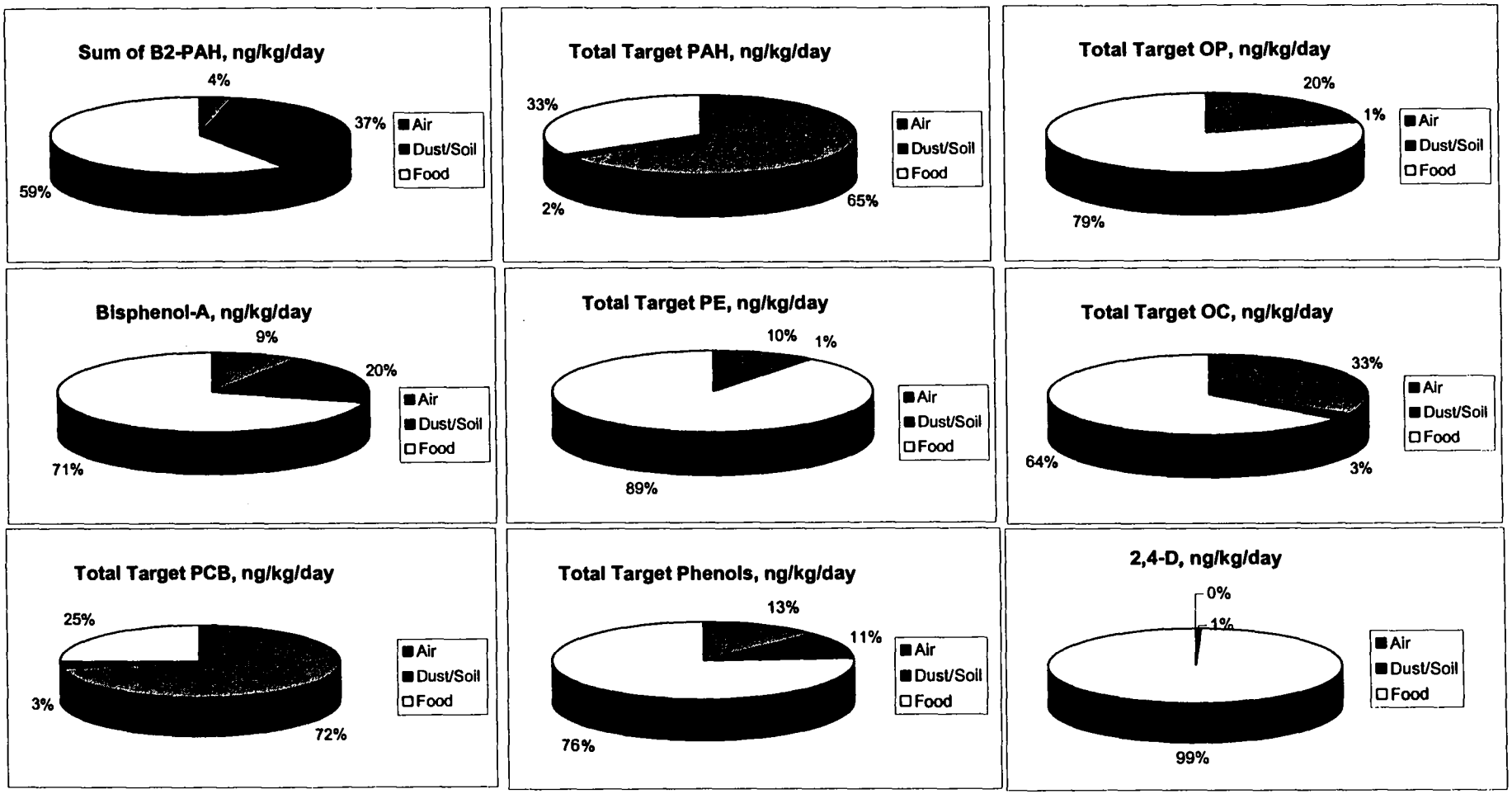


Figure 5.4. Distributions of average daily potential dose of persistent organic pollutants from daycare centers for nine subjects.

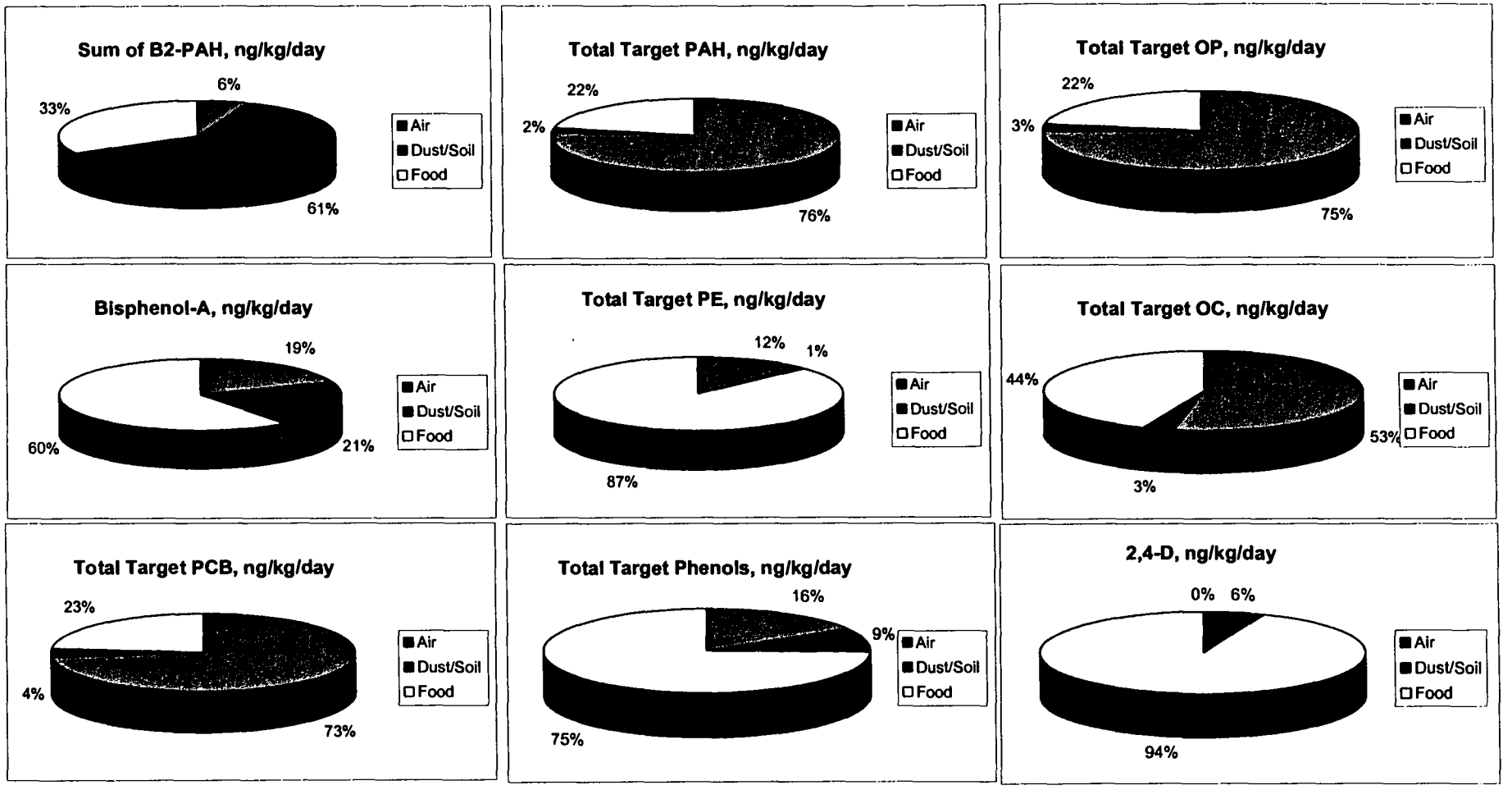


Figure 5.5. Distributions of average daily potential dose of persistent organic pollutants from homes and daycare centers for nine subjects.

Figures 5.6 through 5.8 display the average daily potential dose of POP for the two groups of subjects (low-income vs. middle-income) that resulted from exposures at homes, at centers, and at both locations. Note that the potential dose levels of PE shown in these figures need to be multiplied by a factor of 10 because of the high potential dose levels. In general, the average daily POP potential doses for low- and middle-income subjects were within the same order of magnitude. Slightly higher average daily potential doses of B2 PAH, total PAH, OC, PCB, OP, and Ph were seen in the middle-income subjects from the exposures at homes. The reverse trend was observed for B2 PAH and total PAH from the exposures at daycare centers. The difference between these two groups of subject's average total daily potential doses of POP was small, with slightly higher total potential doses of OP and Ph seen in the middle-income subjects. The general trend for total average potential doses of POP in target compound classes was PE > Ph > total PAH > HA > OP > OC > PCB > B2 PAH.

Concentration Profiles of Urinary Metabolites

The composite urine samples collected from each subject at daycare center and at home were analyzed for target hydroxy-PAH, 2,4-D, PCP, and 3,5,6-TCP. Two different analytical methods were employed, as described in Section 4, one for hydroxy-PAH, PCP, and 2,4-D, and one for 3,5,6-TCP. The concentrations of individual target analyte measured in the urine samples expressed in units of ng/mL of urine and μmole/mole of creatinine are presented in Tables M-9 and M-10 in Appendix M. Summary statistics for the urine data across low-income and middle-income subjects are given in Tables N-28 and N-29 in Appendix N. Among the target analytes, 1- and 3-hydroxy benz[a]anthracene, 1- and 3-hydroxy benz[a]anthracene, and 6-hydroxy indeno[1,2,3-cd]pyrene were detected in some urine samples. The remaining target analytes were found in all urine samples.

The most abundant hydroxy-PAH, urinary PAH metabolites, found in the subjects' urine samples was 1-naphthol. Note that 1-naphthol is an urinary metabolite of naphthalene as well as carbaryl, a widely used commercial insecticide (17). Thus, 1-naphthol in the subjects' urine samples could result from the exposures to both compounds. Levels of 2-naphthol in the urine

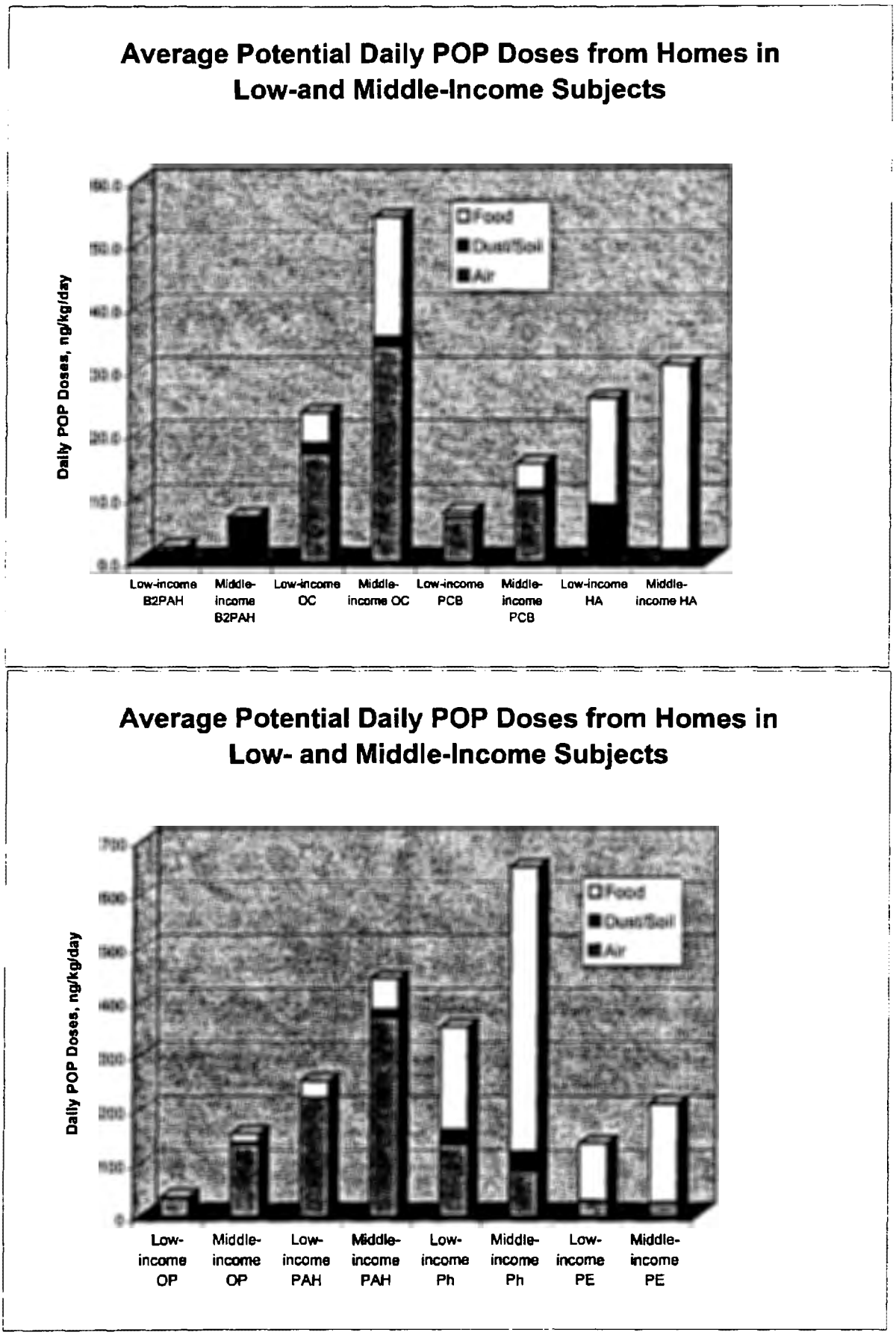


Figure 5.6. Average potential daily persistent organic pollutants doses from at-home exposures in low- and middle-income subjects.

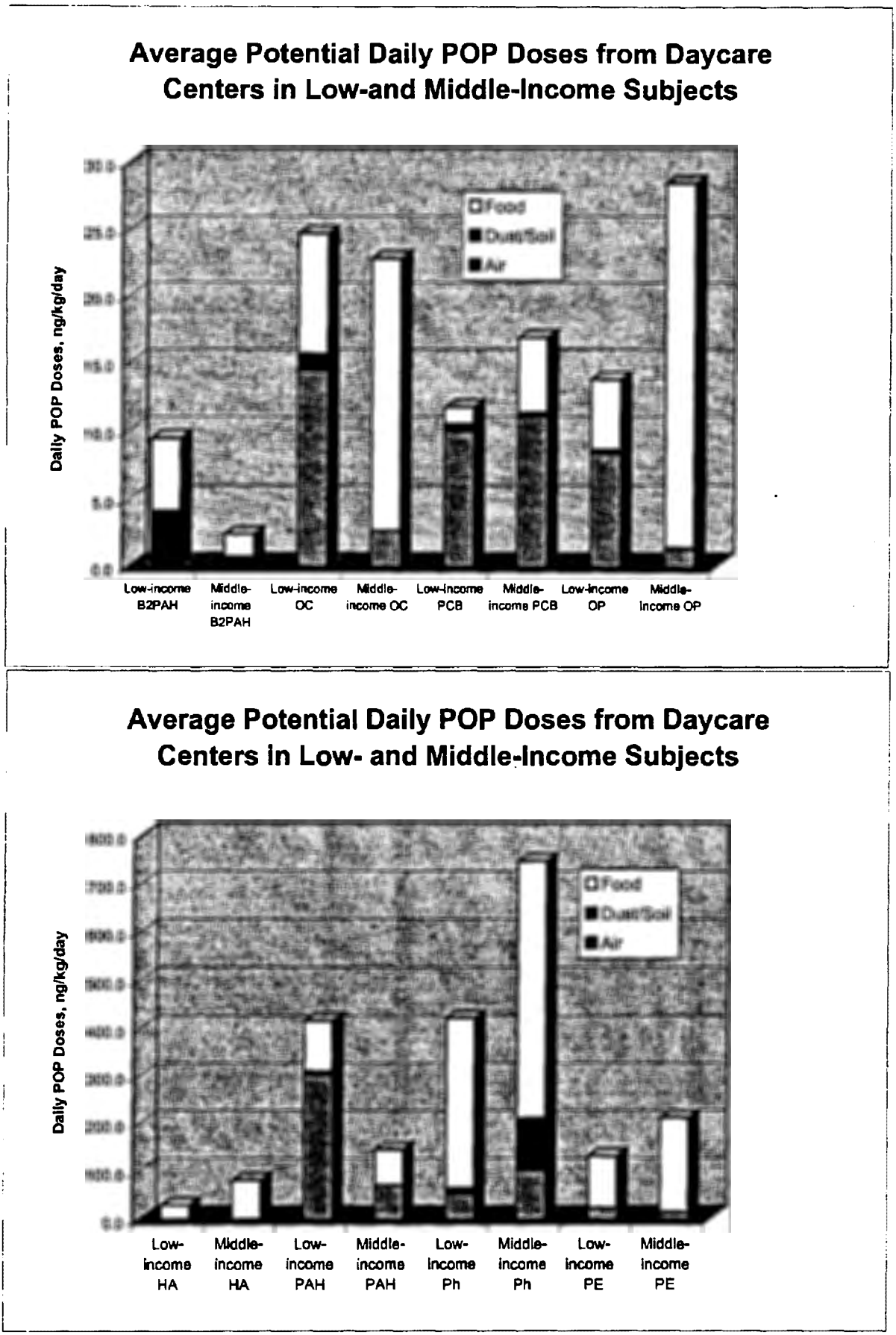


Figure 5.7. Average potential daily persistent organic pollutants doses from at-center exposures in low- and middle-income subjects.

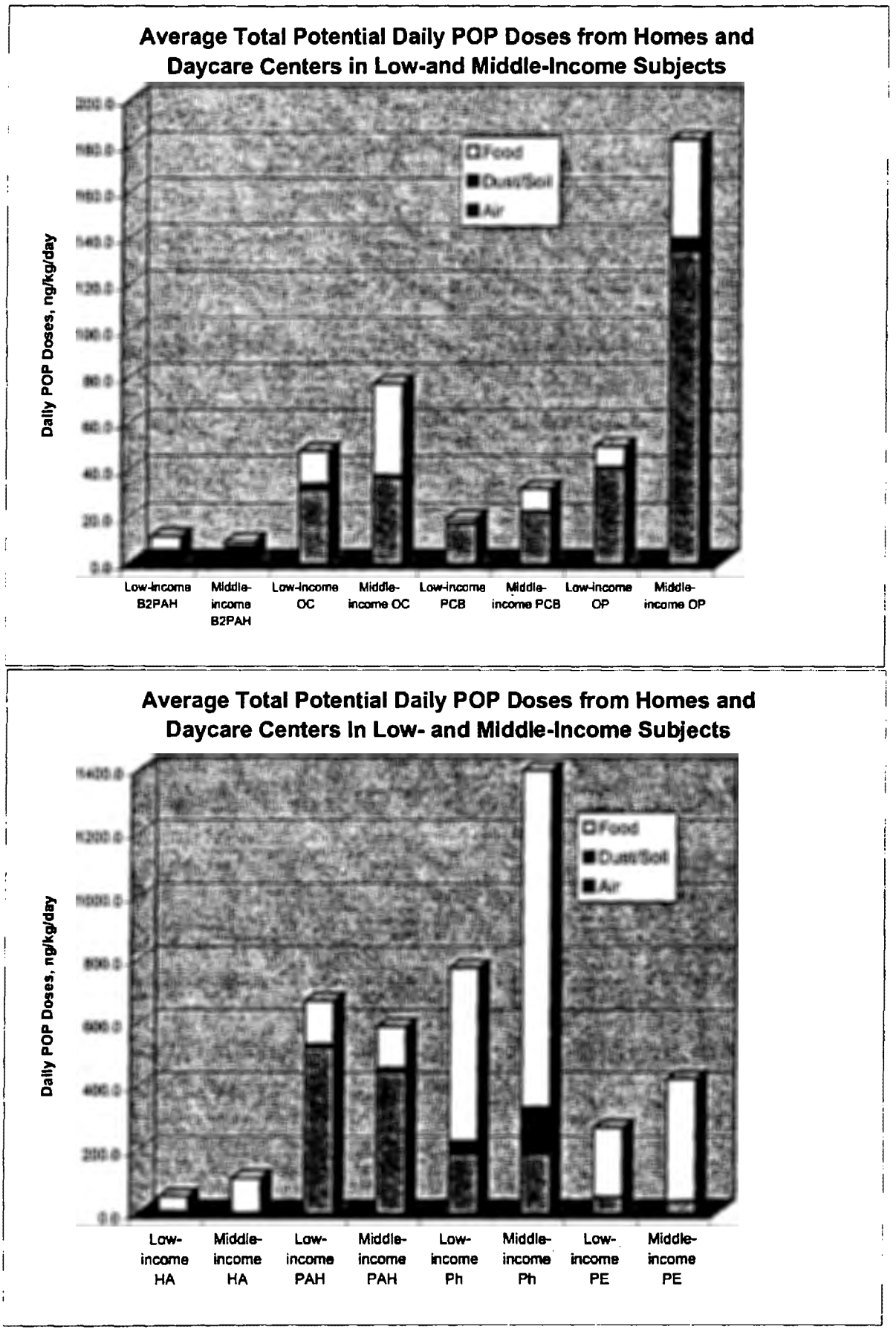


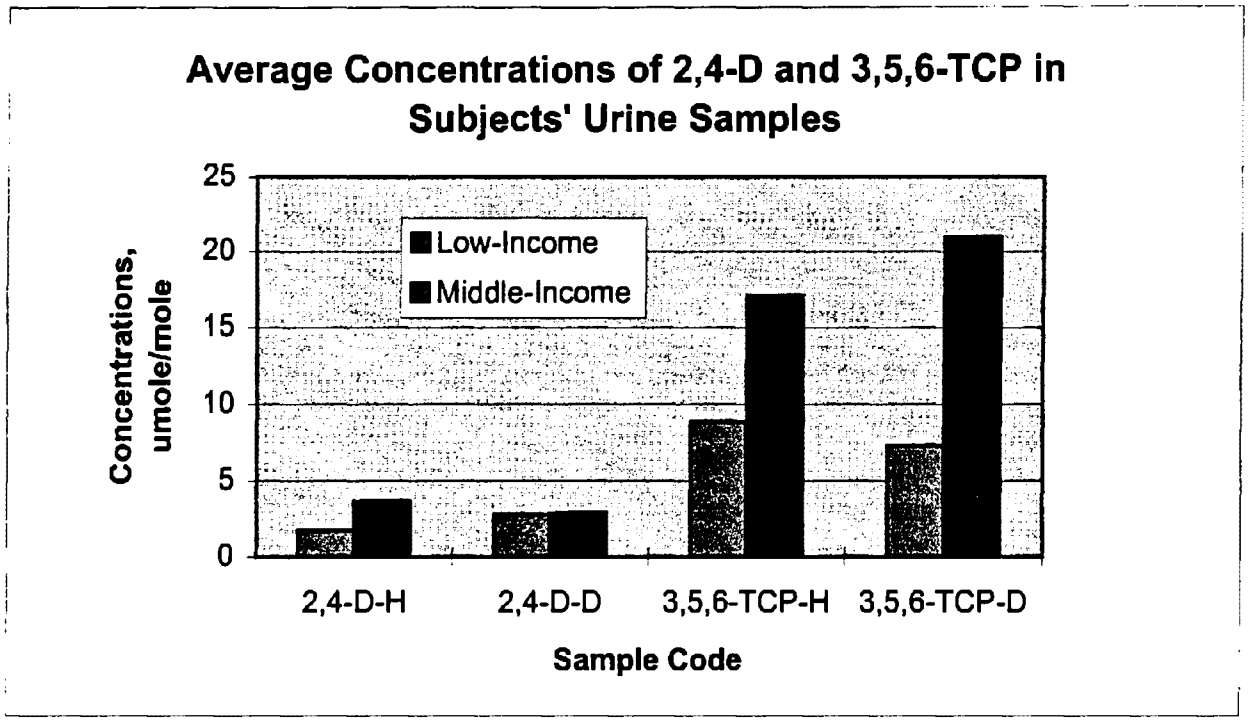
Figure 5.8. Average potential daily persistent organic pollutant doses from at-home and at-center exposures in low- and middle-income subjects.

samples were lower than that of 1-naphthol, but in general were higher than the levels of most other hydroxy-PAH.

The most abundant target analyte found in the urine samples was 3,5,6-TCP, an urinary metabolite of chlorpyrifos. Figure 5.9 displays the average concentrations of 3,5,6-TCP and 2,4-D in the urine samples of the subjects from low- and middle-income families. The concentrations of these analytes expressed in μmole/mole and ng/mL are displayed in the upper and lower portions of the figure, respectively. As shown in Figure 5.9, concentrations (ng/mL and μmole/mole) of 3,5,6-TCP and 2,4-D in the subjects' urine samples collected at their homes were in the same order of magnitudes as those collected at the daycare centers. Similar average concentrations in ng/mL of these two compounds were seen in the urine samples from low- and middle-income subjects. But higher creatinine-corrected concentrations of 3,5,6-TCP in μmole/mole were observed in middle-income subjects, which is consistent with the measured exposures and estimated potential doses of chlorpyrifos. Figure 5.10 displays the average concentrations of 1-naphthol, 2-naphthol, and PCP in the urine samples of the low- and middle-income subjects. Levels of 1-naphthol in the subjects' urine samples collected at their homes were higher in the low-income subjects than that in the middle-income subjects. The reversed trend was observed in PCP in the urine samples collected at homes and at daycare centers in these two subject groups.

Analysis of Variance (ANOVA)

ANOVA models were fitted to B2 PAH, total PAH, OP, OC, PE, Ph and HA as well as selected individual POP. The results of ANOVA models of POP in all sample media on sampling location (daycare center vs. home) are presented in Table Q-1 in Appendix Q. Table 5.28 summarizes the results of ANOVA with significant location effect, at least, at 0.05 level, and the respective geometric mean. As shown in Table 5.28, concentrations of OP in outdoor air in subjects homes were significantly higher than those in the daycare centers. Significantly higher PCB concentrations in indoor and outdoor air in daycare centers were observed. The concentrations of total PAH, total target phenols, and bisphenol-A were significantly higher in liquid food samples collected at daycare centers as opposed to those collected at homes. There were no statistically significant difference in POP concentrations in



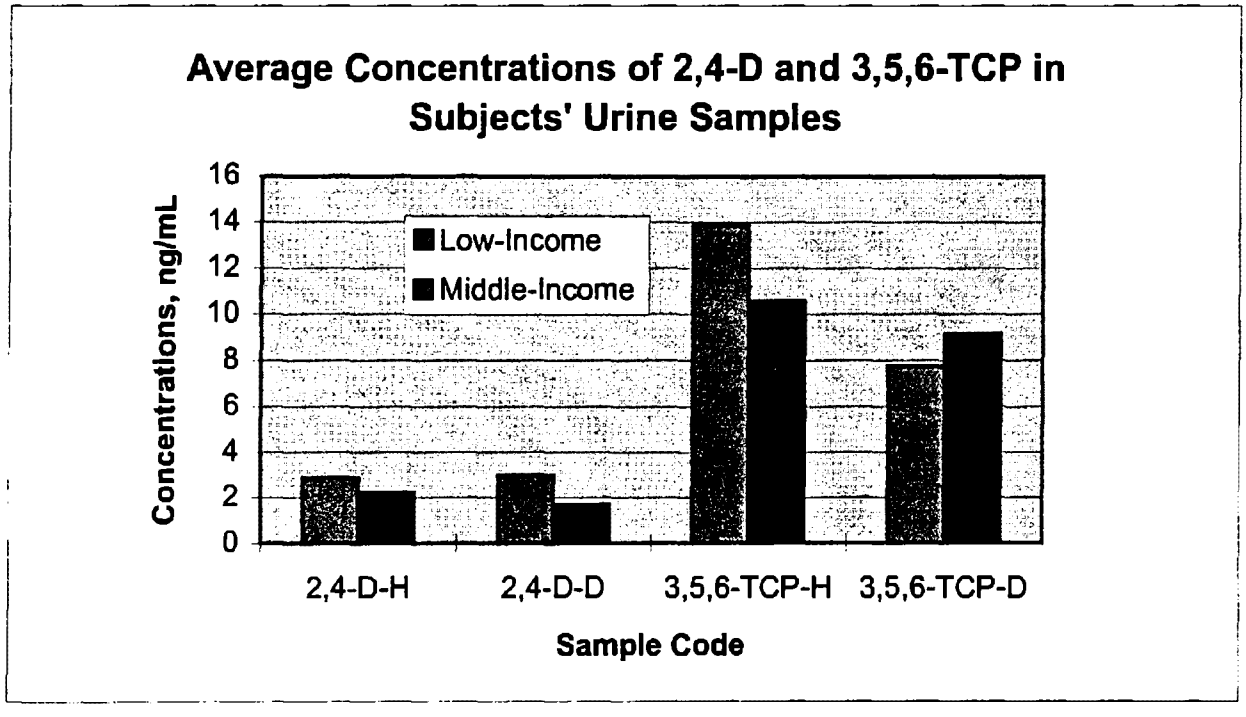


Figure 5.9. Average concentrations of 2,4-D and 3,5,6-TCP in subjects' urine samples. The top plot shows the creatinine-corrected concentrations; the bottom plot shows uncorrected concentrations.

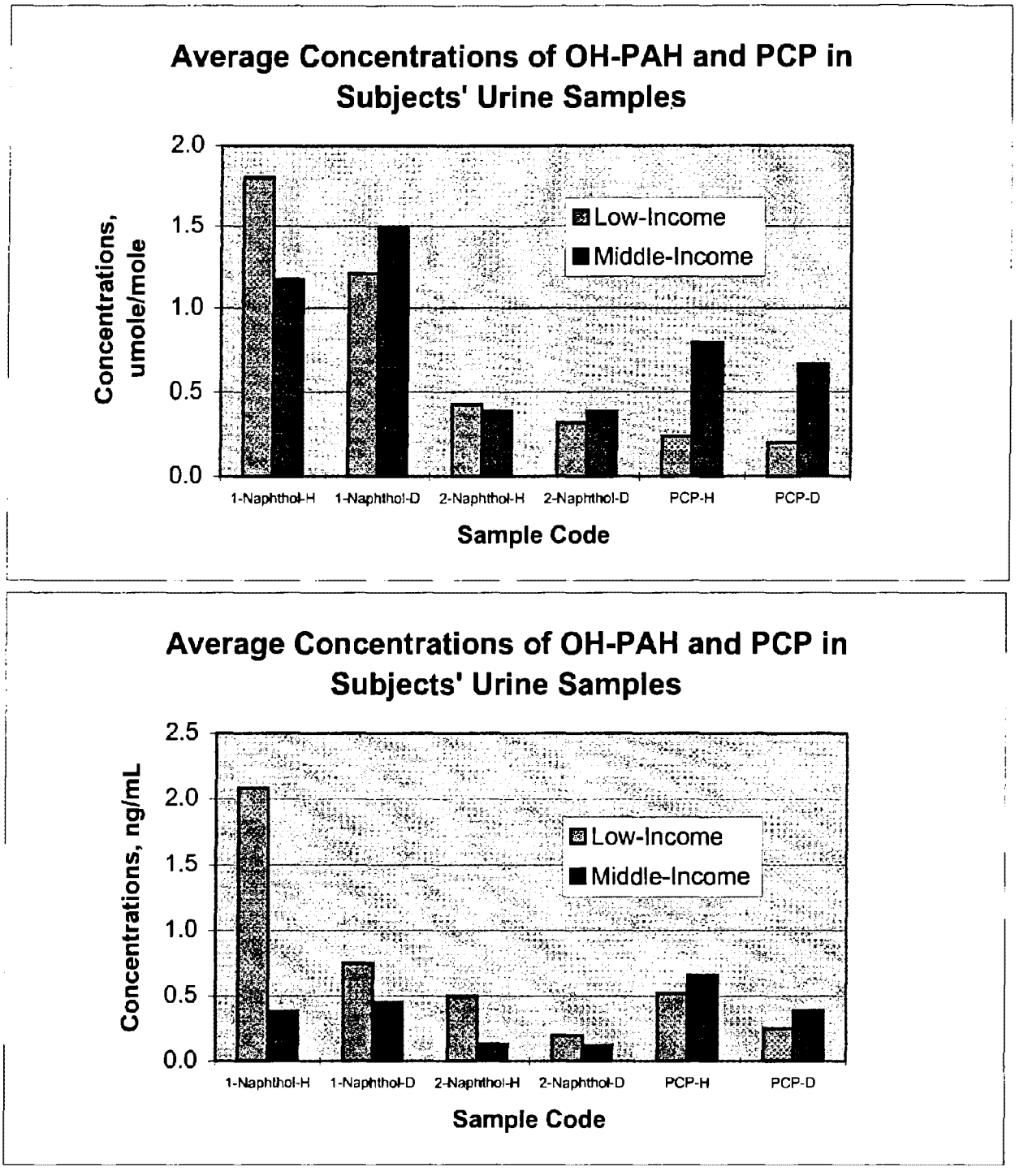


Figure 5.10. Average concentrations of 1-naphthol, 2-naphthol, and pentachlorophenol in subjects' urine samples. The top plot shows the creatinine-corrected concentrations; the bottom plot shows uncorrected concentrations.

TABLE 5.28. SUMMARY OF ANOVA ON THE EFFECT OF SAMPLING LOCATION: DAYCARE CENTERS VERSUS HOMES

Target POP	Sample Medium	Geometric Mean[a]		Daycare Center[b] vs. Home
		Daycare Center	Home	
Total PAH	Liquid food, ppb	0.728	0.225	*
OP	Outdoor air, ng/m^3	1.22	2.16	*
PCB	Indoor air, ng/m^3	35.6	12.0	*
	Outdoor air, ng/m^3	5.12	1.60	**
Ph	Floor dust, ppm	21.3	8.50	*
	Liquid food, ppb	1.63	0.216	*
Bisphenol-A	Liquid Food, ppb	0.198	0.062	*

(a) Sample size = 4 from daycare centers and 9 from homes.
(b) * and ** denote the tested effect is statistically significant at 0.05 and 0.01 level, respectively.

playground soil, solid food, dermal wipe, and urine samples between these two groups of samples.

The effect of family income on concentrations of POP in multimedia samples was also investigated. The results of ANOVA are presented in Table Q-2 in Appendix Q. Table 5.29 summarizes the results of ANOVA having significant effect on family income. Levels of OP in liquid food samples collected at low-income homes were higher than those collected at middle-income homes. Higher concentrations of total target phenols were found in the liquid foods from middle-income families. As mentioned before, the difference seen in the liquid food may be from the types of food they consumed. In addition, significantly higher levels of PCP were found in the urine samples of middle-income subjects. Target POP levels in air, dust, soil, dermal wipe, and solid food between the low- and middle-income groups did not differ significantly.

The ANOVA was also conducted to investigate the differences in POP levels between two groups: Head Start center and low-income families versus private daycare center and middle-income families. The first group is referred to as low-income group and the second one is referred to as middle-income group. The ANOVA results are given in Table Q-3 in Appendix Q. Table 5.30 summarizes the results of ANOVA models showing significant difference in POP concentrations between these two groups. The total phenols concentrations in liquid food were higher in middle-income group as opposed to low-income group. Levels of bisphenol-A in floor dust were also higher in the middle-income group. For dermal wipe samples, significantly higher levels of benzylbutylphthalate and OC but lower levels of total PAH were observed in the low-income group. Concentrations of total target hydroxy-PAH and 2,4-D in the urine samples from the low-income subjects were higher than that from the middle-income subjects. The reversed concentration trend was observed for PCP and 3,5,6-D in the urine samples between these two groups.

Regression Models

The results of the estimated relationships between measured urinary metabolites and measured POP concentrations based on the fitted models are summarized in Table R-1 in

TABLE 5.29. SUMMARY OF ANOVA ON THE EFFECT OF FAMILY INCOME: LOW-INCOME VERSUS MIDDLE-INCOME

Target POP	Sample Medium	Geometric Mean[a]		Low-Income[b] vs. Middle-Income
		Low-Income	Middle-Income	
OP	Liquid food, ppb	0.141	0.020	*
Ph	Liquid food, ppb	0.050	0.696	*
PCP	Urine, μmole/mole	0.299	0.718	**

(a) Sample size = 4 from low-income and 9 from middle-income homes.
(b) * and ** denote the tested effect is statistically significant at 0.05 and 0.01 level, respectively.

TABLE 5.30. SUMMARY OF ANOVA ON THE EFFECT OF FAMILY INCOME AND SAMPLING LOCATION: HEAD START CENTER AND LOW-INCOME VERSUS REGULAR CENTER AND MIDDLE-INCOME

Target POP	Sample Medium	Geometric Mean[a]		Head Start Center/Low-Income[b] vs. Regular Center/Middle-Income
		Head Start Center Low-Income	Regular Center Middle-Income	
Ph	Liquid food, ppb	0.126	1.08	*
Bisphenol-A	Floor dust, ppm	1.11	1.90	*
Total PAH	Wipe, ng/wipe	4.88	13.6	*
Benzylbutylphthalate	Wipe, ng/wipe	186	8.66	*
OC	Wipe, ng/wipe	1.33	0.420	*
OH-PAH	Urine, ng/mL	1.71	0.483	*
2,4-D	Urine, ng/mL	2.89	1.62	*
PCP	Urine, µmole/mole	0.208	0.652	**
3,5,6-TCP	Urine, µmole/mole	7.76	15.4	*

(a) Sample size = 6 from Head Start center and low-income families and 7 from regular center and middle-income families for food and dust samples; 8 from the first group and 10 from the second group for wipe and urine samples.

(b) * and ** denote the tested effect is statistically significant at 0.05 and 0.01 level, respectively.

Appendix R. Each row in the table represents a distinct analysis. The intercepts for the fitted regression models are shown in the second column, and the slopes (estimated parameters) are displayed in column three to six. The slope represents the estimated increase in log-transformed urinary metabolites due to an increase of the log-transformed POP concentration in one sample medium. For each regression model, a test was conducted to determine whether the relationship between the urinary metabolite and the POP concentrations was different between sampling location (at-home vs. at-center). The last column indicates if the test was statistically significant. The regression results of the relationships between measured levels of urinary metabolites and total daily POP potential doses, using the same format as Table R-1, are summarized in Table R-2 in Appendix R. Table 5.31 summarizes the regression models with statistically significant results. Note that the format of Table 5.31 is similarly as described above for Table R-1 except that the last two columns show the r^2 and p- value of the respective regression model.

The results of all regression models showed that there was no statistically significant relationship between sampling location (at-home and at-center) and all measured urinary metabolites. This is partly because POP concentrations in multiple sample media did not vary significantly between homes and daycare centers.

As shown in Table 5.31, the measured values of PCP in urine were significantly related to the measured PCP values in indoor air or floor dust. This positive relationship was also shown between subject's total daily potential dose of POP and PCP level in the subject's urine. This finding suggested that the measured PCP concentrations in indoor air or floor dust in subjects' microenvironment are related to the PCP found in subject's urine. Thus, the measurement of PCP in environmental samples can be an indicator for subject's exposure to PCP. Given the small sample size, more samples are needed to establish such relationships between the PCP in environmental media and PCP in urine.

None of the PAH concentrations in multimedia samples, as well as the total daily potential dose of PAH were significantly related to hydroxy-PAH, urinary metabolites of PAH. A weak relationship was observed between chlorpyrifos in multimedia samples and 3,5,6-TCP, an urinary metabolite of chlorpyrifos, in urine samples. Subjects' total daily potential dose of chlorpyrifos was not related significantly to 3,5,6-TCP in the subjects' urine samples. A

TABLE 5.31. SUMMARY OF REGRESSION MODEL RESULTS

Urinary Metabolite	Parameter Estimates[a]					Regression Model	
						r^2	p-value
	Intercept	IA	OA	FD	FO		
PCP							
ng/mL	-14.585	0.400**	0.261	0.008	-8.640	0.758	0.002
µmole/mole	-0.690	-0.247	0.228	1.042*	-1.891	0.581	0.041

	Parameter Estimates		Regression Model	
	Intercept	Total Daily POP Potential dose	r^2	p-value
PCP				
ng/mL	-1.116**	0.428**	0.649	0.0004
µmole/mole	-1.263**	0.426**	0.261	0.104

(a) * and ** denote that the estimated parameter (slope) is significantly different from zero at 0.05 and 0.01 level, respectively; IA = indoor air, OA = outdoor air, FD = floor dust, and FO = liquid food and solid food.

negative relationship between 2,4-D in urine and total daily potential dose of 2,4-D was obtained, but the r^2 value of this regression model was only 0.351 at the p value of 0.04. The absence of significant relationships between urinary metabolites levels and the respective POP levels in a multimedia samples as well as the metabolite levels and the POP total daily potential dose levels may be due to the small sample size and the variation of elimination rate of urinary metabolites.

Quality Control Data for Phase 2 Study

The recovery data of the spiked POP in Phase 2 multimedia samples are summarized in Appendix S. Acceptable recoveries for spiked POP were obtained in most of the sample media except for food. Greater than 100% recovery (183%) was found in one air sample. This was from the coeluting interference peak in GC/ECD analysis. Recoveries of 3,4-D were low (<50%) in most food samples. It is possible that 3,4-D was lost during the GPC cleanup step. Low recoveries of the spiked ^{13}C-DDE, and ^{13}C-PCB were found in few dermal wipe samples. This may be due to the losses through the SPE cleanup step. For the same reason, slightly lower average recoveries of the spiked POP were found in the dust/soil samples when compared to those obtained from Phase 1 study.

The results of field blanks in each sample medium are given in Appendix T. In general, trace amounts of target POP were found in the field blank except for phthalate esters. The levels of PE in the Phase 2 field blanks were higher than that in Phase 1 field blanks. Among the two target PE, higher background levels were seen of dibutylphthalate as opposed to benzylbutylphthalate. Overall, the field blank data showed that there was no significant contamination due to sample handling and preparation.

References

1. Chuang, J.C., Callahan, P.J., Menton, R.G., Gordon, S.M., Lewis, R.G., Wilson, N.K. Monitoring methods for polycyclic aromatic hydrocarbons and their distribution in house dust and track-in soil. Environ. Sci. Technol. 29(2):494-500, 1995.

2. Nishioka, M.G., Burkholder, H.M., Brinkman, M.C., Gordon, S.M., Lewis, R.G. Measuring transport of lawn-applied herbicide acids from turf to home: correlation of dislodgeable 2,4-D turf residues with carpet dust and carpet surface residues. Environ. Sci. Technol., 30, 3313-3320, 1996.

3. Wania, F. and MacKay, D. Tracking the distribution of persistent organic pollutants. Environ Sci. Technol 30(9):390A-396A, 1996.

4. Stanek, E.J., III and Calabrese, E.J. Daily estimates of soil ingestion in children. Environ. Health Perspectives, 103(3): 276-285, 1995.

5. Chuang, J.C., Callahan, P.J., Lyu, C.W., Pennybacker, M.R. Characterization of polycyclic aromatic hydrocarbon exposure among children of low income families from inner city and rural areas. Final Report (Year 2) to U.S. EPA, Cooperative Agreement CR 822073, October 1995.

6. Chuang, J.C., Callahan, P.J., and Lyu, C.W. Field method evaluation of total exposure of children from low-income families that include smokers to polycyclic aromatic hydrocarbons. Final Report to U.S. EPA, Contract Number 68-D4-0023, Work Assignment No. 9, July 1996.

7. Chuang, J.C. and Kenny, D.V. Method validation for measurement of selected semivolatile phenols in dust and soil, EPA/600/SR-97/027, March 1997.

8. Wilson, N.K., Barbour, R.K., Chuang, J.C., and Mukund, R. Evaluation of a real-time monitor for particle-bound PAH in air, Polycyclic Aromatic Compounds, 5:167-174, 1994.

9. Mukund, R. and Chuang, J.C. Field and laboratory evaluations of a real-time PAH analyzer, EPA/600/SR-97/034, July 1997.

10. High Volume Small Surface Sampler HVS3: Operation Manual. Cascade Stack Sampling Systems (CS_3), Inc., Bend, Oregon, January 13, 1992.

11. Standard Practice for Collection of Dust for Chemical Analysis. Standard Method D.5438-94, Annual Book of ASTM Standards Volume 11.03, American Society for Testing and Materials, Philadelphia, pp. 517-523, 1997.

12. Occupational and Residential Exposure Test Guidelines (1994, 1997). U.S. Environmental Protection Agency Office of Prevention, Pesticides, and Toxic Substances, Washington, DC, Series 875.

13. Barclays Official California Code of Regulations (Barclays Law Publishers. South San Francisco, CA, 1996). "Level of exposure to carcinogens." Vol. 28, § 12721.

14. Lewis, R.G., Fortmann, R.C., and Camann, D.E. Evaluation of methods for monitoring the potential exposure of small children to pesticides in the residential environment, Arch. Environ. Contam. Toxicol. 26:37-46, 1994.

15. Stanek III, E.J. and Calabrese, E.J. Soil ingestion estimates for use in site evaluations based on the best tracer method, Human and Ecological Risk Assessment, 1(2):133-156, 1995.

16. Chuang, J.C., Hannan, S.W., and Wilson, N.K. Field comparison of polyurethane foam and XAD-2 resin for air sampling for polynuclear aromatic hydrocarbons. Environ. Sci. Technol. 21(8):798-804, 1987.

17. Shealy, D.B., Barr, J.R., Ashley, D.L., Patterson, Jr., D.G., Camann, D.E., and Bond, A.E. Correlation of environmental carbaryl measurements with serum and urinary 1-naphthol measurements in a farmer applicator and his family, Environ. Health Perspectives 105(5):510-513, 1997.

NERL-RTP-0-579 TECHNICAL REPORT DATA

1. REPORT NO. 600/R-98/164a	2.	3. PB99-134934
4. TITLE AND SUBTITLE Evaluation and Application of Methods for Estimating Children's Exposure to Persistent Organic Pollutants in Multiple Media Volume I: Final Report		5. REPORT DATE 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Jane C. Chuang et al.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Memorial Institute 505 King Avenue Columbus, Ohio 43201		10. PROGRAM ELEMENT NO. Projects E0608 and E0460 11. CONTRACT/GRANT NO. Contract 68-D4-0023
12. SPONSORING AGENCY NAME AND ADDRESS National Exposure Research Laboratory U. S. Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Research Report 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Field methods for determining children's exposure to selected persistent organic pollutants (POP), including polycyclic aromatic hydrocarbons and other semi-volatile organic compounds (SVOC) were evaluated and applied to estimate the ranges of potential exposures through air, dust, and food, of a small set of children from low-income and middle-income families. A field study was conducted at nine day care facilities, and a second field study was conducted which measured the total exposures to multiple compound classes – polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), phthalate esters (PE), phenols (Ph), organochlorine (OC) pesticides, organophosphate (OP) pesticides, and a herbicide acid (HA) – of nine children selected from two of the day care centers. Ingestion, both dietary and nondietary, was a primary route of exposure for many of the compounds, but other routes were also important, depending on the compound class.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/ OPEN ENDED TERMS	c. COSATI

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This Page)* Unclassified	22. PRICE