



An assessment of the data quality for NHEXAS-Part I: exposure to metals and volatile organic chemicals in Region 5

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A National Human Exposure Assessment Survey (NHEXAS) was performed in U.S. Environmental Protection Agency (U.S. EPA) Region V, providing population-based exposure distribution data for metals and volatile organic chemicals (VOCs) in personal, indoor, and outdoor air, drinking water, beverages, food, dust, soil, blood, and urine. One of the principal objectives of NHEXAS was the testing of protocols for acquiring multimedia exposure measurements and developing databases for use in exposure models and assessments. Analysis of the data quality is one element in assessing the performance of the collection and analysis protocols used in NHEXAS. In addition, investigators must have data quality information available to guide their analyses of the study data. At the beginning of the program quality assurance (QA) goals were established for precision, accuracy, and method quantification limits. The assessment of data quality was complicated. First, quality control (QC) data were not available for all analytes and media sampled, because some of the QC data, e.g., precision of duplicate sample analysis, could be derived only if the analyte was present in the media sampled in at least four pairs of sample duplicates. Furthermore, several laboratories were responsible for the analysis of the collected samples. Each laboratory provided QC data according to their protocols and standard operating procedures (SOPs). Detection limits were established for each analyte in each sample type. The calculation of the method detection limits (MDLs) was different for each analytical method. The analytical methods for metals had adequate sensitivity for arsenic, lead, and cadmium in most media but not for chromium. The QA goals for arsenic and lead were met for all media except arsenic in dust and lead in air. The analytical methods for VOCs in air, water, and blood were sufficiently sensitive and met the QA goals, with very few exceptions. Accuracy was assessed as recovery from field controls. The results were excellent ($\geq 98\%$) for metals in drinking water and acceptable ($\geq 75\%$) for all VOCs except *o*-xylene in air. The recovery of VOCs from drinking water was lower, with all analytes except toluene (98%) in the 60–85% recovery range. The recovery of VOCs from drinking water also decreased when comparing holding times of < 8 and > 8 days. Assessment of the precision of sample collection and analysis was based on the percent relative standard deviation (% RSD) between the results for duplicate samples. In general, the number of duplicate samples (i.e., sample pairs) with measurable data were too few to assess the precision for cadmium and chromium in the various media. For arsenic and lead, the precision was excellent for indoor, and outdoor air ($< 10\%$ RSD) and, although not meeting QA goals, it was acceptable for arsenic in urine and lead in blood, but showed much higher variability in dust. There were no data available for metals in water and food to assess the precision of collection and analysis. *Journal of Exposure Analysis and Environmental Epidemiology* (2001) 11, 140–154.

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1. Abbreviations: AAS, atomic absorption spectroscopy; GC-MS, gas chromatography–mass spectrometry; GFAAS, graphite furnace atomic absorption spectroscopy; HGAFS, hydride generation atomic fluorescence spectroscopy; ICP-MS, inductively coupled plasma–mass spectrometry; IOM, Institute of Occupational Medicine; LWW, Lioy–Wainman–Weisel sampler; MDL, method detection limit; NHEXAS, National Human Exposure Assessment Survey; NIST, National Institute of Science and Technology; NOPES, Nonoccupational Pesticide Exposure Study; PFT, perfluorotoluene; PM_{2.5}, particulate matter with a cut point of 2.5 μm aerodynamic diameter; PM₁₀, particulate matter with a cut point of 10 μm aerodynamic diameter; QA, quality assurance; QC, quality control; QL, quantification limit; QSIP, Quality Systems Implementation Plan; SOPs, standard operating procedures; RSD, relative standard deviation; TEAM, Total Exposure Assessment Methodology; U.S. EPA, United States Environmental Protection Agency; VOCs, volatile organic chemicals; WWT, Wet Wipe towelette.

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Introduction

The National Human Exposure Assessment Survey (NHEXAS) Region V study is a scoping study, the first of its nature conducted on a regional scale, that assembled a cadre of protocols for making comprehensive population exposure estimates (Pellizzari et al., 1995). This NHEXAS built on the past experiences of studies such as the Total Exposure Assessment Methodology (TEAM) and Non-occupational Pesticide Exposure Study (NOPES). TEAM (Hartwell et al., 1987; Wallace et al., 1987) and NOPES (Whitmore et al., 1994) provided the basis for much of the statistically based population survey and analytical methodology employed in NHEXAS Region V. TEAM and NOPES focused on only a few pathways leading to inhalation and ingestion of pollutants, and on a single chemical class.

People are exposed to chemicals from a variety of sources that contaminate air, water, and food involving a variety of pathways and media. Exposure to a pollutant is potentially a complex process as it can occur from contact with several environmental media (e.g., air, water, dust), *via* several pathways (e.g., surface-to-hand-to-mouth transfers), and through several routes (i.e., inhalation, oral, dermal). To conduct aggregate exposure assessments, measurements must be made at key points in the exposure process. In addition, an individual's exposure can be to multiple pollutants through the above processes. This is the basis for estimating cumulative risks from exposures to chemicals with common endpoints and mechanisms of toxicity. The NHEXAS studies were conceptually designed with the above processes in mind (Buck et al., 1995; Callahan et al., 1995; Lebowitz et al., 1995; Lioy and Pellizzari, 1995; Pellizzari et al., 1995; Sexton et al., 1995).

The principal objectives of the NHEXAS scoping studies have been previously discussed (Sexton et al., 1995). Among these objectives was the testing of protocols for acquiring population distributions of exposure measurements and developing databases for use in exposure models and assessments. An analysis of the data quality would also lend itself to an assessment of performance for the collection and analysis protocols used in this study. As the NHEXAS Region V database becomes available to the scientific public further analyses will be performed by secondary investigators. For this reason, it is important that the quality of the NHEXAS Region V data be described to assist and guide investigators in their data analysis efforts.

Several laboratories were responsible for the analysis of samples for metals and volatile organic chemicals (VOCs) collected by a single organization. Quality control (QC) data were provided and included in the database. The precision and bias of these data are the subject of this paper.

Methods

A brief description is presented of the study design and analytical procedures that were used for metals and VOC analysis in the NHEXAS Region V Study. The data quality assessment pertains to the use of these methods. Details for each of the methods may be found in the NHEXAS Quality Systems and Implementation Plan (QSIP)¹ that was prepared before implementing the field study. Included in the QSIP were quality assurance (QA) goals for the sample collection and the analysis that were established at the beginning of the study. These are given in Table 1. The

¹The QSIP document contains a full description of the analytical protocols and quality control and assurance procedures employed. It is available from the U.S. EPA, NERL (HERB), P.O. Box 93478, Las Vegas, NV 89193.

Table 1. NHEXAS Region V QA goals for sample collection and analysis.

Matrix	Contaminant	Precision (% RSD)	Bias (%)	MDL or QL ^a
Air	Metals (P, I, O) ^b	<10	<20	<1 ng/m ³ (As), 10 ng/m ³ (Pb)
	VOCs (P, I, O)	<25	<25	1.0 µg/m ³ (benzene)
	Particles	<25	<25	~25 µg/m ³
Water	Metals	<10	<15	0.2 µg/l (As), 1 µg/l (Pb)
	VOCs	<25	<25	0.05 µg/l (benzene)
Food and Beverages	Metals	<20	<20	5 ng/g (As), 5 ng/g (Pb)
Dust/ Soils	Metals	<20	<20	1 µg/g (As), 1 µg/g (Pb)
Blood	Metals	<10	<30	6 µg/l (As), 10 µg/l (Pb)
	VOCs	<25	<25	0.03 ng/ml (benzene)
Urine	Metals	<10	<30	6 µg/l (As)

^aMDL=method detection limit, QL = quantifiable limit.

^bP=personal, I=indoor, O=outdoor.

performance of the methods was compared against these QA goals.

A single organization collected all samples, while several laboratories were responsible for analyzing the samples for metals and VOCs. These laboratories are anonymously coded and listed in Table 2. The QC data received from each laboratory were incorporated into the database. Each laboratory instituted its own QC procedures, which created an uneven quantity of QC information collected; moreover, not all QC data were provided for inclusion into the database (Table 2). Statistical analyses were conducted on available QC data.

Study Design and Data Collection

The target population for the Region 5 study consisted of all noninstitutionalized persons residing in households in six states (Illinois, Indiana, Ohio, Michigan, Minnesota, Wisconsin) during the time of data collection (July 1995–May 1997). The sampling design utilized for the Region 5 study was a stratified, four-stage probability sampling design. Details on the study design, its rationale, and the hypotheses tested are given in Pellizzari et al. (1995). The types of samples collected and a general description of the sampling methods have been described elsewhere (Pellizzari et al., 1995; Clayton et al., 1999; Thomas et al., 1999).

Analysis of Metals in Air Particulate Matter

Sample preparation and analysis were carried out in batch sizes that were convenient to process as one group at a time by the analyst. A typical batch for the analysis of metals in

Table 2. QC data available from laboratories performing sample analyses.

Medium	Contaminant	Lab A	Lab B	Lab C	Lab D	Lab E	Lab F
Air	Metals	DL, DS ^a					
	VOCs	DL, FC, DS					
	Particles	DS					
Water	Metals			DL, FC, DS			
	VOCs				DL, DS		
Food and beverages	Metals					DL	
Dust/soils	Metals	DL, DS	DL				
Blood	Metals						DL, DS
	VOCs						DL, DS, SS
Urine	Metals						DL, DS

^aDL=detection limit, DS=duplicate sample, FC = field control, and SS=split sample.

air particulate matter included 15 samples, two method blanks, and one method control. Field blanks were also included in the batch, but they were unknown to the analyst and thus treated (and coded) as samples.

Filters laden with air particulate matter were extracted by adding 10 ml of 50% HNO₃ and shaking for 30 min. The extract was decanted into a 50-ml Teflon beaker and the extraction was repeated twice with a fresh portion of acid (total extract volume=30 ml). All three extracts were combined in the 50-ml beaker. Fifteen milliliters of the extract was pipetted into a clean 50-ml Teflon beaker and evaporated down to about 0.5 ml on a hot plate. The beaker was cooled and 12.5 ml of 50% HCl was added. The solution was warmed and filtered through Whatman filter paper into a 25-ml volumetric flask, diluted with deionized water, transferred to a clean plastic storage bottle, and stored in a refrigerator until analysis for arsenic by hydride generation atomic fluorescence (HGAF).

The remainder of the extract (15 ml) was used for lead, cadmium, and chromium analyses. It was evaporated down to about 5 ml on a hot plate and 0.25 ml of H₂O₂ was added. The solution was evaporated to about 0.5 ml and cooled to room temperature. The solution was filtered into a 5-ml volumetric flask and diluted to volume with deionized water. The final solution was transferred to a clean plastic

storage bottle and was stored in a refrigerator until analysis by graphite furnace atomic absorption spectrophotometry (GFAAS).

Calibration blank and calibration standards were analyzed by HGAF (for As) and by GFAAS (for Pb, Cd, and Cr) starting from the lowest concentration to the highest. Each solution (blank and standards) was analyzed at least in duplicate. If the relative standard deviation (RSD) was greater than 10% for any calibration standard, further aliquots of that solution were analyzed or necessary steps were taken to improve the performance of the instrument. The operating parameters for HGAF and GFAAS are given in Tables 3 and 4, respectively.

Absorbance or fluorescence was measured for each calibration standard, and a least-squares linear regression calibration curve, $y = a + bx$, was constructed for each analyte by the instrument software. The QC check standard was analyzed before the first sample, after every 10 samples, and at the end of the sample batch analyses. All QC check standards had to be within 10% of their nominal values for the data to be accepted. Samples for which the QC checks differed by more than 10% of their nominal values were re-analyzed.

Table 3. Operating parameters for HGAF.

Instrument settings	
Element	As
Source	BDHCL
Power current (mA)	Iry, 27.5; boost, 35
Sample volume (ml)	10–12
Measurement mode	Peak ht.
Reductant	1.3% NaBH ₄ in 0.1 M NaOH
Blank	25% HCl in 1% KI and 0.05% ascorbic acid
Carrier gas flow (l/min)	0.3 (Ar)

Table 4. Operating parameters for GFAAS.

Instrumental settings	Pb	Cd	Cr
Source	HCL	HCL	HCL
Power current (mA) ^a	5	4	12
Graphite tube and platform		Pyrolytically coated	
Sample size (μl)	20	20	20
Wavelength (nm)	217.0	228.8	357.9
Slit width (nm)	0.7	0.7	0.7
Matrix modifiers	Mg(NO ₃) ₂ , NH ₄ H ₂ PO ₄	Mg(NO ₃) ₂ , NH ₄ H ₂ PO ₄	Mg(NO ₃) ₂

^aManufacturer recommended, depends on the manufacturer.

The method detection limit (MDL) was defined as three times the standard deviation of the method blank. MDLs were calculated for each analyte using the following equation:

$$\text{MDL} = 3 \times \text{SD}_{\text{bl}} \quad (1)$$

where MDL = method detection limit, ng/ml or ppb; SD_{bl} = standard deviation of method blanks, ng/ml or ppb.

Analysis of Metals in Water

For inductively coupled plasma–mass spectrometry (ICP-MS) determination of metals in tap and drinking water samples, 1 ml of concentrated nitric acid was added to 100 ml of filtered, acid-preserved sample. Internal standards, scandium, yttrium, indium, terbium, and bismuth in ASTM Type I water were added, the sample mixed, and analyzed. An internal standardization procedure was used for the quantification of the elements of interest. Multielement calibration solutions were prepared in ASTM Type I water containing 1% (v/v) nitric acid.

The ICP-MS conditions used for sample analysis are given in Table 5.

Analysis of Metals in Food and Beverage Samples

The food homogenate was blended and immediately a 1- to 7-g analytical portion was weighed into a tared, clean microwave digestion vessel liner. Nine milliliters of double distilled concentrated nitric acid was added to each liner. The microwave digestion vessels were placed into the microwave and digested under programmed conditions. After cooling and releasing the pressure, the digest was transferred to a 250-ml high-density polypropylene sample bottle. The analytical solution was brought to 250 ml total volume with ASTM Type I water, and internal standards were added.

The high-resolution ICP-MS operating conditions are given in Table 6. Internal standardization was used in all

Table 5. Operating conditions for ICP-MS.

Instrument	VG PlasmaQuad Type I
Plasma forward power	1.35 kW
Coolant flow rate	13.5 l/min
Auxiliary flow rate	0.6 l/min
Nebulizer flow rate	0.78 l/min
Solution uptake rate	0.6 ml/min
Spray chamber	15°C
Detector mode	Pulse counting
Replicate integrations	3
Mass range	8–240 amu
Dwell time	320 μ s
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 min/sample

Table 6. High resolution ICP-MS operating parameters.

ICP conditions	
Incident RF power	1300 W
Reflected RF power	<10 W
Argon pressure	>80 psi
Coolant argon flow	13 l/min
Auxiliary (plasma) Ar flow	0.7 l/min
Aerosol carrier Ar flow	1.00 l/min
Sample uptake rate	0.7 ml/min

analyses to correct for instrument drift and physical interferences. The four internal standard elements (scandium, yttrium, indium and bismuth) in 2% nitric acid were added to the calibration blank, standards, and sample digest solutions.

The calibration check sample was run every sixth sample and at the end of the batch run. The MDL was established for each element by analysis of 12 laboratory reagent blanks. The MDL was calculated as follows:

$$\text{MDL} = t \times 3S \quad (2)$$

where t = Student's t value for a 99% confidence level based on 11 degrees of freedom, and S = standard deviation of the replicate analyses.

Analysis of Metals in Dust and Soil

The house dust [Lioy–Wainman–Weisel (LWW) and Wet Wipe towelette (WWT)] samples, deposition plates, dust from carpets, and soil were prepared using procedures compatible with HGAF spectroscopy (HGAFS) and ICP-MS analyses. The LWW and WWT wipe samples were dried for 24 h in a controlled humidity room, weighed, and then extracted for either As analysis by HGAF or Cr, Cd, and Pb analysis by ICP-MS. The settled dust from plates was recovered from the surface using the LWW method, thereby creating a wipe sample. Side by side samples were collected, one for As analysis and one for Cr, Cd, and Pb analysis.

Before they were prepared for analysis, soil samples were dried for 24 h in a controlled-humidity room. The carpet was vacuumed and a subsample of dust was removed for As analysis. The remaining portion of dust was extracted with a dilute acid solution in an ultrasonic bath.

The wipe, carpet, and soil samples slated for HGAFS analysis were extracted for As by placing the samples in separate 35-ml polypropylene test tubes and adding 10 ml of 50% HNO_3 to each tube. Sample containers were rinsed with 1 ml of deionized water to recover any dislodged particles and added to the respective test tubes. Tubes were sealed with airtight plastic screw caps and placed on a horizontal shaker for 30 min. The extract was decanted into a 50-ml Teflon beaker, and the extraction was repeated twice with a fresh portion of acid each time (total extract vol. = 30 ml). All three extracts representing a sample were

combined in a 50-ml beaker and evaporated down to about 0.5 ml on a hot plate. The beaker was cooled and 12.5 ml of 50% HCl was added.

The solution was warmed and filtered into a 25-ml polypropylene volumetric flask and diluted to full volume with deionized water. The final solution was transferred to a clean plastic storage bottle and was stored in a refrigerator until analysis.

The wipe, plate, carpet, and soil samples slated for ICP-MS analysis were extracted for Cr, Cd, and Pb by placing the sample (0.5 g of soil) in a polysulfone Oak Ridge centrifuge tube and adding 10 ml of extraction solution (200 ml of HNO₃ plus 800 ml of Type I water) and then capping the tube tightly. The tube was placed in a 120-ml Teflon microwave digestion vessel, which contained 31 ml of Type I water. The microwave oven was programmed for a time of 23 min and a power of 82% (522 W). The Oak Ridge centrifuge tubes were opened and 10 ml of Type I water was added. The tubes were tightly capped and mechanically shaken for 5 min, centrifuged 25 min at 2000 rpm, and then opened, and the clear solution pipetted into an acid-cleaned scintillation vial for analysis.

An HGAFS was used for As analysis. The procedure and instrumental conditions employed were the same as for the air particulate described above.

A VG Fisons Plasma Quad Model (PQS) ICP-MS was calibrated by analyzing a series of eight calibration solutions (containing Pb, Cd, and Cr) covering a concentration range of two orders of magnitude. Sample, reagent, and standard blanks were run with each sample data set and subtracted from the appropriate signals when they are found to be significant (>10% of the lowest measurable sample concentration). A National Institute of Science and Technology (NIST) calibration standard at nominal concentration for the analytes of interest, was run after every 10 samples to ensure that the analytical precision remained within predetermined limits.

The estimated MDL was determined as

$$MDL = 3 \times S/b \quad (3)$$

where *S* = standard deviation of the 15 replicate measurements, and *b* = slope of the calibration line.

Sample runs in which the QC checks differed by more than 20% from their certified value or more than 10% from one of the value limits were repeated.

Analysis of Metals in Blood and Urine

The analytical method used was based on a Zeeman effect background correction GFAAS. The biological fluid was diluted with an appropriate matrix modifier, and vaporized thermally in a graphite furnace by electrical resistive heating. The resulting ground state neutrally charged atoms were then measured by absorbance of resonance radiation from a "line" source — either a hollow cathode lamp or

electrodeless discharge lamp. Quantification was accomplished by measurement of standards (external calibration) carried through the same analytical processes as specimens. The detection limits for the metals of interest were calculated by estimation of the standard deviation of a "blank" or a low-concentration processed specimen, usually with 10 replicate measurements. The detection limit was the concentration equal to three standard deviations of the mean. The basic approach was the analysis of blood or urine with known target values in duplicate with each analytical run (blanks, standards, and unknown specimens).

Volatile Organic Compounds in Air

Samples (3M passive badges) received from the field or retrieved from storage were first inspected for (a) the closure cap being firmly snapped to the passive monitor body and (b) the closure cap plugs being firmly sealed in the cap ports. If these conditions were violated, the sample was compromised and discarded. The sample was also discarded if the diffusion barrier was torn after use.

The center port of the cap was opened, and 1.5 ml of acetone/carbon disulfide (2:1 v/v) desorption solvent (which contained three internal standards, octafluorotoluene, hexafluorobenzene, and bromopentafluorobenzene, each 5 μg/ml) were injected. The rim port was opened to allow venting. Both ports were resealed. With occasional gentle agitation, the monitor was allowed to stand for 0.5 h.

Both ports were carefully opened. The decanting spout was inserted into the rim port and the liquid was carefully transferred into a sampler vial used with the automatic sampler of the gas chromatograph/mass spectrometer (GC-MS) system. The vial was immediately sealed, and was ready for analysis.

The GC-MS analysis conditions are given in Table 7. Table 8 lists the ions used for quantification for all selected

Table 7. Operating parameters for capillary GC-MS.

Parameter	Setting
<i>GC</i>	
Column	60×0.32 mm DB-5 fused silica capillary column
Temperature program	0°C (3 min) to 150°C at 4°C/min
Carrier gas flow	1.0 ml/min
Capillary injector	1 min splitless
Sample injection	1–2 μl
Injector temperature	200°C
<i>MS</i>	
Ionization mode	Electron ionization selected ion monitoring
Emission current	0.3 mA
Source temperature	200°C

^aTypical value.

Table 8. Selected analyte ions for SIMS GC-MS.

Compound	Primary ion	Secondary ion
Benzene	78	74
Chloroform	83	85
Perchloroethylene	166	94
Trichloroethylene	130	95
Methyl chloroform	61	97
Methylene chloride	84	86
Styrene	104	78
Toluene	91	92
<i>m/p</i> -Xylene	91	106
<i>o</i> -Xylene	91	106
<i>p</i> -Dichlorobenzene	146	148
Octafluorotoluene	236	186

compounds and internal standard. Upon analysis of calibration solutions, the response for each analyte was ratioed to the octafluorotoluene (PFT) internal standard to construct a response factor vs. mass curve.

Demonstration and documentation of acceptable initial calibration were required before any samples were analyzed and were required intermittently throughout sample analysis, as dictated by results of continuing calibration checks. After initial calibration, a continuing calibration check was performed at the beginning and end of each 8-h period during which analyses were conducted.

Complete chromatographic resolution was not necessary for accurate and precise measurements of analyte concentrations if *unique* ions with adequate intensities were available for quantification. Analyte and surrogate concentrations were calculated using the GC-MS system software to compute the concentrations of the analytes and surrogates from first- or second-order regression curves. The lowest calibration point chosen for each of the VOCs gave a signal-to-noise ratio of ~20:1. This VOC level, after taking into consideration the sampling volume employed, was defined as the quantification limit (QL).

Volatile Organic Compounds in Water

A purge and trap technique coupled with capillary GC-MS was used for the analysis of VOCs in drinking water samples. A 25-ml water sample was purged with helium gas at 40 ml/min for 11 min at ambient temperature. Standards and samples were analyzed in exactly the same manner.

Full-scan GC-MS data were acquired over the nominal mass range of 35–260 Da with a total cycle time of 2 s or less. A single-ramp linear temperature program with a narrow bore column and a cryogenic interface was used. The helium carrier gas flow rate was 4 ml/min, and the column temperature was 10°C for 5 min from the beginning of vaporization from the cryogenic trap, programmed at 6°/min for 10 min, then 15°/min for 5 min to 145°C, and held

until all components were eluted. The GC-MS system software was used to compute the concentrations of the analytes and surrogates from the linear or second-order regression curves.

Volatile Organic Compounds in Blood

The method used was a purge GC method using high-resolution isotope dilution mass spectrometric detection in the full-scan mode. Stable isotopically labeled analogs of the compounds of interest were added to 10 ml of blood, and the entire sample was injected into a specially designed sparging vessel attached to the purging apparatus. Prepurified helium gas was bubbled through the blood, which was heated to approximately 35°C. The purged volatile compounds were passed into and captured by a Tenax trap.

Once the 15-min purge cycle was complete, the Tenax trap was purged with dry helium gas for 6 min to remove absorbed water. The trap was then heated to 180°C for 4 min to desorb all VOCs. As the compounds were desorbed, they were trapped at the GC injection port by a liquid nitrogen trap at –150°C. Subsequently, the site was ballistically heated to 200°C, which injected the VOCs onto the DB-624 capillary column interfaced to a mass spectrometer. The MS was operated in the full scan-mode (40–200 amu), with one scan collected per second. Quantification was accomplished from specific ion responses relative to those of the corresponding isotopically labeled analogs. Final concentrations were calculated based on six-point calibration curves.

The detection limits for the VOCs of interest were determined from the plot of the standard deviation of calculated concentration of standards versus concentration. The y -intercept of the least-squares fit of this line equaled S_0 , with $3 \times S_0$ being the calculated MDL.

Results and discussion

Samples Collected and Completion Statistics

A QA goal in NHEXAS was to assess the performance of the collection and analysis procedures and to describe the quality of the data derived from the study. It was important to provide results regarding the robustness of the data that are available for modeling and data analyses. Documentation of the completion rate for the various steps of the study implementation is important information for designing future large-scale population-based exposure studies (Whitmore et al., 1999).

Table 9 provides the inventory for all sample types collected in the NHEXAS Region V study and the corresponding completion statistics. The minimum requirements to participate in this study were to provide samples of water and dust, and of badges for indoor, outdoor, and personal air. The provision of the other sample types (e.g.,

Table 9. Inventory of samples collected and completion statistics for the initial monitoring period.

Medium	Subsample type	Contaminant	No. of samples scheduled for collection	No. of samples collected	No. of samples analyzed	No. of samples with valid data ^a
Personal air	IOM	Particles and metals	228	175 (77) ^b	174 (76) ^b	169 (74) ^b
		VOCs	249	248 (99)	244 (98)	244 (98)
Indoor air	PM ₁₀	Particles and metals	33	33 (100)	33 (100)	33 (100)
	IOM	Particles and metals	229	222 (97)	222 (97)	220 (87)
Outdoor air	PM ₁₀	VOCs	249	249 (100)	248 (99)	247 (99)
		Particles and metals	30	30 (100)	30 (100)	30 (100)
		Particles and metals	90	89 (99)	89 (99)	89 (99)
Beverages	Days 4, 5, 6, 7	VOCs	97	97 (100)	97 (100)	97 (100)
		Metals	164, 164, 165, 163	159 (97), 158 (96), 159 (96), 155 (95)	159 (96)	159 (96)
		Metals	163, 164, 164, 163	157 (96), 157 (96), 158 (96), 155 (95)	157 (96)	157 (96)
Drinking water	VOCs	215	214 (99)	213 (99)	213 (99)	
Tap water	Flush	Metals	249	248 (99)	248 (99)	248 (99)
	Standing	Metals	248	248 (100)	247 (99)	247 (99)
Dust, LWW	Surface Dust	Metals	248	248 (100)	247 (99)	245 (99)
	Window Sill	Metals	248	241 (97)	241 (97)	240 (97)
Dust, LM	Surface Dust	Metals	247	247 (100)	246 (99)	244 (99)
	Window Sill	Metals	248	241 (97)	241 (97)	239 (96)
Dust, WWT	Surface Dust	Metals	64	64 (100)	64 (100)	63 (98)
	Window Sill	Metals	64	63 (98)	63 (98)	62 (97)
Soil	Entranceway	Metals	64	64 (100)	64 (100)	64 (100)
	Yard	Metals	64	63 (98)	63 (98)	64 (100)
Blood		Metals	179	165 (92)	165 (92)	165 (92)
		VOCs	178	160 (94)	160 (94)	151 (85)
Urine	Days 3, 7	Metals	204, 205	200 (98), 198 (97)	200 (98)	200 (100)

IOM=Institute of Occupational Medicine.

^aMaximum number of samples with valid data for one or more contaminants.

^bPercent of scheduled.

personal air-metals, beverages, food, blood, and urine) by the participants was optional.² In addition, a few subsample types [e.g., nonoccupational and occupational personal air, indoor and outdoor PM₁₀, dust (WWT), and entranceway and yard soil] were collected for only selected subsets of homes, but their selection were not probability based. The result was a stratified level of participation with several possible combinations of sample types provided across the participants and a variable number of samples collected across the sample types. The samples scheduled for collection were based on the participants' agreeing to provide the samples or permit the study investigators to collect these samples during the initial enrollment visit (Pellizzari et al., 1995). The maximum number of participants for any measurement in the study was 249.

Except for blood, the samples collected as a percentage of those scheduled ranged from 77% to 100% (Table 9),

which was the goal for the study. In general, those samples collected by the participants resulted in only a slightly lower completion percentage (e.g., food and beverage) than those collected by the study investigators, an indication of compliance by the participants. The percent of beverage and food samples collected was calculated for daily composites. The completion percentage was a relatively narrow range of 95% to 97%. Because the burden to the participant for providing an equal portion of beverage and food consumed for all meals over a 4-day period is substantial, the completion percentage was remarkably good.

Blood samples designated for VOC and metal analyses were collected sequentially in separate vacutainers. The first collection was for VOCs, the second for metals. The completion percentage for blood VOCs was a little higher than for blood metals because either participants refused or difficulties occurred in collecting the second blood sample. The high completion percentages for all sample types suggest that once a participant agreed to participate, he/she was likely to continue to comply.

²The use of human subjects in the study was approved by RTI's Institutional Review Board (IRB).

Table 10. Inventory of samples collected in longitudinal phase and completion statistics.

Medium	Subsample type	Contaminant	No. of samples scheduled for collection		No. of samples collected		No. of samples analyzed		No. of samples with valid data ^a	
			2nd visit	3rd visit	2nd visit	3rd visit	2nd visit	3rd visit	2nd visit	3rd visit
Personal air		VOCs	98	87	94 (96) ^b	85 (98) ^b	92 (94) ^b	81 (93) ^b	87 (89) ^b	74 (85) ^b
Indoor air		VOCs	97	86	96 (99)	86 (100)	96 (99)	81 (94)	90 (93)	77 (79)
Outdoor air		VOCs	8	5	7 (88)	5 (100)	7 (88)	5 (100)	7 (88)	5 (100)
Tap water	Flush	Metals	108	91	107 (99)	91 (100)	107 (99)	91 (100)	106 (98)	91 (100)
	Standing	Metals	110	92	107 (97)	91 (99)	107 (97)	91 (99)	106 (96)	91 (99)
Dust, carpet		Metals	119	96	112 (94)	92 (96)	112 (94)	91 (95)	105 (88)	84 (88)
Dust, plate		Metals	122	97	120 (98)	97 (100)	119 (98)	96 (99)	118 (97)	93 (96)

^aMaximum number of samples with valid data for one or more contaminants.

^bPercent of scheduled.

Of the samples collected, very few samples were lost in transport to the laboratory or during storage, as indicated by the percent of samples analyzed (Table 9). The percentages given in parentheses are based on samples scheduled for collection; thus, they are cumulative percentages. The percentage of samples that yielded valid data (data that met all of the analytical QC requirements) after analysis for at least one target analyte was also very high. In general, the sample and analysis procedures used in this NHEXAS Region V study were very effective in providing a high yield of valid data.

Although the attrition of samples and data are relatively low for most sample types, these statistics can be used as a guideline in defining data quality objectives and in

designing future exposure studies. For example, for VOC determinations in blood, an adjustment in the number of samples scheduled might be made because an attrition rate of 15% would be expected.

The study design also included a second and third longitudinal follow-up for a few selected sample types and participants. The follow-up procedures prescribed the mailing of a sampling kit containing instructions to each selected participant who agreed to further participate in the study. Table 10 lists the samples obtained in this phase of the study and the associated completion statistics. Similarly to the first home visit (Table 9), the percentage of samples collected relative to those scheduled was high for both the second and third times of participation. In contrast, the

Table 11. Median detection limits for metals in air, water, dust, blood, and urine samples.

Medium	Units for DL ^a	Arsenic			Lead			Cadmium			Chromium		
		N ^b	Median DL	Percent measurable	N	Median DL	Percent measurable	N	Median DL	Percent measurable	N	Median DL	Percent measurable
Personal air (IOM)	ng/m ³	522	0.19	94	518	6.3	80	515	0.63	75	517	28	11
Indoor air (IOM)	ng/m ³	85	0.32	85	85	13	51	85	2.3	46	81	15	7.2
Outdoor air (IOM)	ng/m ³	85	0.32	96	85	13	74	85	2.3	19	81	15	5.7
Tap water	µg/l	46	0.2	96 ^c	104	0.1	99 ^c	750	0.1	35 ^c	202	0.22	80 ^c
Beverages	µg/l	138	0.31	92	138	0.26	93	137	0.26	73	137	5.2	92
Food	µg/Kg	137	1.4	99	137	1.2	100	137	1.2	99	137	24	82
LWW surface and sill dust (loading)	ng/cm ²	519	0.57	31	545	0.5	88	545	0.5	30	545	0.5	87
WWT surface dust (loading)	ng/cm ²	140	0.089	81	159	0.5	89	159	0.5	42	159	0.5	69
Dust, carpet	µg/g	190	3.4	100	194	0.5	29	195	0.5	0	194	0.5	28
Dust, plate	µg/g	211	13	100	212	0.5	72	212	0.5	20	212	0.5	60
Soil, entrance	µg/g	63	3.4	32	66	0.5	92	67	0.5	72	66	0.5	98
Soil, yard	µg/g	63	0.36	56	66	0.5	91	67	0.5	6.0	66	0.5	94
Blood	µg/l	- ^d	-	-	6	0.6	94	68	0.3	63	-	-	-
Urine	µg/l	249	4.0	60	-	-	-	84	0.1	85	230	0.4	67

^aDL=detection limit.

^bNumber of observations for median detection limits.

^cFor standing water sample.

^dNot measured.

Table 12. Percent recovery for metals in tap water field controls as a function of sample storage time.

Metal	Overall			<75 days			>75 days		
	N ^a	Median	CV (%)	N	Median	CV (%)	N	Median	CV (%)
Arsenic	29	100	12	8	102	15.7	21	100	10.1
Lead	29	99	6.1	11	98	4.4	18	99	7.0
Cadmium	29	102	6.3	11	102	6.0	18	102	6.5
Chromium	29	98	6.3	11	99	2.1	18	98	8.0

^aNumber of observations (field control samples).

percentage of personal and indoor air samples that were analyzed for VOCs were lower. This was attributed to the participant not carefully following or understanding the instructions on how to package and ship the samples, which produced more invalid samples. For example, a few of the 3M badges for the air VOCs were not properly sealed in their containers before return shipment, resulting in potential contamination. As a result, the percentage of samples with valid data ranged from 88% to 98% for the second follow-up and from 79% to 100% for the third.

Even though the percent of samples with valid data were less for the second and third follow-up compared to the first visit, the percent completions were acceptable. The use of this procedure was feasible for certain types of samples. The mail-in approach was limited to those sample types that involved minimal burden to the participant, were simple to implement by the participant and did not have special packaging and shipping requirements (e.g., cold packs, hazardous materials). The cost effectiveness of the mailing approach was an attractive feature when compared to the costs associated with the study investigators returning to each of the homes to collect the samples.

Limits of Detection for Metals Analyses

The influence of detection limits becomes evident during data analysis. The percent of observations that fall below measurable values can provide special challenges in data analysis and modeling. As the percent of nonmeasurable values increases, the uncertainty in estimating the central tendencies in the data also increases. Also, the term “detection limit” generically encompasses the more specific terms of MDL and the QL, both have been used in NHEXAS and identified in the methods section. The calculation of MDLs incorporates method blanks in the procedure and for this reason the blank data are not reported here.

The detection limits should be sufficiently low to permit the full range of health risk assessment for the target analytes of interest. Table 1 lists detection limit goals for one or two target analytes for each sample type. The median detection limits for metals in air, dust, blood, and urine sample analysis that were achieved in this NHEXAS are shown in Table 11. The detection limits for arsenic, lead and cadmium across all media were comparable, whereas the detection limit for chromium differed by as much as an order of magnitude. For air samples, the detection limits were adequate for arsenic and cadmium, whereas chromium detection limits were relatively high, yielding a low percentage of samples with measurable values ($\leq 11\%$). The detection limits for tap water, beverages, and food composites were sufficiently low such that the metals were measurable in most samples. The quantity of house dust collected coupled with the analytical detection limits yielded a high percentage of samples with measurable lead and chromium, but $< 50\%$ of the samples had measurable levels of arsenic and cadmium. These results suggest that the methods had adequate sensitivity for arsenic, lead, and cadmium in all media but not for chromium (e.g., air samples).

Table 13. Precision for the collection and analysis of metals in duplicate samples of air, dust, blood, and urine.

Medium	Arsenic		Lead		Cadmium		Chromium		Particles ^a	
	N ^b	Median %RSD	N	Median %RSD	N	Median %RSD	N	Median %RSD	N	Median %RSD
Indoor air	22	9.1	13	9.1	11	4.6	– ^c	–	25	3.7
Outdoor air	16	10	10	13	–	–	–	–	17	3.1
Tap water	31	2.7	28	5.7	–	–	23	44	–	–
LWW sill dust (loading)	4	29	14	57	3	66	14	64	–	–
LWW sill dust (conc)	4	23	14	57	3	44	14	51	–	–
LWW surface dust (loading)	–	–	15	25	–	–	16	28	–	–
LWW surface dust (conc)	–	–	15	26	6	21	16	22	–	–
WWT sill dust (loading)	4	49	3	37	–	–	–	–	–	–
WWT surface dust (loading)	9	22	10	28	–	–	6	41	–	–
Blood	–	–	11	14	8	24	–	–	–	–
Urine	15	15	–	–	40	8.9	–	–	–	–

^aFrom IOM particle sampling.

^bN=number of pairs where both measurements were above the detection limit.

^cNo data.

Percent Recovery for Metals from Field Controls

Field controls that were prepared during the study and analyzed along with field samples were used to assess the percent recovery or bias for the analysis of metals in water. Table 12 shows the number of such control samples, the median of these percent recoveries, and the variation of these percent recoveries, expressed as a coefficient of variation (CV), in percent. Table 12 also presents comparable statistics for those field controls stored less than and greater than 75 days from the time of their preparation. The median percent recoveries across the entire time period of analysis for arsenic, lead, cadmium, and chromium were 98% to 102% with a CV ranging from 6.1% to 12%. The range of CVs was slightly larger when examined over the two time periods, i.e., for field controls stored less than and greater than 75 days before analysis. These overall results indicate that the QA goals listed in Table 1 for arsenic and lead were met and the results for cadmium and chromium, although not stated, were comparable. In general, these data suggest that samples could be stored for up to 4 months without introducing appreciable bias in the results.

Precision of Duplicate Collection and Analysis for Metals

As part of the QC program in NHEXAS, duplicate samples were collected and analyzed to assess precision of collection and analysis. To accomplish this assessment, the samples were limited to those having measurable levels of the target metal in both replicate samples. Thus, the number of sample pairs satisfying this criterion varied across sample types and across metals. The precision was expressed as the median % RSD between duplicate samples. Table 13 presents the precision for the analysis of metals in duplicate samples of air, dust, blood, and urine. Also included is the precision for measuring the mass of particles in air samples. For arsenic and lead the median RSD was $\leq 13\%$ for air and tap water measurements. The results were within the QA goal specifications. The precision for chromium in tap water was relatively poor; however, this may be due to the low levels observed, i.e., most of the data were near the detection limit of the method. Duplicate dust samples (surface wipes collected by the LWW and WWT methods) entailed the collection of a second sample near the first one. The median RSD for duplicate dust loading measurements (ng/cm^2) ranged from 22% to 66% whereas the median RSD for duplicate dust concentration measurements ($\mu\text{g}/\text{g}$) (for LWW) ranged from 21% to 57%. The higher variability of dust sample measurements relative to the other media cannot simply be attributed to the sample analysis step, because the results possibly reflect the reproducibility of dust collection as well as the uneven deposition of dust over a given surface area. Nevertheless, the precision for arsenic and lead did not meet the QA goals of the study.

Results on the precision of metals analyzed in blood and urine were limited as shown in Table 13. For the measurement of cadmium in urine, the median % RSD was within the QA goals whereas arsenic in urine was not. There were no duplicate measurable data available from these samples for chromium, so no assessment could be made about its precision.

The precision for the analysis of lead in blood was 40% higher than the QA goal (Table 13). The median % RSD for cadmium was over a factor of two higher than the QA goal.

Precision of Duplicate Analysis for Metals Over Time

In this NHEXAS Region V Study, samples were collected from participants from July 1995 through May 1997.

Table 14. Precision for the analysis of duplicate samples over the course of the study.

Medium	Chemical	July 1995 to May 1996		June 1996 to May 1997	
		N ^a	Median % RSD	N	Median % RSD
Indoor air	Particles ^b	7	3.6	18	3.9
	Arsenic ^b	6	6.9	16	10
	Cadmium ^b	6	3.1	5	13
	Lead ^b	5	9.1	8	10
Outdoor air	Particles ^b	5	4.9	12	3
	Arsenic ^b	4	5.3	12	15
	Lead ^b	3	1.4	7	19
Outdoor PM ₁₀	Particles	3	16	7	10
	Arsenic	3	5.5	6	8.3
Tap water	Arsenic	11	4.4	20	2.1
	Lead	10	16	18	3.6
	Chromium	11	45	12	41
	Manganese	11	2.1	21	3.3
LWW surface dust (loading)	Nickel	12	2.8	20	4.9
	Lead	6	57	9	21
LWW surface dust (conc)	Chromium	6	32	10	28
	Lead	6	34	9	18
LWW window sill dust (loading)	Chromium	6	9.6	10	40
	Lead	5	86	9	34
LWW window sill dust (conc)	Lead	5	84	9	36
	Chromium	5	55	9	21
Blood	Lead	4	16	7	9.4
	Cadmium	4	29	4	21
Urine	Arsenic	3	15	12	16
	Cadmium	5	20	35	5.9
	Creatinine	13	3.1	37	2.0

^aNumber of observations where both measurements were above the detection limit.

^bAir particles and metals are from IOM samples.

Table 15. Detection limits and percent measurable data for VOCs in personal air.

VOC	Total			Nonoccupational			Occupational		
	N ^a	Median QL ^b	Percent measurable	N	Median QL	Percent measurable	N	Median QL	Percent measurable
Benzene	386	0.75	100	53	1.00	100	52	3.0	96
Chloroform	381	1.09	62	52	1.46	69	49	4.5	69
Tetrachloroethylene	362	1.60	63	49	2.15	69	46	6.6	84
Trichloroethylene	362	1.06	33	47	1.43	36	41	4.4	36
1,1,1 - Trichloroethane	385	1.39	78	52	1.87	75	51	5.7	88
<i>p</i> -Dichlorobenzene	382	0.78	58	53	1.05	47	52	3.2	77
Styrene	375	0.83	83	50	1.13	90	49	3.5	94
Toluene	386	3.54	100	53	4.77	100	52	14	98
<i>m,p</i> -Xylenes	386	0.97	100	53	1.31	100	52	4.0	100
<i>o</i> -Xylene	386	0.90	100	53	1.22	100	52	3.8	100

^aNumber of observations for median.

^bQuantification limit ($\mu\text{g}/\text{m}^3$).

Because of the long-term nature of sample analysis, it was important to assess the precision of analysis over the 2-year period. The precision for the collection and analysis of duplicate samples was used to assess whether the performance of the methods remained relatively constant. Table 14 presents the median % RSD for the analysis of particles and metals in a variety of sample types and for cases where sufficient data existed to make this comparison. Except for chromium (tap water) and cadmium (blood), the median RSDs for particles and metals were $\leq 21\%$ in air, tap water, blood, and urine. The RSDs were much larger for metals measured in dust samples, especially those collected from the window sill. It should be noted that flakes of paint on the window sills were occasionally observed during sampling, which may explain some of the variability between duplicate samples. Excluding the noted exceptions, the precision did substantially exceed the QA goals, i.e., the precision was better than the goals.

Limits of Detection for VOCs Analyses

The detection limits and percent measurable data for VOCs in personal — total, nonoccupational, and occupational — air are given in Table 15. Four of the VOCs were measured in all of the total exposure samples. Four of the VOCs were measured in over half of the samples. Trichloroethylene was the lowest, with 33% of the samples yielding measurable values. Comparable statistics were obtained for nonoccupational and occupational personal samples, even though the median detection limits were as much as 4.5 times higher. This occurred because the exposure time for the badges for nonoccupational and occupational samples were a fraction of the total exposure samples. These results indicate that the collection and analysis of personal air samples using the 3M badge with an exposure period of 6 days was sufficiently sensitive for segregating the components into total, nonoccupational, and occupational exposure in this study.

Table 16. Detection limits and percent measurable data for VOCs in indoor and outdoor air, drinking water, and blood.

VOC	Indoor air			Outdoor air			Drinking water			Blood		
	N ^a	Median QL ^b	Percent measurable	N	Median QL ^b	Percent measurable	N	Median QL ^b	Percent measurable	N	Median MDL ^c	Percent measurable
Benzene	442	0.74	99	121	0.74	100	282	0.031	5.9	33	0.068	91
Chloroform	438	1.09	73	121	1.09	48	282	0.04	81	108	0.019	41
Tetrachloroethylene	409	1.59	57	103	1.60	50	282	0.015	6.9	151	0.047	39
Trichloroethylene	421	1.06	36	117	1.07	26	282	0.03	8.1	218	0.009	7.0
1,1,1 - Trichloroethane	437	1.39	73	119	1.39	56	282	0.056	1.4	198	0.054	13
<i>p</i> -Dichlorobenzene	438	0.79	36	118	0.78	1	282	0.053	4.1	102	0.082	54
Styrene	427	0.83	79	118	0.84	70	282	0.059	0.6	120	0.019	54
Toluene	443	3.54	100	121	0.76	98	282	0.038	60	2	0.032	98
<i>m,p</i> -Xylenes	443	0.97	99	121	0.97	100	282	0.098	9.2	14	0.041	94
<i>o</i> -Xylene	442	0.91	96	121	0.91	94	282	0.028	14	154	0.053	50

^aNumber of observations for median.

^bQuantification limit ($\mu\text{g}/\text{l}$).

^cMDL ($\mu\text{g}/\text{l}$).

Table 17. Percent recovery of VOCs in field controls for air and drinking water as a function of sample storage time.

VOC	Air									Drinking water								
	All samples			<75 days			>75 days			All samples			<8 days			>8 days		
	N ^a	Median	CV (%)	N	Median	CV (%)	N	Median	CV (%)	N	Median	CV (%)	N	Median	CV (%)	N	Median	CV (%)
Benzene	22	90	29	8	82	47	14	92	14	23	73	18	8	86	19	15	69	17
Chloroform	29	94	25	9	116	28	20	91	10	23	83	14	8	90	15	15	82	14
Tetrachloroethylene	29	94	19	9	94	28	20	94	13	23	70	22	8	81	24	15	69	22
Trichloroethylene	29	94	21	9	93	31	20	94	11	23	74	19	8	79	21	15	68	17
1,1,1-Trichloroethane	29	88	26	9	118	26	20	86	12	23	85	19	8	104	20	15	81	18
<i>m,p</i> -Xylene	29	77	38	9	90	32	20	59	28	23	77	18	8	82	19	15	69	16
<i>o</i> -Xylene	29	74	35	9	104	29	20	70	14	23	74	28	8	83	16	15	67	32
<i>p</i> -Dichlorobenzene	– ^b	–	–	–	–	–	–	–	–	23	59	28	8	64	17	15	58	33
Styrene	–	–	–	–	–	–	–	–	–	23	60	20	8	63	21	15	59	18
Toluene	–	–	–	–	–	–	–	–	–	23	98	45	8	113	37	15	96	49

^aNumber of observations.^bNo Data.

The median detection limits achieved for indoor and outdoor air were very close to those for total personal air exposure (Table 16). However, because the VOC levels were lower for indoor and outdoor air, the percent of the data above the detection limit was lower than for personal air. The percent measurable data for chloroform, trichloroethylene, and *p*-dichlorobenzene in indoor and outdoor air samples were below 50%. Nevertheless, the collection and analysis method was adequate for VOC measurements in indoor and outdoor air.

Table 16 also gives the detection limits and percent measurable statistics for VOCs in drinking water and blood samples. Except for chloroform and toluene, the VOC levels in drinking water were very low, as reflected by the low detection limits and low percent measurable values. The drinking water method was sufficiently sensitive for this study to identify high-end exposures and potential health risks.

The detection limits for VOCs in blood were very low (Table 16). For the 10 VOCs measured, three had data with over 90% of the values above the detection limit, three VOCs at or above 50%, and two were under 15%. This method was deemed sufficiently sensitive for the purposes of this NHEXAS.

Percent Recovery for VOCs from Field Controls

The recovery of VOCs from field controls (3M badges loaded with known amounts of each VOC) was used as a measure of bias for their analysis. Table 17 presents these results for air and drinking water samples. Across all air samples, the median percent recovery and % Cvs for field controls for air samples ranged from 74 to 94 and 19 to 38, respectively. Except for *o*-xylene, the bias was within QA goals.

When the data were partitioned into field controls stored for less than and greater than 75 days before analysis, the

percent recoveries for *m,p*-xylenes and *o*-xylene appeared to decrease with the longer storage time. Though their recovery levels are higher, chloroform and 1,1,1-trichloroethane also dropped about the same amount as the xylenes, whereas the remaining VOCs gave similar recoveries regardless of storage time. Also, the Cvs appeared slightly smaller for the longer storage times. The results suggest that samples should be analyzed within 75 days to meet the more stringent bias requirements. Except for *m,p*-xylenes, the QA goals were met, even with storage of over 75 days.

For drinking water, and with the exception of *p*-dichlorobenzene and styrene, the median percent recovery of VOCs from field controls (reagent water spiked with known quantities of VOCs) met the goals of the study (Table 17). However, when the data were partitioned into samples stored less than and greater than 8 days before analysis, only 7 of the 10 VOCs met the QA goals of the study. The analytical protocol prescribed the analysis of samples within 14 days of collection; however, these data

Table 18. Percent recovery for VOCs from field controls for air as a function of two instruments.

VOC	GC-MS No. 1			GC-MS No. 2		
	N ^a	Median	CV (%)	N	Median	CV (%)
Benzene	16	86	34	6	95	6.8
Chloroform	23	94	27	6	94	8.1
Tetrachloroethylene	23	90	22	6	95	4.3
Trichloroethylene	23	94	23	6	93	5.2
1,1,1-Trichloroethane	23	88	27	6	86	9.7
Toluene	14	92	17	6	96	4.1
<i>m,p</i> -Xylenes	23	69	43	6	82	11
<i>o</i> -Xylene	23	77	38	6	73	3.1

^aNumber of observations.

Table 19. Precision for the analysis of VOCs in duplicate samples of air, drinking water, and blood.

VOC	Personal air		Residential indoor air		Residential outdoor air		Drinking water		Duplicate blood samples		Split blood samples ^a	
	N ^b	Median %RSD	N	Median %RSD	N	Median %RSD	N	Median %RSD	N	Median %RSD	N	Median %RSD
Benzene	16	3.8	31	18	9	38	— ^c	—	5	35	60	7.5
Chloroform	10	2.2	10	2.4	3	0.3	27	3.0	—	—	—	—
Tetrachloroethylene	6	5.4	16	9.2	3	8.8	—	—	—	—	22	9.9
Trichloroethylene	3	22	6	1.9	—	—	3	4.9	—	—	6	12
1,1,1 - Trichloroethane	10	3.4	20	4.6	5	4	—	—	—	—	—	—
<i>p</i> -Dichlorobenzene	12	3.8	9	9.9	—	—	—	—	4	7.2	40	10
Styrene	11	3.3	17	24	3	5.4	—	—	—	—	39	9.6
Toluene	16	6.5	30	8.9	11	16	18	18	8	17	73	11
<i>m,p</i> -Xylenes	16	2.6	29	10	10	19	6	6.1	8	22	69	14
<i>o</i> -Xylene	16	3.4	29	16	9	26	3	9.9	—	—	24	16

^aA second aliquot of blood sample was reanalyzed.

^bNumber of observations where both measurements were above the detection limit.

^cNo data.

suggest that the data quality deteriorates appreciably even after 8 days of storage. In large exposure studies the number

Table 20. Precision for the analysis VOCs in duplicate samples over the course of the study.

Medium	Chemical	July 1995 to May 1896		June 1996 to May 1997	
		N ^a	Median %RSD	N	Median %RSD
Personal air	Benzene	3	3.7	13	4.6
	Chloroform	3	0.4	7	3.7
	Tetrachloroethylene	3	7.1	3	4.9
	1,1,1 - Trichloroethane	3	1.5	7	3.6
	Styrene	3	2.2	8	3.9
	Toluene	3	10	13	4.8
	<i>m,p</i> -Xylene	3	5.5	13	2.6
	<i>o</i> -Xylene	3	3.7	13	3.2
Indoor air	Benzene	17	22	13	18
	Tetrachloroethylene	13	9.2	3	1.8
	1,1,1 - Trichloroethane	12	9.8	8	3.6
	Styrene	9	29	8	15
	Toluene	17	6.4	13	11
	<i>m,p</i> -Xylene	17	14	12	9.2
	<i>o</i> -Xylene	17	16	12	15
Outdoor air	Toluene	7	16	4	17
	<i>m,p</i> -Xylene	7	20	3	4.5
Drinking water	Chloroform	12	3.2	15	2.1
	Carbon tetrachloride	4	2.0	4	4.0
	Toluene	6	15	12	23
	<i>m,p</i> -Xylene	3	6.0	3	6.2
Blood	Toluene	4	11	4	25
	<i>m,p</i> -Xylene	4	18	4	32

^aNumber of observations where both measurements were above the detection limit.

of samples collected can often exceed the capacity for a single instrument to analyze all of the samples within the prescribed maximum storage times. This was the case in NHEXAS. Therefore, two GC-MS instruments of identical models operated by different persons were used to provide the needed capacity. Table 18 gives the median recoveries for VOCs analyzed in field controls for air samples on two different GC-MS instruments. Even though the percent median recoveries were comparable between the two systems, the % CV was considerably larger on GC-MS No. 1. It should be noted that the first system was in operation over the entire course of the study, whereas the second system was pressed into operation for only a few months and analyzed about one-fourth of all field controls and field samples. As such, the analytic bias for each VOC as

Table 21. Precision for the analysis of VOCs in split blood samples over the course of the study.

VOC	July 1995 to May 1996		June 1996 to May 1997	
	N ^a	Median % RSD	N	Median % RSD
Benzene	26	7.1	34	7.7
Chloroform	5	5.8	9	11
Ethyl benzene	16	9.7	25	17
Styrene	14	6.5	25	11
Tetrachloroethylene	6	30	16	7.5
Toluene	36	6.4	37	16
Trichloroethylene	3	10	3	13
<i>m,p</i> -Xylene	35	12	34	15
<i>o</i> -Xylene	12	13	12	20
<i>p</i> -Dichlorobenzene	16	7.0	6	11

^aNumber of observations.

Table 22. Precision for the duplicate sample analysis of VOCs for air as a function of two GC-MS instruments.

Medium	VOC	GC-MS No. 1		GC-MS No. 2	
		N ^a	Median %RSD	N	Median %RSD
Indoor air	Benzene	12	41	17	4
	Tetrachloroethylene	7	9	8	7
	1,1,1-Trichloroethane	7	71	12	3
	<i>p</i> -Dichlorobenzene	3	32	7	2
	Styrene	4	50	12	5
	Toluene	12	19	17	7
	<i>m,p</i> -Xylenes	11	17	17	5
	<i>o</i> -Xylene	11	30	17	5
Outdoor air	Benzene	4	40	5	9
	Toluene	6	17	5	14
	<i>m,p</i> -Xylenes	5	21	5	4
	<i>o</i> -Xylene	4	51	5	3

^aNumber of observations where both measurements were above the detection limit.

measured by median percent recovery was within the QA goals of NHEXAS.

Precision of Duplicate Analysis for VOCs

The quality of VOC data was also evaluated in terms of precision by analyzing samples collected in duplicate. To accomplish this assessment, both duplicate samples needed to exhibit measurable levels of a VOC. Table 19 presents the precision for the analysis of VOCs in duplicate samples of personal air, residential indoor and outdoor air, drinking water, and blood. Duplicate blood samples consisted of two vacutainer samples taken in sequence from the participant, whereas split blood samples were aliquots of blood from the same vacutainer. The median % RSD was excellent for most sample types. With the exception of benzene, the precision of collection and analysis methods for VOCs were within the QA goals of NHEXAS.

Precision of Duplicate Analysis for VOCs Over Time

As with metals, the precision of analysis of VOCs over the course of the study was assessed to determine if quality of data was relatively constant for the 2-year period of sample collection and analysis. Table 20 presents these results. As expressed by the median % RSD, there appeared to be no appreciable deterioration of the precision of data over the 2-year span. Except for the measurement of *m,p*-xylene in blood, all of the medians met the QA goals.

Table 21 gives the precision for split blood samples analyzed over the 2-year period. All of the VOCs exhibited median % RSDs within the QA goals of $\pm 25\%$. Although there was a slight increase in the median % RSD in the second year compared to the first, all VOCs met the NHEXAS QA goals in the second year.

Similarly to field controls, the precision of duplicate sample analysis for VOCs in air was determined as a function of two GC-MS instruments (Table 22). The median % RSD experienced with GC-MS No. 2 was considerably better than with GC-MS No. 1. The reason for the difference was not evident.

Summary

The achieved detection limits were a function of the sample size available for analysis and the sensitivity of the instrument used for quantifying the analytes. The methods employed for the collection and analysis of particles, metals, and VOCs in air samples had sufficiently low detection limits to quantify them. Most analytes were measurable in more than 50% of the samples analyzed. For tap water, dust, and soil samples, cadmium occurred at levels below the detection limit in more than 50% of the samples. With the exception of chloroform and toluene, the VOC levels in drinking water were measurable in less than 10% of the samples. Approximately half of the VOCs were measured in over 50% of the blood samples.

In general, the precision of the collection and analysis methods was excellent. The noted exception was chromium, which often did not meet the QA goals. The precision could not be established for all analytes in all sample types. The QC goals prescribed that 10% of the samples be collected in duplicate. Furthermore, at least four duplicate pairs needed to contain an analyte above the detection limit to assess precision of collection and analysis. For cases when the percent of samples with measurable levels was below 25%, there was insufficient number of observations to assess precision. This was particularly the case for VOCs in drinking water where the precision for only chloroform and toluene could be calculated.

The bias, to the extent it could be determined, was low for most analytes for all of the samples.

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