

Relationship of Indoor, Outdoor and Personal Air (RIOPA) study: study design, methods and quality assurance/control results

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The Relationship of Indoor, Outdoor and Personal Air (RIOPA) Study was undertaken to evaluate the contribution of outdoor sources of air toxics, as defined in the 1990 Clean Air Act Amendments, to indoor concentrations and personal exposures. The concentrations of 18 volatile organic compounds (VOCs), 17 carbonyl compounds, and fine particulate matter mass (PM_{2.5}) were measured using 48-h outdoor, indoor and personal air samples collected simultaneously. PM_{2.5} mass, as well as several component species (elemental carbon, organic carbon, polyaromatic hydrocarbons and elemental analysis) were also measured; only PM_{2.5} mass is reported here. Questionnaires were administered to characterize homes, neighborhoods and personal activities that might affect exposures. The air exchange rate was also measured in each home. Homes in close proximity (<0.5 km) to sources of air toxics were preferentially (2:1) selected for sampling. Approximately 100 non-smoking households in each of Elizabeth, NJ, Houston, TX, and Los Angeles, CA were sampled (100, 105, and 105 respectively) with second visits performed at 84, 93, and 81 homes in each city, respectively. VOC samples were collected at all homes, carbonyls at 90% and PM_{2.5} at 60% of the homes. Personal samples were collected from nonsmoking adults and a portion of children living in the target homes. This manuscript provides the RIOPA study design and quality control and assurance data. The results from the RIOPA study can potentially provide information on the influence of ambient sources on indoor air concentrations and exposure for many air toxics and will furnish an opportunity to evaluate exposure models for these compounds.

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Introduction

Communities are exposed to a complex mixture of air toxics that include solid-, liquid-, and gas-phase compounds generated in different microenvironments and emitted by a variety of sources. A chemical or complex air contaminant (e.g., diesel particulate matter) is classified as a hazardous air pollutant (HAP; 1990 Clean Air Act Amendments) or air toxic on the basis of its presence in the atmosphere and the results from toxicological and clinical studies performed in controlled environments, as well as epidemiological studies in

occupational settings and communities that have investigated the toxicity and health effects of many components of this complex mixture. The mixture includes a large number of volatile organic compounds (VOCs) and carbonyl compounds (aldehydes and ketones), as well as semi-volatile and particle-bound organic and inorganic compounds and elements that comprise fine airborne particulate matter (PM). Exposure to several of these air toxics has been associated with neurological, teratological, carcinogenic, or cardiovascular effects (Kjaergaard et al., 1991; Dockery et al., 1993; Caldwell et al., 1998; Lovett et al., 1999; Morello-Frosch et al., 2000; Pope, 2000; Samet et al., 2000; Suh et al., 2000). A number of exposure studies have found that concentrations of personal exposures to VOCs and particulate matter (PM) are frequently higher than outdoor concentrations and, typically, are better correlated with indoor concentrations, suggesting that indoor sources and personal activities strongly influence human exposure to these

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constituents (Wallace et al., 1984, 1985, 1986; Gordon et al., 1999; Pellizzari et al., 1999; Rojas-Bracho et al., 2000; Bonanno et al., 2001; Jurvelin et al., 2001a,b; Koistinen et al., 2001; Rodes et al., 2001). Results from the Total Exposure Assessment Methodology (TEAM) studies suggested that small sources of VOCs located close to the individual, usually inside the home, are major contributors to personal exposures (Wallace et al., 1985, 1986, 1987). However, contaminants generated by outdoor sources are transported to and penetrate into homes resulting in a baseline exposure to airborne contaminants to which emissions from indoor sources and personal activities add. Knowledge of the outdoor source contributions to indoor and personal air concentrations is needed to guide regulatory decision-making and public health protection efforts. Notably, little is known about community and personal exposure to carbonyl compounds other than formaldehyde. Except for exploring the influence of proximity to highways (Huang and Batterman, 2000; Pless-Mulloli *et al.*, 2000; Jo and Oh, 2001; Singh et al., 2003), few prior studies have been designed to investigate the impact of proximity to outdoor sources of air toxics on indoor and personal air concentrations. The RIOPA study was designed to investigate this impact. The database from this study is one of the most comprehensive sets of compound class measurements performed simultaneously in indoor, outdoor and personal air to date. As this database is further explored, it is likely that additional hypotheses about the relationship between concentration and exposure can be examined. This manuscript presents the study design, methodology, and quality assurance and control results for the measurement of VOCs, carbonyls, and PM_{2.5} mass, and AER, as well as questionnaire responses. Future manuscripts will describe PM_{2.5} speciation, air concentration results and the evaluation of the initial study hypotheses.

Objectives and study design

The RIOPA study was designed to address three general hypotheses, including:

- (1) In residences immediately adjacent to outdoor sources, a measurable and significant proportion of the indoor and personal air concentration for selected VOCs, carbonyl compounds and/or PM_{2.5} are contributed by outdoor stationary and mobile sources.
- (2) The residential air exchange rate (AER) is a major determinant of the relative influence of outdoor air concentrations on indoor air and personal exposure levels; therefore the influence of outdoor air on indoor and personal concentrations of air toxics can be predicted from the outdoor air concentration and air exchange rate using a relatively simple steady state, nonlinear model for individual compounds or compound classes, and

- (3) Other determinants of the association between indoor and outdoor air concentrations besides air exchange rate can be identified from the RIOPA data by using auxiliary information collected on season, location, housing characteristics, and household and personal activities; these determinants can be used to develop mixed models for predicting indoor and personal air concentrations.

To assess the role of ambient emissions on indoor concentrations and exposures, homes located close (defined as <0.5 km) to ambient sources of the target compounds were preferentially selected (~2:1) to homes more distant from sources. Sampling was conducted in three geographically distinct locations (Houston, Texas; Los Angeles, California; and Elizabeth, New Jersey) with different climates and housing characteristics (Table 1) and throughout the year, providing homes with a wide distribution of air exchange rates. This design is conducive to a mechanistic examination of the data and appropriate for model development and/or testing. Outdoor, indoor and personal air samples were collected for 48 h in more than 300 nonsmoking homes equally divided among the three cities. The homes were sampled twice about three months apart throughout the year. VOC and carbonyl compound concentrations, air exchange rate, temperature, relative humidity, time-activity information, and home characteristic data were collected at each home, while PM_{2.5} mass was obtained from a subset of homes. PM_{2.5} samples were also analyzed for a suite of chemical species. Prior to commencing the 300 home sampling effort, a pilot study was conducted in 10 homes in each city to test and optimize each component of the field and laboratory analysis protocols and procedures. The pilot study was conducted in two phases, first in NJ and TX, then in CA after modifications to the initial sampling protocols were made. The revised sampling and analytical methodologies applied during the second phase of the pilot study were found to be adequate to measure the target species at existing environmental concentrations, and to recruit nonsmoking participants from nonsmoking households with a wide range of housing types, and determine air exchange rates.

Methods

IRB Approval

All sampling and analyses protocols were approved by the Institutional Review Boards of the University of Medicine and Dentistry of New Jersey; Rutgers, The State University of New Jersey; and the University of Texas-Houston Health Science Center. Human consent procedures met governmental guidelines. Informed consent was obtained from each participant and/or his or her parent or guardian for minors.

Table 1. General description of sampling sites.

	Elizabeth, NJ		Houston, TX		Los Angeles, CA	
Communities selected (near — community selected for homes near sources, none — homes not near sources, mixed — community had homes near and far from sources)	Entire City — mixed		Houston Ship Channel — mixed Pasadena — mixed Galena Park — mixed Channel View — mixed Baytown — mixed Medical Center — none		West Los Angeles — near Pico Rivera — near Burbank — none Newhall — none	
Emission sources targeted	Industrial, mobile, area, airport		Industrial (petro-chemical)		Mobile	
Climate ^a						
Average Temp. (°F, °C)						
January	31.2, -0.4		51.4, 10.8		56.0, 13.2	
April	52.1, 11.2		68.7, 20.4		59.5, 15.3	
July	76.8, 24.9		83.1, 28.4		69.3, 20.6	
October	57.2, 14.0		69.7, 20.9		66.3, 19.1	
Annual Precipitation (in)	42.3		44.8		12.1	
Number of days with ppt	122		105		36	
Housing Characteristics (%) ^b						
Single family detached	17		47		39	
Single family attached	6		5		7	
Two units	25		2		3	
Four units	15		4		6	
Five or more units	37		40		44	
Year built after 1990	5		11		6	
1970–1989	16		45		26	
1960–1969	16		19		18	
1940–1959	33		20		34	
Before 1940	31		5		17	
Population ^b (%)	City	RIOPA	City	RIOPA	City	RIOPA
White (non-Hispanic)	6	19	14	43	37	54
African American	20	8	25	3	10	0
Asian	2	1	5	0	9	18
Hispanic (any race)	50	72	37	54	39	23
Other	22	1	18		5	5

^aData from NOAA Averaged over 20 years.

^bData from 2000 Census Fact Sheet for Each City <http://factfinder.census.gov> for entire city, not just sections sampled in RIOPA.

Questionnaires

The National Human Exposure Assessment Survey (NHEXAS) was used as a basis for developing RIOPA-specific questionnaires (Sexton *et al.*, 1995). Three distinct questionnaires were developed, a Baseline Questionnaire, a Technician Walk-Through Questionnaire, and a Time Diary and Activity Questionnaire. The Baseline Questionnaire included sections on household and participant characteristics; demographics of the participant; family income; housing characteristics, facilities and usage; and personal exposure activities before the study period. The Technician Walk-Through Questionnaire included an evaluation of the house and exposure-relevant furnishings and

other contents, a floor plan and measurements of the home, and a description of possible neighborhood point sources located closer than the 0.5 km criterion. The Time Diary and Activity Questionnaire included a 48-h activity log listing the time spent indoors and outdoors, and a detailed series of questions related to personal and household activities, duration of the activities, and use of consumer products. Each questionnaire was available in English and Spanish and an English or Spanish-speaking field staff member was available for each household dependent upon the household's native language. A copy of the questionnaires can be obtained by contacting the investigators.

Recruitment

It was determined during the pilot study that while random recruitment of participants in each city was possible and followed in Los Angeles, CA, the effort required to recruit a population-based sample in Elizabeth, NJ and Houston, TX was beyond the resources available and not justified in terms of accomplishing the main goal of the study, that is, to evaluate the effect of proximity to ambient sources on indoor and personal air concentrations and the mechanistic associations between ambient emissions and exposures. This objective could be accomplished by recruiting nonsmoking participants that lived in nonsmoking residences with a wide range of air exchange rates, in areas with ambient sources in near proximity to residences that had a varied housing stock. A population-based sample of 100 homes in each city that met these criteria would not be representative of the population as a whole in each city, but only small selective sections of each city that are close to ambient sources. It was therefore decided that recruitment in NJ and TX would use a convenience sampling approach. Although the indoor air concentrations and exposures measured in RIOPA cannot be directly extrapolated to the populations in these cities, the findings from the analysis of the relationship among the indoor, outdoor and personal air concentrations of air toxics can be used in the development or evaluation of exposure models across factors such as the housing type, climatic conditions and air exchange rates included in the study. Such models are generic and should be applicable to air toxic exposures in general.

Once the target areas close to ambient sources were identified, a number of different approaches were used to identify and recruit subjects. These included seeking support from governmental, community and religious leaders in the target neighborhoods, interviews with local newspapers, radio and television stations, mailings with follow-up telephone calls, direct canvassing of residences in targeted areas, presentations at community centers and word of mouth contact through local organizations. After an individual in the selected residence was contacted in their native language (Spanish or English), they were administered a brief screening questionnaire to determine if they met the study eligibility criteria. These criteria included being a nonsmoker living in a nonsmoking household, being at home for more than 14 h per day, willingness to wear personal samplers for 48 h, except when sleeping or bathing, and no current plans to move from the home within the next three months. The requirement of a minimum time spent at home was to assure that the personal samples could be related to the impact of ambient emissions near the home, though exposures at other indoor locations and outdoor air environments would also impact the exposure when the participant was away from home. The actual times at home, at other locations, and the activities engaged in during the 48-h sample collection period were recorded, so that, it would be

possible to examine the relative influence of different locations on the personal air concentrations. If the selection criteria were met and the residents agreed to participate an appointment was made and the home visited on three days for the purpose of data collection. During the first day, the study was explained, informed written consent to collect the samples and questionnaire responses was obtained, the Baseline and Technician Walk-Through Questionnaires were completed (if possible, otherwise an additional appointment was made to administer the questionnaires), perfluorocarbon tracer (PFT) sources for the air exchange rate measurement (AER) were placed in the home, and an appointment was made to set up the samplers at least 48 h after the placement of PFT sources. During the second day visit at least 48 h later, the indoor/outdoor and personal samplers were setup and instructions on how to complete the time-activity log were provided; an appointment was made for a third day visit 48 h later. During this last day, the samples and all monitoring equipment were retrieved, the Time Diary and Activity Questionnaire was administered, the time activity log was reviewed with the participant, and a small study fee was provided to the participants. Both the initial recruitment of participants and follow up retention activities for the repeat sampling was often a time-consuming process that required multiple telephone calls and contacts to complete, even after participants initially committed to participate.

Sampling

A single set of detailed sampling protocols was developed and used for sampling at all sites. Indoor, outdoor and personal air samples were collected and analyzed for VOCs, carbonyl compounds and PM_{2.5}, with simultaneous collection of perfluorocarbon tracer for estimation of AER in each home. Carbonyl samples were also collected from inside vehicles (data not presented here). Temperature and relative humidity were continuously measured indoors and outdoors during the sampling period. A field audit of the sites was conducted at the beginning of the study by one of the study investigators and later during the study by an independent auditor appointed by the funding organizations. Laboratory audits were conducted by independent auditors at the beginning and end of the study.

Selection of sampler locations was based on the following criteria. The indoor samplers were placed in a rack assembled in the main living area of the residence, 1–2 m above the floor and at least 1 m from the nearest wall. The samples were positioned as far as possible from clearly identified indoor emission sources, such as portable heaters, fireplaces, or kitchen stoves. The outdoor samplers were placed on similar racks in a secure location sheltered from rain and direct sunlight, at least 1 m away from a wall or other objects. Placement under a low roof or patio attached to an upper floor of the residence was considered acceptable if required for security concerns or practical logistics (e.g., access

to electrical power, or second floor apartment with a balcony).

A personal air monitoring set was designed to hold and carry all personal collection devices at breathing zone level. The personal air monitoring set consisted of a suspender, a belt, a bag for a personal pump and its battery, and sample holders designed to keep the actual monitors near the breathing zone of the participant. Participants were instructed to wear the personal air monitoring set whenever awake, except when showering, bathing or swimming; they were instructed to leave the set just outside the bathroom or pool area to minimize exposing the samplers to sources of high humidity. It is recognized that this approach may result in underestimating the exposure to volatile chemicals emitted from shower or pool water. The sampler was placed next to the bed when the participant was sleeping. Adults and children 10 years and older were eligible to participate in personal VOC, carbonyl, and PM_{2.5} monitoring. Children under 10 years of age wore only passive samplers attached to their shirt/jacket collar or pocket. Field sampling forms that recorded the home and participant identification code (ID), sampler ID, start date and time, end date and time were designed and used for all field sampling. The home and subject code and was used as the main link relating all information collection instruments.

Air Exchange Rate (AER) The passive measurement method used in this study was designed to provide an estimate of the total exchange of indoor air with outdoor air in relatively small enclosures such as homes, apartments, or small offices (Dietz et al., 1986). Briefly, AER measurements were accomplished by first releasing perfluorinated methyl cyclohexanone (PMCH) at a known rate during a minimum of 48 h to allow tracer equilibration from at least four permeation tube sources placed in distinct locations in the house. The tracer source strength was above that previously reported in order to detect AER levels from zero to 5 volume changes per hour. The tracer was then sampled for 48 h (while the air toxics monitoring was performed) using a charcoal adsorption tube (CAT) which was later analyzed by gas chromatography with an electron capture detector (GC/ECD). The CAT consists of a short length of glass tubing (6.35 cm L × 0.6 cm OD × 0.4 cm ID) containing a small amount of a carbonized adsorbing material sandwiched between stainless steel screens. An identification number was permanently engraved on each CAT. The ends of the CAT were capped with either a polyurethane or polyethylene cap. AER estimates are expressed as the number (or fractions) of indoor air volumes replaced each hour with outdoor air in the home. The AERs estimates were based on the average 48 h temperature calculated from the temperature measurements recorded every 5 min using a HOBO Sensor (HOBO, Onset Computer Corp, Bourne, MA, USA), which also recorded relative humidity (RH).

Passive Volatile Organic Compounds (VOCs) Sampling Organic vapor monitors (Model No. OVM3500, 3 M Company, St. Paul, MN, USA) were used for passive VOC sampling. This selection was based on results from the comparative evaluation of the OVM 3500 (single charcoal pad) and the OVM 3520 (double charcoal pad) during the pilot study for the 18 target VOCs that included: 1,3-butadiene, methylene chloride, methyl *tert* butyl ether, chloroprene, chloroform, carbon tetrachloride, benzene, trichloroethylene, toluene, tetrachloroethylene, ethylbenzene, *m/p*-xylene, *o*-xylene, styrene, α -pinene, β -pinene, D -limonene, and 1,4-dichlorobenzene. These VOCs are air toxics commonly found in indoor and outdoor urban settings, and include aldehyde precursors (i.e., α - and β -pinene and D -limonene.) No discernable breakthrough of these compounds to the backup charcoal pad of the OVM 3520s was detected during the pilot study, which included extreme temperature and humidity conditions typical of summertime in Houston, TX. The OVM 3500 which requires half the number of analyses was, therefore, the sampler of choice. It was subsequently determined that 1,3-butadiene and chloroprene cannot be reliably measured using OVMs at environmental levels (Stock et al., 2002).

The VOC sampling and analyses methods as described by Chung et al. (1999a, b) were performed by both laboratories. The target VOCs are air toxics commonly found in indoor and outdoor urban settings, and the aldehyde precursors (terpenes) α - and β -pinene and D -limonene. The OVMs were specially ordered without their labels preattached as emissions from the glue and/or ink in these labels within the closed aluminum shipping containers tend to increase the blank levels for some of the target aromatic hydrocarbons. The labels were attached to each OVM after the dosimeter was removed from its sealed container at the beginning of the sampling period. The personal sampler was worn with the windscreen (sampling side) facing outwards and not covered by any clothing. The need to leave the sampling surface exposed to the air was communicated to the participants verbally and as written instructions. After sampling was completed, the OVMs were retrieved from the subject or sampling setup, capped with the analytical cover (which was kept in the original container) and placed back into that container. The containers were transported to the laboratory in a cooler containing blue ice packs, and stored in a dedicated refrigerator until analyzed within four weeks of collection.

Passive Carbonyl Sampling The original RIOPA protocol called for sampling airborne carbonyl compounds with the active DNPH method, and this procedure was used during the first third of the study. The DNPH-coated cartridges were set to sample at a flow rate of 200 cm³/min for indoor and outdoor samples, 50–80 cm³/min for personal samples, and 800 cm³/min for in-vehicle samples. The flow rate for all

sampling was <1 l/min to avoid potential breakthrough (Zhang et al., 1994). The flow rate for the personal samples was lower than for the indoor or outdoor samples because the cartridges were connected in parallel with the $PM_{2.5}$ samplers using the same sampling pump. During the RIOPA study a new passive sampler was developed to measure multiple carbonyl compounds at typical environmental levels based on 24–48 h of sample collection. This new sampler, called Passive Aldehydes and Ketones Sampler (PAKS) employs a fluorogenic reagent, dansylhydrazine (DNSH), to derivatize aldehydes and ketones into the corresponding DNSH-hydrazones (Nondek et al., 1992). Similar to DNPH-carbonyl derivatives, individual DNSH-carbonyl derivatives can be separated by reverse-phase HPLC. However, the sensitivity and selectivity of the DNSH technique is enhanced over DNPH derivatization due to the use of fluorescence detection, which is more sensitive than the UV detection method used for the DNPH derivatives; in addition it permits sampling and analysis for acrolein more effectively than DNPH derivatization (Zhang et al., 2000). The carbonyls measured were formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, benzaldehyde, hexaldehyde, glyoxal and methylglyoxal.

The participants were instructed that the open end of the PAKS should neither be covered with clothing nor any objects, nor should be placed faced down against any surface. At the end of the sampling period, the PAKS was removed from the subject and securely capped. PAKSs for indoor or outdoor sampling were placed in the racks holding the rest of the sampling equipment, with the cap open during the sampling period. Unexposed cartridges (capped) were deployed as field blanks indoors and outdoors. The exposed cartridges, along with field blanks, were shipped to the laboratory in a cooler containing blue ice packs, and stored in a refrigerator until analysis.

PM Mass Microenvironmental indoor and outdoor $PM_{2.5}$ samples for gravimetric mass concentration analysis, were collected for 48 h at 10 l/min on 37 mm stretched Teflon filters mounted in Harvard Impactors downstream from the single-jet 2.5 μ m cutpoint impactor. These samplers were mounted in the indoor/outdoor sampling rack. Personal samples for $PM_{2.5}$ mass were collected at 3.2 l/min on 25 mm stretched Teflon filters with modified MSP personal environmental monitors (PEM; MSP Co., Minneapolis, MN, USA) using BGI Personal Sampling Pumps (BGI Incorporated, Waltham, MA, USA) for 48 h as described in detail by Meng et al. (2004). PEMs were mounted in the participants breathing zone on the personal air monitoring set. Filters were loaded and unloaded into the samplers in the laboratory, and the samplers were leak checked. They were transported to the field with a field blank that was placed in the indoor or outdoor sampling rack and returned to the laboratory with the samples. Flow rates were measured at the

beginning and end of each sampling period, and samplers were leak-checked again at the end of the sampling period, particularly if the flow rate had changed by more than $\pm 5\%$. All collected samples and field blanks were returned to the laboratory in coolers with blue ice packs and stored frozen until analysis. Collocated microenvironmental samples ($n=35$ pairs) were collected with side-by-side Harvard Impactors sited on the indoor or outdoor sampling rack. In addition, 14 collocated samples were collected with PEMs that were placed on the indoor sampling rack with the Harvard Impactor.

Chemical Analysis

Air Exchange Rates The PFT sources and CATS were supplied under a contract to Harvard University School of Public Health. The Harvard Laboratory performed PFT emission rate check measurements, and analyzed the CATS (Dietz et al., 1986). The CATs were cleaned prior to use by thermally desorbing any remaining adsorbed compounds at an elevated temperature in an inert nitrogen atmosphere. After sampling, the amount of PFT adsorbed on the CATs was determined by GC-ECD (Varian Model 6000) analysis.

VOCs samples collected in NJ were analyzed at EOHSI, those collected in TX were analyzed at the University of Texas School of Public Health-Houston (UTSPH) and those collected in CA were split between the two laboratories for analysis. To maximize comparability between the two laboratories analyzing the VOCs (EOHSI and UTSPH), both groups followed identical protocols using a common Standard Operating Procedures (SOPs) along with direct training in the techniques developed by the UTSPH laboratory to the EOHSI staff prior to the pilot study. In addition, the same source of supplies (solvents and standards) and instrumentation was used in both laboratories. The procedures for sampling and analysis of the target VOCs have been previously described (Chung et al., 1999a, b). Briefly, VOCs collected on the charcoal pad of each OVM 3500 were extracted by ultrasonication into a high purity 2:1 acetone/carbon disulfide solvent mix containing a surrogate (bromochloromethane) and two internal standards, chlorobenzene *D*-5 and 1,4-difluorobenzene in methanol (Supelco Inc., PA, USA). Calibration curves were prepared from commercially purchased certified standards (Accustandard Inc., New Haven, CT, USA) of the target VOCs. The purity of each lot of acetone and carbon disulfide was pretested to confirm that they did not contain more than trace amounts of any of the target compounds prior to their use in the analysis. Blanks and calibration check samples were analyzed together with the samples. Samples were blank corrected prior to calculating the air concentration. The average load (i.e., total μ g of VOC in the charcoal pad) of each VOC present in the blanks was calculated from field and laboratory blanks of the same OVM lots as the samples and

extracted with the same solvent lot. If a new lot of OVMs, or a series of OVMs within the same lot, or solvents presented statistically significant different blank background concentrations than previous lots or solvents, a new average blank value was determined.

Carbonyl Compounds Carbonyl compounds were measured using two methods, the DNPH active method and the DNSH passive method.

DNPH samples collected in TX were analyzed by the UTSPH laboratory, and those collected in CA and NJ were analyzed by the EOHSI laboratory. All PAKSs were analyzed by the EOHSI laboratory. The DNPH method used in the EOHSI laboratory and UTSPH has been reported in detail earlier (Zhang et al., 1994, 2000). Briefly, Sep-Pak C₁₈ cartridges (Waters Corp., Milford, MA, USA) were coated with DNPH and stored in a freezer before use. The DNPH-carbonyl derivatives were extracted with acetonitrile (ACN) when returned from the field and analyzed by HPLC/UV (Zhang et al., 2000). Calibration curves were prepared using certified standard solutions of DNPH-carbonyl derivatives purchased commercially (Supelco, Inc., Bellefonte, PA, USA; Accustandard, Inc., New Haven, CT, USA). All sample concentrations were corrected for field blank mass and carbonyl recovery rates.

The PAKSs were prepared by coating a custom-made C₁₈ cartridge (Supelco, Inc., Bellefonte, PA, USA) with a DNSH (Aldrich Chemical Co., Milwaukee, WI, USA) solution in ACN. The exposed or blank PAKSs were extracted with ACN. The extracts were analyzed by HPLC with fluorescence detection as described in detail by Zhang et al. (2000). Standards of DNSH-carbonyl derivatives were prepared *in situ* by spiking a known amount of carbonyl compounds into DNSH-coated C₁₈ cartridges. The spiked cartridges were treated and extracted in an identical manner as the samples and served as external standards for identification and quantification of the carbonyl compounds.

PM_{2.5} Mass Teflon filters (samples and field blanks) were weighed on a Cahn C-30 (Cahn Instruments Inc., Cerritos, CA, USA) or a Mettler MT5 (Mettler Toledo Inc., Columbus, OH, USA) microbalance in the EPA-audited laboratory at EOHSI, following EPA protocols (USEPA, 1994). Each filter was equilibrated before and after sampling for at least 24 h at 30–40% relative humidity (RH) and 20–23°C, and weighed twice under those conditions. Conditions for postcollection analysis were within 5% RH and 2°C of those for precollection analysis. Pre- and post-collection analyses were conducted by the same operator on the same balance, with few exceptions. The balance was calibrated daily prior to filter weighing with a 200 ± 0.025 mg primary mass standard traceable to NIST mass standards, and an independent standard (50 mg) was analyzed after every 10 filters. At least one laboratory blank was also weighed daily.

Results

Number of Samples Collected

The number of homes that had first and second visits, along with the number of valid indoor, outdoor, in-vehicle and personal samples collected and analyzed for each type of measurement are provided in Table 2. In NJ, TX and CA a second set of samples were obtained from 84%, 89% and 77% of the homes, respectively. Reasons for refusal of a second visit included, in decreasing order of importance, loss of interest/burden too large, moved, and illness. Actively pumped PM_{2.5} and carbonyl samples were considered valid if the flow rate changed less than 15% during sampling, and collection times were greater than 42 h (87.5% of the target duration). Valid active samples comprised approximately 82%, 83% and 91% of those collected in NJ, TX and CA, respectively.

Quality Control Measures Load minimum detection limits (MDLs) (i.e., µg per sample) for the passive samplers were calculated as the mean blank plus the standard deviation of the blanks mass distribution multiplied by the Student's *t*-value for $\alpha = 0.01$ at $n - 1$ degrees of freedom, where n is the number of blanks used in the calculation, typically 7 or more. For compounds with no background present in the samplers, the MDLs were estimated applying the same approach to the distribution of at least seven replicates of the lowest concentration standard. Field blank distributions were used for mean blank corrections for calculating air concentrations. If there was a batch-to-batch variation in blank concentrations, batch means were used, otherwise the overall means from the entire study were used for blank subtraction or MDL estimation. MDLs for PM_{2.5} were also estimated based on the distribution of blanks, as the mean plus 3 standard deviations from the mean. The air concentration MDLs were calculated using the estimated load MDLs and nominal sample duration of 48 h and the target flow for active samples or the diffusive sampling rate at 25°C for passive samples. The detection limits for VOCs and carbonyls are presented in Table 3. The detection limits for PM_{2.5} were 0.55 µg/m³ for indoor and outdoor samples and 1.4 µg/m³ for personal samples.

The ability to measure air exchange rate is limited by the amount of PMCH on the CATs. The higher the air exchange rate, the lower the collected PMCH. Therefore, the lower detectable limit for PMCH measurement determines the maximum measurable air exchange rate for a given residence and sampling protocol. A total of 158 blank samples were analyzed to estimate the minimum detectable PFT (or the maximum determinable air exchange rate). The distributions of the blank CATs for the three cities were tested by ANOVA and no differences were found in mean value of blanks among the cities. Accordingly, blank values were pooled and a mean blank value of 0.54 pl was subtracted

Table 2. Number of home visits and samples collect by city and sample type.^a

Variable	City	Visits (1st 2nd)	Indoor (1st 2nd)	Outdoor (1st 2nd)	Personal (1st 2nd)	In-vehicle (1st 2nd)					
Homes	Elizabeth	100	84	NA	NA	NA					
	Houston	105	93	NA	NA	NA					
	Los Angeles	105	81	NA	NA	NA					
Participants	Elizabeth	120	93	NA	NA	NA					
	Houston	165	169	NA	NA	NA					
	Los Angeles	119	89	NA	NA	NA					
<i>Main measurements</i>											
Ventilation	Elizabeth	94	81	NA	NA	NA					
	Houston	86	67	NA	NA	NA					
	Los Angeles	101	78	NA	NA	NA					
VOC	Elizabeth	318	258	100	82	99	83	119	93	NA	
	Houston	379	352	105	93	105	94	169	165	NA	
	Los Angeles	314	242	98	76	98	77	118	89	NA	
Aldehydes	Elizabeth	305	256	88	79	90	80	120	93	7	4
	Houston	309	307	75	79	75	78	129	147	30	3
	Los Angeles	309	307	92	78	92	71	119	83	40	22
PM _{2.5}	Elizabeth	180	140	57	46	61	48	62	46	NA	
	Houston	200	172	69	58	58	59	73	55	NA	
	Los Angeles	210	151	72	55	71	52	67	44	NA	

^aThe number of samples does not include either collocated/duplicate samples or field blanks. Number of valid measurements collected in each city. "Homes" and "Participants" indicate number of homes or participants sampled (first visit), and the number of homes or participants sampled twice (second visit) for at least some air toxics. For each class of air toxics the total number of measurements (sum of indoor, outdoor, personal, and in-vehicle) during all first visits and during all second visits are provided, as well as the number collected broken down by type of sample. NA — not applicable.

from all sample CATs. The maximum AER resulting from the LOD for the samplers. The LOD was determined as 3 × SD, resulting in 4.67 pl. Depending on the house volume and sampling conditions, this translates approximately to a maximum measurable air exchange of 5 ACH.

Analytical precision was calculated as a pooled coefficient of variation of replicate sample analyses, and measurement precision is expressed as a pooled coefficient of variation of collocated (duplicate) sample concentrations. The pooled coefficient of variation is given by the pooled standard deviation (σ_{pooled}) divided by the mean value of the pairs. For the general case:

$$\sigma_{\text{pooled}} = \left[\frac{\sum (n_i - 1) \sigma_i^2}{\sum (n_i - 1)} \right]^{1/2}$$

and for paired data:

$$\sigma_{\text{pooled}} = \left[\frac{\sum d_i^2}{2n} \right]^{1/2}$$

where σ_i is the standard deviation of replicate set i , d is the difference between paired i values, n_i is the number of data points used to calculate σ_i and n is the number of pairs. The overall measurement precision by sample type is given in Table 4. To assess whether there were losses of any compounds while the samples were collected, field positive control results were calculated from the analysis of samples spiked with a known quantity of target species and placed with field samples for the designated sampling duration (48 h

nominal; VOCs and carbonyl compounds only). The results are expressed as the percentage difference between measured and actual (spiked) species mass (Table 5). Recovery rate expressed as the ratio of the measured concentration to the concentration generated in a test chamber or the ratio of the measured quantity to the quantity spiked on the sample (Table 6). The recovery rate determined using the gas chamber reflects recovery for the collection and the extraction process (carbonyls), whereas the recovery rate using the spiked method reflects recovery only for the extraction process (VOCs)

Interlaboratory Comparisons

To evaluate the consistency between the analytical laboratories (EOHSI and UTSPH), extracts of both VOCs and carbonyls of samples, blanks, and standards were exchanged for independent analyses at both labs. The concentration data from UTSPH were regressed against the concentration data from EOHSI (the nondetectable values were excluded) since the two laboratories had different detection limits.

VOCs A laboratory intercomparison for VOC analyses was made by exchanging extracts from OVM samples and spikes between the laboratory at EOHSI and the laboratory at UTSPH (Table 7). The laboratories had slightly different MDLs (Table 3). Results from a regression fit of the paired

Table 3. Detection limits ($\mu\text{g}/\text{m}^3$) expressed as a nominal 48-h sample.

VOCs	EOHSI		UTSPH	
1,3-Butadiene	3.1		4.02	
Methylene chloride	2.1		0.29	
Methyl <i>tert</i> butyl ether	0.68		0.38	
Chloroprene	0.51		0.51	
Chloroform	0.42		0.28	
Carbon tetrachloride	0.27		0.34	
Benzene	1.1		0.54	
Trichloroethylene	0.44		0.24	
Toluene	6.7		7.12	
Tetrachloroethylene	0.42		0.22	
Ethyl benzene	0.74		0.22	
<i>m,p</i> -Xylene	1.4		0.65	
<i>o</i> -Xylene	0.85		0.29	
Styrene	0.84		0.34	
α -Pinene	2.04		0.28	
β -Pinene	1.01		2.09	
D-Limonene	1.27		0.74	
1,4-Dichlorobenzene	0.91		0.43	
Carbonyls	In/out	Personal	In-vehicle	In/out/ personal passive
Formaldehyde	0.96	1.75	4.65	0.10 & 0.28 ^a
Acetaldehyde	0.75	1.37	3.63	0.74
Acetone	2.75	5.04	13.38	0.40
Acrolein	0.57	1.04	2.76	0.14
Propionaldehyde	0.52	0.95	2.53	0.05
Crotonaldehyde	0.51	0.93	2.48	0.13
Benzaldehyde	1.03	1.88	4.99	0.24
Hexaldehyde	0.90	1.65	4.39	0.06
Glyoxal	0.53	0.96	2.56	0.09
Methylglyoxal	0.59	1.09	2.88	0.20

Detection limits calculated as three times the standard deviation of the field blank, or when the species are absent in field blanks, a low concentration calibration standard was used to determine the detection limits. The estimated air concentration detection limit ($\mu\text{g}/\text{m}^3$) uses a nominal 48-h sampling period.

^aBlank values changed due to new procedure to two different detection limits exist for formaldehyde.

data, excluding pairs where both values were below the detection limit, are presented in Table 7. The slopes of all but three of the regressions for VOCs were between 0.8 and 1.2 with an $R^2 > 0.95$, indicating biases of $< 20\%$ (since the values of the intercepts are small) and a high correlation between the results from the two laboratories. The exceptions were methylene chloride, styrene and toluene. Inconsistent blank contributions were observed for methylene chloride at EOHSI, which may have resulted from contamination of some extracts during analysis at EOHSI. It is not clear why styrene values had a bias of a factor of two, thus these values need to be reviewed carefully before used. Toluene had a lower than optimal correlation, but slope was in the acceptable range, suggesting no bias but a lower overall agreement between the two laboratories than for the other compounds.

Carbonyl Compounds The samples collected in NJ, CA, and TX using the DNPH active method were extracted at EOHSI, UCLA, and UTSPH-Houston. The slopes of the regression lines were all between 0.9 and 1.2, except for glyoxal and methylglyoxal. The R^2 values were > 0.95 , except for acetone (0.90). All intercepts were small. See Table 7. An inter-laboratory comparison with Daniel Grosjean and Associates (DGA, Inc., Ventura, CA, USA) of the analysis of DNPH-carbonyl derivatives was also conducted. In this effort, 12 extracts (three field blanks, two indoor samples, two outdoor samples, two in-vehicle samples, and three personal samples) were prepared by the EOHSI lab and aliquots were analyzed by both laboratories. The DGA laboratory used an HPLC-MS method, whereas the EOHSI laboratory used an HPLC-UV analysis. Regression analysis results for the compounds for which both laboratories reported detectable concentrations in the same extract are also shown in Table 7. The slopes and R^2 for formaldehyde, acetaldehyde, acetone, propionaldehyde, butyraldehyde, and benzaldehyde were within 15% and > 0.85 , respectively, and considering the small intercepts, indicative of agreement in the results. Except for crotonaldehyde, the R^2 for the other measured carbonyl compounds are greater than 0.7, but the slopes of the regression lines deviated significantly from unity, suggesting a potential bias between the two laboratories. The reason for the discrepancies is not known at this time.

Discussion

VOCs

Detection limits at sub- $\mu\text{g}/\text{m}^3$ concentrations were achieved for most compounds, except methylene chloride ($2.1 \mu\text{g}/\text{m}^3$ EOHSI) and toluene ($6\text{--}7 \mu\text{g}/\text{m}^3$), which had relatively high and variable blank concentrations, due to contributions from either the solvent or the charcoal in the OVM pad.

Comparison of field and laboratory blanks showed small, if any, differences for the majority of the VOCs, indicating that minimal contamination occurred during collection and shipment of samples. The extraction efficiencies determined by both laboratories were similar to those reported by the manufacturer for higher VOC concentrations and generally exceeded 90%. Styrene had an extraction efficiency closer to 70% which may reflect losses due to chemical reactions across its double bond once adsorbed onto the badge charcoal pads. Consistent with this observation, large losses of 1,3 butadiene and chloroprene, highly reactive unsaturated compounds, have been found during the storage of OVMs spiked at environmentally relevant levels (Stock et al., 2002).

The overall measurement precision for VOCs was similar for the three types of samples collected — outdoor, indoor and personal — with most compounds having a precision of 10–20%, based on collocated sample analysis. Some

Table 4. Species measurement precision.^a

	Active (N)	All data combined passive (N)	Indoor passive (N)	Outdoor passive (N)	Personal passive (N)
Air exchange rate		16			
PM _{2.5}	17.0 (35)				
Formaldehyde	8.0 (11)	18.7 (108)	12.4 (41)	20.5 (41)	21.9 (26)
Acetaldehyde	13.5 (11)	30.2 (108)	32.5 (41)	22.5 (41)	15.7 (26)
Acetone	17.9 (10)	22.2 (105)	16.6 (40)	31.5 (39)	20.0 (26)
Acrolein	13.8 (5)	29.1 (86)	29.0 (31)	30.8 (33)	26.7 (22)
Propionaldehyde	19.1 (11)	26.8 (108)	27.8 (41)	26.9 (41)	24.1 (26)
Crotonaldehyde	14.8 (7)	26.4 (92)	22.0 (37)	34.5 (32)	22.4 (23)
Benzaldehyde	9.7 (11)	20.1 (108)	21.4 (41)	19.3 (41)	17.3 (26)
Hexaldehyde	14.0 (10)	21.4 (108)	23.4 (41)	17.7 (41)	17.4 (26)
Glyoxal	43.0 (11)	18.6 (104)	17.3 (39)	21.4 (41)	17.4 (24)
Methylglyoxal	10.1 (10)	18.8 (97)	13.5 (37)	23.8 (38)	21.1 (22)
1,3-Butadiene		ND ^b	ND ^b	ND ^b	ND ^b
Methylene chloride		7.9 (171)	4.9 (62)	15 (67)	12 (42)
Methyl <i>tert</i> butyl ether		10 (171)	7.9 (62)	7.8 (67)	13 (42)
Chloroprene		ND ^b	ND ^b	ND ^b	ND ^b
Chloroform		16 (171)	11 (62)	22 (67)	20 (42)
Carbon tetrachloride		9.4 (171)	13 (62)	7.9 (67)	8.0 (42)
Benzene		11 (171)	11 (62)	8.7 (67)	13 (42)
Trichloroethylene		42 (171)	32 (62)	22 (67)	22 (42)
Toluene		17 (171)	12 (62)	21 (67)	18 (42)
Tetrachloroethylene		13 (171)	18 (62)	11 (67)	11 (42)
Ethyl benzene		11 (171)	10 (62)	17 (67)	9.4 (42)
<i>m,p</i> -Xylene		10 (171)	9.4 (62)	11 (67)	9.1 (42)
<i>o</i> -Xylene		11 (171)	11 (62)	15 (67)	10 (42)
Styrene		15 (171)	11 (62)	15 (67)	16 (42)
α -Pinene		42 (171)	44 (62)	32 (67)	35 (42)
β -Pinene		15 (171)	21 (62)	30 (67)	9.2 (42)
D-Limonene		7.9 (171)	7.4 (62)	17 (67)	8.0 (42)
1,3-Dichlorobenzene		5.7 (171)	3.6 (62)	19 (67)	34 (42)

^aMeasurement precision, expressed as the pooled coefficient of variation of *N* pairs of collocated measurements (%)

^bND more than 90% the values are below detection, so CV not determined.

individual compounds had poorer precision, for some sample types. Compounds present at concentrations close to the MDL would tend to produce high percent deviations even though the absolute error was small. A high coefficient of variation was also calculated for α -pinene and trichloroethylene, compounds with a wide range of concentrations and a large proportion of very low concentrations. Lower variability was observed if extreme concentrations were excluded. The lower precision for toluene and methylene chloride is probably a function of higher and more variable blank contributions from charcoal pad background or from the extract solvent compared to the other compounds. The instrumental analysis precision (data not shown) was better than 20% for all compounds except methylene chloride, which had variable solvent blank values. These quality assurance measures suggest that sub- $\mu\text{g}/\text{m}^3$ concentrations of VOCs can be measured and concentration differences of approximately 20% can be identified except for trichloroethylene and α -pinene, which have measurement precision closer to 30–40%.

Carbonyl Compounds

The distribution of all the field blanks indicates that either most carbonyl compounds were not detected in the blanks or had small batch-to-batch differences in DNPH or DNSH cartridge background concentrations. Therefore, the specific compound overall mean from all the blank cartridges was used to determine the MDLs and to perform blank correction for the samples. One exception was the formaldehyde blank concentrations in the DNSH cartridges which were lower later in the study than during the first 1/3 of the study. This decrease in formaldehyde blank values is explained by initially using a commercially available high purity DNSH reagent (>97% purity) directly to prepare the coating solution, while in the latter part of the study the DNSH reagent was recrystallized in HPLC grade ethanol/ACN prior to use. No significant batch-to-batch differences in DNSH field blanks for formaldehyde were found within each preparation method. Therefore, two overall DNSH blank concentration means (and thus two estimates of MDLs) for formaldehyde were determined (see Table 3).

Table 5. Field positive controls.^a

	DNPH-active (<i>N</i> = 5)	DNSH-passive (<i>N</i> = 17)
Formaldehyde	9.8	11.5
Acetaldehyde	21.4	34.2
Acetone	7.4	31.8
Acrolein	100.0	43.2
Propanal	2.6	10.6
Crotonaldehyde	77.2	29.2
Benzaldehyde		15.3
Hexaldehyde		14.3
Glyoxal	60.5	13.0
Methylglyoxal	35.8	23.9
	OVM3500 Badges (<i>N</i> = 12)	
1,3-Butadiene		33
Methylene chloride		89
Methyl <i>tert</i> butyl ether		127
Chloroprene		104
Chloroform		79
Carbon tetrachloride		104
Benzene		104
Trichloroethylene		79
Toluene		91
Tetrachloroethylene		71
Ethyl benzene		85
<i>m,p</i> -Xylene		82
<i>o</i> -Xylene		85
Styrene		79
1,4-Dichlorobenzene		68

^aField positive controls expressed as the % difference between measured and spiked mass, average from *N* controls.

For the DNPH active method, the measurement precision was generally comparable to the analytical precision, indicating that the deployment of DNPH cartridges to the field (processes including sample handling, transport, storage) and extraction of the cartridges did not cause significant amount of additional error. In contrast, the DNSH passive method had higher measurement uncertainty than analytical uncertainty, mainly because of increasing baseline concentrations in cartridge extracts. This suggests that the field deployment process had a relatively stronger impact on the passive samplers than the active samplers.

The positive control results for active carbonyl sampling indicate a large difference between the measured and spiked amounts for acrolein and crotonaldehyde. This is consistent with stability test results showing that acrolein and crotonaldehyde disappeared rapidly on DNPH cartridges/extracts. Because all the samples were collected during a 48-h (nominal) period and several hours passed before the sampled cartridges were extracted in a laboratory, acrolein and crotonaldehyde might have been lost partially or completely lost during sample transportation and even during sample collection. Hence, the concentrations of acrolein and crotonaldehyde measured using the DNPH active method

Table 6. Species recoveries (%).

	Active % (<i>N</i>)	Passive % (<i>N</i>)
Air exchange rate		90–100
Formaldehyde ^a	81.4 (6)	101.1 (6)
Acetaldehyde ^a	95.8 (6)	87.2 (6)
Acetone ^a	109.1 (6)	80.3 (6)
Acrolein ^a	20.0 (6)	60.3 (6)
Propionaldehyde ^a	85.4 (6)	107.5 (6)
Crotonaldehyde ^a	38.6 (6)	76.3 (6)
Benzaldehyde ^a	95.2 (6)	98.3 (6)
Glyoxal ^b	87.0 (6)	90.0 (6)
Methylglyoxal ^b	93.0 (6)	95.0 (6)
Hexaldehyde ^a	85.9 (6)	94.2 (6)
		EOHSI^b UTSPH^b
1,3-Butadiene		74 79
Methylene chloride		120 90
Methyl <i>tert</i> butyl ether		83 99
Chloroprene		96 70
Chloroform		95 100
Carbon tetrachloride		130 96
Benzene		71 95
Trichloroethylene		87 97
Toluene		110 98
Tetrachloroethylene		98 91
Ethyl benzene		90 97
<i>m,p</i> Xylene		87 82
<i>o</i> Xylene		83 84
Styrene		71 60
α -Pinene		100
β -Pinene		100
D-Limonene		100
1,4-Dichlorobenzene		110 75

Species recoveries (%) expressed as the ratio of measured concentration or mass to gas concentration or spiked mass.

^aThe recovery rate was determined using the gas concentration in a gas chamber, and therefore, represents the recovery for sample collection and extraction.

^bThe recovery rate was determined by liquid spike onto the sampling media, and therefore, it only represents the recovery for sample extraction.

are suspect. Problems were also identified for a fraction of the samples in accurately quantifying the DNPH-derived hexaldehyde hydrazone.

The MDLs for carbonyls collected using DNSH are generally five to ten times lower than observed from DNPH ranging between 0.05 and 0.74 $\mu\text{g}/\text{m}^3$. The instrumental analytical uncertainties are mostly below $\pm 10\%$, and the overall measurement precision varied between 12% and 30% across the different compounds and sample types. A similar magnitude percent deviation from unity slope in the comparison between laboratories was observed. These quality assurance measures suggest that sub- $\mu\text{g}/\text{m}^3$ concentrations of carbonyls can be measured in outdoor, indoor and personal air, and that concentration differences of approximately 20% can be identified.

Table 7. Inter-laboratory comparisons for analysis of VOCs and carbonyls.

UTSPH vs. EOHSI	Slope	Standard Error of Slope	Intercept	Standard Error of Intercept	R ²
VOCs (n = 26)					
Methylene chloride	0.62	0.07	1.1	0.37	0.77
MTBE	1.08	0.04	0.009	0.041	0.96
Chloroform	1.39	0.08	0.006	0.056	0.92
Carbon tetrachloride	1.16	0.01	0.040	0.007	0.99
Benzene	1.16	0.06	0.092	0.054	0.95
Trichloroethene	1.14	0.02	0.013	0.017	0.99
Toluene	1.12	0.11	0.19	0.28	0.81
Tetrachloroethene	1.16	0.04	0.072	0.037	0.97
Ethyl benzene	0.829	0.026	0.15	0.03	0.98
<i>m,p</i> -Xylene	0.985	0.039	0.18	0.09	0.96
<i>o</i> -Xylene	0.942	0.028	0.11	0.02	0.99
Styrene	2.28	0.03	0.084	0.014	0.99
1,4-Dichlorobenzene	1.06	0.05	0.11	0.05	0.95
Carbonyls UTSPH vs. EOHSI					
Formaldehyde (n = 21)	1.17	0.06	0.051	0.032	0.951
Acetaldehyde (n = 19)	1.12	0.05	0.028	0.019	0.969
Acetone (n = 19)	1.08	0.09	0.068	0.037	0.900
Acrolein (n = 5)	0.99	0.03	0.029	0.020	0.997
Propionaldehyde (n = 5)	0.96	0.02	0.033	0.011	0.999
Crotonaldehyde (n = 3)	1.03	0.02	0.020	0.013	0.999
Butyraldehyde (n = 4)	1.00	0.05	0.036	0.039	0.994
Benzaldehyde (n = 5)	1.02	0.05	0.057	0.033	0.992
Valeraldehyde (n = 5)	0.909	0.03	0.13	0.02	0.996
Glyoxal (n = 5)	2.08	0.03	-0.012	0.024	0.999
Methylglyoxal (n = 4)	2.36	0.10	-0.009	0.070	0.996
Hexaldehyde (n = 4)	1.02	0.03	0.14	0.02	0.998
DGA vs. EOHSI					
Formaldehyde (n = 12)	1.05	0.01	-0.008	0.020	0.998
Acetaldehyde (n = 12)	0.982	0.054	0.013	0.046	0.970
Acetone (n = 12)	1.06	0.02	-0.009	0.012	0.995
Propionaldehyde (n = 11)	0.862	0.034	0.003	0.006	0.986
Crotonaldehyde (n = 7)	0.612	0.359	0.002	0.005	0.368
Butyraldehyde (n = 10)	0.943	0.034	0.006	0.004	0.990
Benzaldehyde (n = 11)	0.969	0.134	-0.017	0.041	0.853
Isovaleraldehyde (n = 9)	0.318	0.076	0.009	0.006	0.717
Valeraldehyde (n = 10)	0.712	0.040	-0.008	0.009	0.976
Glyoxal (n = 10)	0.558	0.074	-0.016	0.006	0.875
Methylglyoxal (n = 10)	0.408	0.077	0.008	0.009	0.777
Hexaldehyde (n = 10)	0.675	0.124	0.072	0.086	0.786

The percent of samples that had detected levels for each sample type and VOC or aldehyde is given in Table 8. More than 80% of the samples of each type had detectable levels of 14 compounds. As found in other studies, outdoor air samples had more nondetectable values than did indoor or personal samples. This is expected since outdoor concentrations are lower and is consistent with outdoor air providing a background for many of these compounds from ambient sources to which indoor emissions and personal activities add. Only acrolein, crotonaldehyde, methylene chloride and trichloroethylene were detected in less than 80% of the personal air samples. Styrene was the additional compound detected in less than 80% of the indoor air samples. In the

outdoor air samples, acetone, methyl glyoxal, hexaldehyde, chloroform, β -pinene, D-limonene and 1,4-dichlorobenzene were detectable in less than 80% of the samples.

PM_{2.5} Mass

Field blank weights were not significantly different before and after transport to the field based on paired *t*-tests ($\alpha=0.05$, $n=452$, $P=0.24$). Therefore, no blank subtraction was performed for PM_{2.5} mass measurements. PM_{2.5} mass measurements are dominated by uncertainties introduced by sample handling, transport, storage, and sampling methods rather than by analytical uncertainties as evidenced by extremely small estimates of analytical accuracy and

Table 8. Percent of samples that were above the detection limit stratified by compound and sample type for all sites combined.

	Outdoor % detected	Indoor % detected	Personal % detected
PM _{2.5}	100	100	100
<i>Carbonyls (whole data)</i>			
Formaldehyde	96	99	99
Acetaldehyde	96	97	99
Acetone	76	80	92
Acrolein	58	62	70
Propionaldehyde	81	91	97
Crotonaldehyde	51	62	64
Benzaldehyde	82	87	93
Glyoxal	81	99	100
Methylglyoxal	77	87	88
Hexaldehyde	72	87	90
<i>Carbonyls (partial data)</i>			
Butyraldehyde	65	77	75
Isovaleraldehyde	33	71	60
Valeraldehyde	68	86	79
<i>o</i> -Tolualdehyde	5.7	6.8	11
<i>m, p</i> -Tolualdehyde	3.3	6.8	6.2
2,5 Dimethylbenzaldehyde	17	14	18
<i>VOCs</i>			
Methylene chloride	54	65	68
Methyl <i>tert</i> butyl ether	97	97	98
Chloroform	56	87	93
Carbon tetrachloride	96	85	96
Benzene	99	99	99
Trichloroethylene	67	67	75
Toluene	88	97	98
Tetrachloroethylene	92	97	97
Ethyl benzene	96	97	97
<i>m, p</i> -Xylene	97	99	99
<i>o</i> -Xylene	98	99	99
Styrene	48	77	85
α -Pinene	83	97	97
β -Pinene	25	81	87
D-Limonene	58	90	92
1,4-Dichlorobenzene	76	94	96

precision (i.e. better than 1%). The measurement precision of indoor and outdoor PM_{2.5} concentrations was 17% based on analysis of 35 pairs of collocated Harvard samples inside and outside of study residences. Collocated PEM and Harvard mass measurements were highly correlated ($R^2 = 98\%$; 92% without highest concentration pair). However, mass concentrations measured with the PEMs were significantly greater ($P < 0.5$) than those measured with the Harvard samplers according to a *t*-test on the log-transformed data. The linear least-squares regression of PEM mass measurements on collocated Harvard Impactor (HI) measurements is given by

$$[\text{PEM}] = 0.92[\text{HI}] + 4.33$$

and without the highest concentration pair:

$$[\text{PEM}] = 1.15[\text{HI}] + 1.51$$

A single laboratory weighed all the samples, so complete compatibility should exist across the sampling sites. Differences of less than 20% should be determinable between samples of the same type or between indoor and outdoor samples, since both used the Harvard Impactor Sampler. The apparent bias between the Harvard Impactor and PEM samplers will result in only larger difference between personal samples and either indoor or outdoor samples being statistically significant.

Detectable Concentrations

The percent of samples that had detected levels for each sample type and compound is given in Table 8. More than 80% of the samples of each type had detectable levels of 14 compounds. As found in other studies, outdoor air samples had more nondetectable values than did indoor samples, than did personal samples. This is consistent with outdoor air providing the background sources for these compounds to which indoor and personal emissions then contribute additional concentrations. Only acrolein, crotonaldehyde, methylene chloride and trichloroethylene were detected in less than 80% of the personal air samples. Styrene was the only additional compound detected in less than 80% of the indoor air samples. In the outdoor air samples, acetone, methyl glyoxal, hexaldehyde, chloroform, β -pinene, D-limonene and 1,4-dichlorobenzene were additional compounds detectable in less than 80% of the samples.

Questionnaire Response

Questionnaire responses were obtained to characterize the house, surrounding area and activities of the participants in general and specifically for each sampling period. All questionnaire data were entered into an ACCESS database designed with entry cells to only accept entries that were of the correct format, numeric or text, and to be within predetermined acceptable ranges. An individual different from the original data entry person visually verified each entry for accuracy of transcription. During the external audit, the error rate for entry was found to be $< 0.3\%$, based on a random check of several hundreds of entries. The database was run through internal checks within ACCESS to identify any duplicate entries and missing data, with any error identified fixed.

Conclusions

The RIOPA study successfully collected and analyzed air toxic concentrations along with information on air exchange rates, personal and household activities, and other questionnaire responses for 310 homes, equally divided among

three distinct cities in different regions of the US; 280 homes were sampled a second time approximately three months after the first visit. The homes were selected with an emphasis on homes closer to ambient emission sources. The measured air toxics included VOCs, carbonyl compounds; PM_{2.5} concentrations were monitored in approximately 1/2 of the homes. The carbonyl data represent the most comprehensive collection of concentrations of these compounds to date in outdoor, indoor and personal air, and inside vehicle cabins. The use of the passive sampler with DNSH provided a more accurate measurement of acrolein and lower detection limits for many carbonyls than previously reported. The collection of data occurred throughout the year in each city, another unique aspect of this data set. The samples were collected in homes with a wide range of air exchange rates so that the data can be used for development and evaluation of exposure models. Overall measurement precision for most compounds was better than 20% and no or small biases were identified for most compounds in the measurements made between the two laboratories participating the study so comparisons between cities and personal, indoor and outdoor measurements can be reliably made. The range of distributions measurements for the VOCs, carbonyls, PM_{2.5}, and air exchange rates, are consistent with values reported previously in the literature. Thus, extrapolation of the associations or models based on the RIOPA data set that may link the influence of ambient sources with indoor air should be relevant to general urban settings.

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