United States
Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

EPA/600/R-97/069
August 1997

EPA

Ostrava Human Exposure and Biomarker Study

EPA/600/R-97/069
August 1997

OSTRAVA HUMAN EXPOSURE AND BIOMARKER STUDY

by

R. W. Williams, R. R. Watts, T. A. Hartlage, L. Phillips and J. Lewtas
U.S. Environmental Protection Agency, Research Triangle Park, NC, USA

L. Dobias, J. Havrankova and J. Volf
Regional Hygiene Institute, Ostrava, Czech Republic

R. B. Kellogg and R. D. Willis
ManTech Environmental Technology, Inc., Research Triangle Park, NC, USA

J. Novak
Czech Hydrometeorological Institute, Prague, Czech Republic

Principal Investigator

R. Williams
Human Studies Division
National Health and Environmental Effects Research Laboratory
Research Triangle Park, NC 27711, USA

National Health and Environmental Effects Research Laboratory
Office of Research and Development
Human Studies Division
Research Triangle Park, NC 27711, USA

Printed on Recycled Paper

Disclaimer

A portion of the research described in this document has been funded by the United States Environmental Protection Agency under Contract 68-D50049 to ManTech Environmental Technology, Inc. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Abstract

A four week repeated measures personal air pollution exposure study was conducted in the city of Ostrava, Czech Republic, during October and November 1995. Personal exposure monitoring with 30 participants was conducted to determine the relationship between individual air particulate exposures and subsequent biomarkers of exposure and dose to DNA (not reported here). The 24 hour exposure periods for each individual were divided into day time at the central work site (KHS-Ostrava) and night time (e.g., at home) away from the central work site. Each individual was repeatedly monitored one day per week for four weeks. Individual blood and urine specimens, along with a 24 hour activity log, were collected in addition to fine ambient air particulate matter during each sampling period. Stationary indoor and outdoor monitoring of fine ambient air particulate matter at the central site was also conducted. Outdoor ambient monitoring at several sites across the city of Ostrava was conducted simultaneously (Willis et al., 1997).

Personal exposure concentrations of fine particulate matter ($PM_{2.5}$), measured during participant daytime working hours at a central site (KHS-Ostrava), indicated particle exposure concentrations as high as 474.6 $\mu g/m^3$. The 30 day daytime average for all study participants was 90.3 $\mu g/m^3$. The nighttime average fine particle concentration of 43.2 ug/m^3 for the same 30 individuals was approximately 50% of the daytime value. These higher exposures during working hours may result from the work site being situated downwind from industrial emission sources. This central site was located in an area of Ostrava that had previously been found to have annual mean PM_{10} ambient concentrations in excess of the Czech Republic standard of 60 $\mu g/m^3$. The mean 24 hour individual $PM_{2.5}$ particle exposure in this 30 day study was 57.3 ug/m^3.

Carcinogenic PAH concentrations from the 30 day personal sampling showed central work site daytime ambient concentrations of benz(a)pyrene [B(a)P] that were also higher than those for the nighttime periods. The daytime B(a)P mean for all participants was 4.7 ng/m^3 as compared to 3.5 ng/m^3 for nighttime periods. The overall 24 hour average exposure concentration for B(a)P was 3.9 ng/m^3. Total carcinogenic PAHs were determined by summing individual concentrations of carcinogenic PAHs. Ambient B(a)P concentrations from personal monitoring correlated with total carcinogenic PAH concentrations (r^2=0.77). No correlation was found for $PM_{2.5}$ particle concentrations and B(a)P concentrations.

$PM_{2.5}$ particle concentrations from indoor stationary monitoring were approximately one-half of those observed in matched outdoor sampling. Analysis of this same sample set revealed a high degree of correlation between indoor and outdoor pollution levels using several elements and individual PAHs. Concentrations of individual species, B(a)P for example, measured outdoors of the participants work site on various days of the study, were within the same order of magnitude with those collected by different sampling techniques at three Ostrava ambient monitoring sites. This would indicate that pollutant concentration data from the primary monitoring sites should relate to exposure biomarkers for individuals working at the KHS-Ostrava central study site.

This report covers the period from November 1995 to January 1997. Biomarker studies will be reported at a later date.

Contents

Abstract iii
Figures v
Tables vi
Acknowledgment vii

1. Introduction 1
2. Summary 3
3. Recommendations for Future Work 5
4. Experimental 6
   - Personal Exposure Monitoring Study Design and Testing Regimen 6
   - Indoor/Outdoor Study Design 6
   - Sample Processing 8
   - Use of Personal Monitors 8
   - PEM XAD-2 Extraction 9
   - PEM Filter Extraction and PAH Sample Preparation 9
   - Indoor/Outdoor Filter Extraction and PAH Sample Preparation 10
   - XRF Elemental Analysis Procedures 10
   - PEM and Indoor/Outdoor PAH Analysis Procedures 10
   - Biological Sample Processing and Analysis 11
5. Results and Discussion 12
   - PEM and Biomarker Sample Collection 12
   - PEM $PM_{2.5}$ Mass Analysis 12
   - PEM $PM_{2.5}$ PAH Analysis 13
   - Indoor/Outdoor $PM_{2.5}$ Mass and PAH Analysis 16
   - Indoor/Outdoor $PM_{2.5}$ XRF Elemental Analysis 17

References 19

Figures

Figure		Page
1.	Fine Particulate Matter Personal Monitor	20
2-11.	$PM_{2.5}$ Mass Concentrations from Personal Monitoring	21
12-15	$PM_{2.5}$ B(a)P Concentrations from Personal Monitoring	31
16-19.	$PM_{2.5}$ Total Carcinogenic PAH Concentrations from Personal Monitoring	35
20.	Correlation of Personal Monitoring $PM_{2.5}$ B(a)P and Total Carcinogenic PAH	39
21.	Correlation of Personal Monitoring $PM_{2.5}$ Mass and B(a)P	40
22-31.	$PM_{2.5}$ Mass and B(a)P Concentrations Depicted by Residence Locations	41
32.	Daily Variation of Indoor and Outdoor $PM_{2.5}$ Mass Concentration at KHS-Ostrava from Stationary Monitoring	46
33.	Daily Variation of B(a)P and Total Carcinogenic PAH Concentration at KHS-Ostrava From Stationary Monitoring	47
34.	Daily Variation of B(a)P to Lead Ratio at KHS-Ostrava From Stationary Monitoring	48

Tables

Table		Page
1.	Personal Monitoring and Biomarker Study Design	49
2.	HPLC Conditions for PAH Analysis	50
3.	Collection Results of Environmental and Biological Samples	51
4.	Results from Fine Particulate Matter Personal Monitoring	53
5.	Results from PAH Personal Monitoring	54
6.	Total Carcinogens Measurements from Personal Monitoring	55
7.	Indoor/Outdoor Sample Collection Results	56
8.	Comparison of Regional Outdoors B(a)P Concentration	57
9.	Elemental Analysis Results from Indoor Monitoring	58
10.	Elemental Analysis Results from Outdoor Monitoring	59
11.	Correlation of Paired Elemental Species from Indoor and Outdoor Monitoring	60
12.	Indoor/Outdoor Metal Concentration Ratios	61

Acknowledgment

The authors would like to thank Anna Phillips and Jane Metcalf of the U.S. Environmental Protection Agency (USEPA) for their administrative and financial support throughout the scope of the study. The authors also acknowledge the contributions of J. Kusova, M. Lorkova, R. Rakusova, M. Skopalova, J. Tvrda, M. Adamcik, and J. Lvoncikova from KHS-Ostrava for their contribution in the collection of environmental and biomarker samples described in this report; James Scott (USEPA) for assisting in PAH filter extraction; Dina Schreinmachers (USEPA), Debra Walsh (USEPA) , Debra Costa (UNC-CH), and for their technical review of the document; Robert Stevens (Florida Department of Environmental Protection) and Rebecca Calderon (USEPA) for their editorial and technical comments.

Section 1
Introduction

A collaborative research program involving the Czech Ministry of Environment, the Czech Institute of Hygiene (KHS-Ostrava) and the U.S. Environmental Protection Agency (EPA) has been ongoing since 1992. The objective of this program is to reduce the uncertainties in the risk assessment of polycyclic organic matter (POM) and polynuclear aromatic hydrocarbons (PAH) adsorbed to respirable particles through research on human exposure, biomarkers of exposure, dose, susceptibility and cancer risk. The best human cancer risk data is based on studies of coke oven workers, therefore Ostrava was selected for these studies since the town includes several large active coke ovens. Previous studies conducted as part of this research program have focused on the highest human exposures found in coke oven workers. Results from these studies show that coke oven workers are exposed to extremely high and variable levels of fine particulate matter (30-17,000 $\mu g/m^3$) and polynuclear aromatic hydrocarbons [benz(a)pyrene 6-42,000 ng/m^3]. Supporting data from biomarker studies of these same workers revealed that at high concentrations of environmental exposures the formation of DNA adducts may be nonlinear (Lewtas et al., in press). Other studies have been conducted in the Czech Republic on residents and workers exposed to much lower concentrations of particles and PAH than those from coke oven workers (Watts et al., 1994; Binkova et al., 1995).

The primary objective of this study is to improve our understanding of the relationship between ambient and personal exposures in Ostrava for a typical population not occupationally exposed to coke oven emissions. The PAH exposures were assumed to be substantially lower than observed for coke oven workers and higher than previously reported for ambient exposures in Northern Bohemia. Furthermore, the study was designed to evaluate variability of exposure and dose both within and between individuals over a four week period. This study was conducted through a collaboration between the US EPA Office of Research and Development National Laboratories (National Exposure Research Laboratory, NERL and National Health and Environmental Effects Research Laboratory, NHEERL), Czech Hydrometeorological Institute (CHMI), and the Ostrava Regional Institute of Hygiene (KHS-Ostrava). The Ostrava Exposure Monitoring Project, also known as Project Silesia, involved the collection of a range of continuous real-time as well as time-averaged environmental pollutant measurements. Three stationary monitoring platforms located strategically around three (3) major coke ovens in Ostrava, Czech Republic were utilized to collect ambient pollutant concentrations of PAH, volatile organic compounds, metals, volatile carbon, coarse and fine particulate mass, SO2, NO/NO2/NOX, and CO. Meterological parameters at the sites were also measured.

The personal exposure and biomarker component of this study, reported in part here, was conducted with volunteers from KHS-Ostrava over a 4 week period (The Ostrava Human Exposure and Biomarker Study). KHS-Ostrava is located within the area bracketed by the stationary monitoring platforms. Daytime and nighttime $PM_{2.5}$ measurements were performed on each volunteer and PAH analysis conducted upon the collected particulate matter. Blood and urine specimens were collected from these same 30 individuals for exposure, dose, and susceptibility biomarker analysis (studies in progress). Volunteers were selected to represent a range of distribution of possible nighttime (home) exposures based on the proximity of residences

to the known pollutant point sources (e.g., coke ovens). Individual PAH exposures within the 4 week study were expected to vary due to changing meteorological conditions. This variation in exposure across the 4 repeated sampling periods will be used to evaluate within and between individual variability in both personal exposure and biomarkers of exposure and dose.

A second component of the Ostrava Health Study investigated the relationship between indoor and outdoor concentrations of $PM_{2.5}$ and select subspecies. Matched fine particulate matter samplers were operated at KHS-Ostrava and operated for a 2 week period. Concentrations of $PM_{2.5}$ mass, PAH, and selected elemental species from collected samples were determined during the event.

This report details the study design, sampling and chemical analysis of the personal of personal exposure samples, and collection of the human samples for biomarker studies. Individual as well as average exposures to environmental pollutants are reported here. Comparisons are made between daytime and nighttime personal exposures relating to various geographical locations within the city of Ostrava, Czech Republic. Biomarker studies are in progress and will be reported at a later date. Correlation of outdoor and indoor pollutant concentrations of select species is described. Recommendations for future studies are also provided.

Section 2
Summary

The principal objectives of the Ostrava human exposure and biomarker study were the following:

1. To improve our understanding of the relationship between ambient and personal exposures in Ostrava for a typical population not occupationally exposed to coke oven emissions.
2. To determine individual and population exposures to fine particulate matter ($PM_{2.5}$) and the associated particle-bound polynuclear aromatic hydrocarbons (PAHs).
3. To determine the relationship between indoor and outdoor exposures for this population.
4. To evaluate the relationship between the coke oven source of emissions and personal exposure.
5. To evaluate variability of exposure and dose both within and between individuals over a four week period.

This report provides the detailed sampling and chemical analysis report for the personal exposure and indoor/outdoor component of the Ostrava 30 day study. A second study performed concurrent with this study and not reported here (R. Willis et al., 1997), describes the ambient exposure concentrations across the town of Ostrava over the same 30 day period. The biomarker studies are in progress and will be reported separately at a later time.

An investigation of the relationship between outdoor and indoor air particle concentrations at the participants work site (KHS-Ostrava) was conducted simultaneously with the personal monitoring biomarker exposure assessment study. Results of the studies reported here are summarized below:

- Planned collection of biological and environmental samples as part of the associated health study was successful (99, 85% respectively). A total of 30 volunteers from diverse occupations within the KHS facility participated in the health study over a period of 4 weeks. These participants included nurses, physicians, biologists, tradesmen, etc. All were nonsmokers with no known occupational exposure to PAHs. Their residences were located in geographically diverse areas of Ostrava.

- Personal exposure monitoring (PEM) for fine particle ($PM_{2.5}$) concentrations ranged from 14.5-474 $\mu g/m^3$. Daytime concentrations averaged 90 $\mu g/m^3$ over the 4 week period with nighttime concentrations averaging 43 $\mu g/m^3$. Residential particle exposure concentrations were therefore approximately one-half of daytime concentrations at the KHS facility. The mean 24 hour exposure for the entire study was 57 $\mu g/m^3$. Significant individual variations in particle exposures were observed and explained by 24 hour personal activity logs.

- Total carcinogenic PAH concentrations from individual personal air monitoring were found to vary between 0.4-393 ng/m^3 and averages for all participants over the 4 week study ranged from 17-45 ng/m^3. Concentration of benzo(a)pyrene [B(a)P], as well as

other carcinogenic PAHs, were higher in daytime samples collected from the participants at the central work site (KHS-Ostrava) compared to those from nighttime samples from individual residences located throughout the city (4.7 versus 3.5 ng/m^3 respectively). The average 24 hour exposure to B(a)P was 3.9 ng/m^3. B(a)P concentrations correlated with total carcinogenic PAH but did not correlate with personal fine particle concentrations.

Results from stationary indoor and outdoor monitors at the participants work site (KHS in central Ostrava) showed correlations for particle concentrations and for B(a)P concentrations. X-ray fluorescence (XRF) analysis of indoor and outdoor particles revealed significant concentrations for the elements like barium, zinc, iron, copper, bromine, titanium, manganese and lead among others. The ratios of B(a)P to lead (lead is a tracer for emissions from gasoline powered vehicles) indicates significant PAH sources other than these vehicle emissions.

Section 3
Recommendations for Future Work

1. Complete the analysis of select biomarker samples. This involves work earlier proposed by the research staff at KHS-Ostrava as well as those of NHEERL. Coordination of efforts between the respective laboratories should occur to focus efforts upon prime samples of interest.

2. Personal exposure data should be integrated with both ambient exposure data and individual biomarker concentrations when these data are available. This would include DNA-adduct, albumin adducts or other assays available to investigate the question of individual variation in exposure-biomarker relationship.

3. Perform matched indoor and outdoor exposure monitoring at various Ostrava locations and building types to further investigate fine particle infiltration.

4. Initiate epidemiological studies relating ambient $PM_{2.5}$ concentrations to physiological and biochemical responses in select populations. Variations in $PM_{2.5}$ mass concentrations among study participants and during the course of the study offer an excellent opportunity to investigate presumed physiological health effects resulting from fluctuating $PM_{2.5}$ mass concentrations.

5. Biomarker susceptibility profiles should be performed upon each volunteer involved in the study utilizing metabolic genotyping techniques.

Section 4
Experimental

Personal Exposure Monitoring Study Design and Testing Regimen

A personal exposure monitoring component of the project was conducted using 30 volunteers from the Ostrava Institute of Hygiene (KHS) during October 16th- November 9th 1995. These were non-smokers and non-occupationally exposed adults (age 30-50 years old) who received no compensation for their involvement. The 30 volunteers (12 male, 18 female) were divided into two 15 member groups to permit the KHS Department of Genetic Toxicology a reasonable amount of time to perform ambient personal monitoring as well as collect and process human biological specimens during each week of the study (a total of 4 weeks). The test subjects were issued one flow-calibrated personal exposure monitor (PEM) at approximately 8 am on Monday (group 1) or Thursday (group 2) of each week with instructions as to its operation. The PEMs were placed on each volunteer so that the inlets of the units were within their respective breathing zone. Each volunteer was then given two vessels for collection of urine with instructions to collect their next void specimen and return it to the study coordinators (refrigerated when immediate return was not possible). Volunteers were instructed to collect their first void of the next morning and bring it with them to the study center. Each volunteer returned to the study center at approximately 4:00 pm on the day the PEM was first issued where the existing PEM was replaced with a new PEM. This changing of PEMs was conducted so that $PM_{2.5}$ measurements could be obtained from each group of volunteers during their work hours (hereafter called daytime samples) at the central site (KHS-Ostrava) as well as from their respective non-work residences and habits (hereafter called nighttime samples).

Volunteers returned to the study center on the following morning with a freshly collected urine specimen. Personal monitors were recovered from each individual by the study staff who then administered a questionnaire regarding the past 24 hours (e.g., type of residence, home location, work and home activities, passive smoke exposure). A 20 ml blood specimen was then collected from each respondent (20 ml via an EDTA-treated vacutainer tube). Volunteers were then instructed about returning for the next sampling period (one-24 hour period for four consecutive weeks). Individuals were placed upon either a Monday-Tuesday or a Thursday-Friday schedule at initiation of the study with no changes allowed during the four weeks. A summary of planned environmental and biological specimen collection is presented in Table 1.

Indoor/Outdoor Study Design

Experiments were designed to investigate the relationship between indoor and outdoor air at KHS-Ostrava. The KHS site was selected based upon criteria such as availability of study personnel to operate the samplers, the presence of an existing monitoring platform (with weather protection) and the fact that KHS-Ostrava was in a geographically acceptable location relative to the three NERL/CHMI stationary monitoring sites incorporated into Project Silesia.

One cyclone-equipped $PM_{2.5}$ fine particulate matter sampler (University Research Glassware, Carrboro, NC) was placed at the 2 meter level within an unoccupied office on the ground level of the KHS's main building (hereafter called indoors). This site was co-selected by KHS and EPA investigators on the basis of noise concerns about positioning the accompanying 10 l/min air sampling pump, the relative infrequency of foot traffic into the room and the fact that it was representative of offices found throughout the facility (furnishings). The selected office was separated from a main automotive thoroughfare by a distance of approximately 50 meters with approximately a 60 space employee parking lot located within 10 meters of the office windows. Room temperature was controlled by adjusting radiator controls within the office and by the opening and closing of large windows. At times throughout the study, wind originating outside was easily detectable in the vicinity of the indoor fine particle sampler. This was without doubt the result of air movement passing through the open windows.

A second URG $PM_{2.5}$ fine particulate matter sampler was placed at an outdoor particulate monitoring platform located behind the Department of Genetic Toxicology at an inlet height of 2 meters. Co-located at this site were other KHS-Ostrava particulate monitoring instruments not related to this study. This site was buffered from automotive traffic by a 25 meter wide tree-covered park on one side with a distance of 10 meters separating the monitoring platform from the wall of an adjacent KHS building.

Stationary indoor and outdoor fine particulate matter sampling was performed during the period of October 27th-November 9th to coincide with personal and primary stationary site monitoring that was underway in the overall study. Sampling was performed by placement of a single tared 47 mm Teflon (Gelman) Teflon filter within the filter pack of each sampler at approximately 8:00 am each day. Each sampler's pump was then calibrated to achieve a flow rate of 10 ± 0.1 L/min. Filters were recovered from each sampler after 24 hours and exchanged with fresh filters. Total collected flow (m^3) was determined for each sampling period by direct measurement using an in-line dry gas meter (Schlumberger-Gallas 2000). Collected filters were returned to CHMI laboratories where mass loadings were determined following 24 hour equilibration at constant temperature and humidity.

Area air monitoring was conducted at three monitoring platforms operated by the Czech Hydrometeorological Institute, the Regional Hygiene Institute in Ostrava and NERL (EPA). These sites were located in Privoz, Radvanice, and Zabreh districts of Ostrava. Each was chosen due to their proximity to large, medium and small ambient air pollution point sources and to their respective locations that triangulated the city as a whole. The platforms were operated in a time period to coincide with the personal exposure study. Species monitored included PAH, volatile organic compounds, metals, volatilizable and elemental carbon, coarse and fine particulate mass, SO_2, $NO/NO_2/NOX$, and CO. Meterological parameters at the sites were also measured. Detailed results from this monitoring is reported elsewhere (R. Willis et al., 1997).

Sample Processing

The study staff returned all collected environmental and biological samples to laboratories within the Department of Genetic Toxicology where sample processing and recovery was initiated. Each PEM was audited for a final flow rate which was averaged with the initial calibration flow to yield an average used in calculation of the total collected air volume (the product of the elapsed run time and the average flow rate). Pre-tared Teflon- impregnated glass fiber (TIGF) filters were removed from each PEM using clean stainless steel tweezers and placed within a constant relative humidity chamber for 24 hours to achieve hygroscopic equilibration. $PM_{2.5}$ mass loading was then determined by reweighing each filter using a microbalance sensitive to 0.01mg. Weighed filters were then placed within individual storage vials. XAD-2, contained within the vapor-phase collection module of each sampler, was decanted into separate glass storage vials and sealed with Teflon-lined screw caps. Filter and XAD-2 samples were stored at -40°C awaiting either KHS analysis or transport to US EPA laboratories.

Aliquots from each collected urine sample were transferred by the study staff into plastic vials for future or possible analysis: creatinine (Czech), metabolic genotyping (Czech) 1-hydroxypyrene(Czech), mutagenicity (Czech), cotinine (EPA), metabolic genotyping (EPA), PAH metabolites (EPA), DNA and albumin adducts (EPA). Storage at -40°C was utilized prior to any analysis.

Blood specimens were processed immediately after their collection by the staff using standard KHS clinical procedures for recovery of serum, white and red blood cells. Components of whole blood were processed and ultimately transferred to plastic tubes for storage at -40°C until analysis by KHS-Ostrava investigators or transport to US EPA laboratories.

Use of Personal Exposure Monitors (PEMs)

This study involved use of a $PM_{2.5}$ size-selective impactor to allow for the collection of respirable suspended particulate (RSP). The device selected was one designed by the US Environmental Protection Agency as reported in detail by (Williams et al., 1992; Watts et al., 1994). A depiction of the device is presented in Figure 1. In summary, the PEM consists of a Teflon coated aluminum elutriator operated at a face velocity of 5.1 cm/sec which when connected to a specially designed impactor assembly, focuses particles having an aerodynamic diameter of >2.5 μm onto the impactor surface. The impactor is a removable 4.5 mm borosilicate disc coated with 6 μl of 1:1 (v/v) 400 polyethylene glycol:600 polyethylene glycol. Non-impacted particles (ie, $\leq PM_{2.5}$) are transported past the impactor by aerodynamic forces into a Teflon coated aluminum tube which corrects the flow for non-laminar properties. The coarse particle-denuded airstream then enters a staged 25 mm diameter Teflon filter pack. Each stage of the filter pack is separated by Teflon O-rings and Teflon-coated stainless steel support screens. Only one filter (25 mm TIGF, Pallflex T60A20) was necessary per sampling event and thus only one stage was required. The filter utilized has properties that reportedly collects 99.9% of particles having an aerodynamic diameter of ≥ 0.5 μm. Particle-denuded air was then channeled

into an attached Teflon resin cartridge. The cartridge has an interior void dimension of 1 X 5 cm (width X depth) with a total volume of 3.9 cm^3 available for use. A total mass of 2-2.5 g (dry weight) of 20/40 mesh size styrene-divinylbenzene, having the trade name of XAD-2 (Rohm & Haas, USA) was utilized to collect vapor-phase components in the airstream.

Flow was brought into and through the above connected assemblies (inlet, filter pack, and vapor phase cartridge) by means of a battery powered personal air sampling pump. The Shibata MP-15CF was selected for it's ability to run continuously for 24 hours using a single set of alkaline batteries (8/pump) as well as it's flow constant capabilities. Each sampling pump was calibrated to have a flow rate of 1.5-1.7 l/min after new batteries had been installed and allowed to discharge for 0.5 hours while attached to a blank PEM. Calibration was performed by configuring the flow through an EPA primary standard calibrated flowmeter while a complete PEM (inlet, filter and XAD-2 cartridge) prepared for field use was attached.

PEM XAD-2 Extraction

Chemists from KHS-Ostrava had the responsibility to extract all XAD-2 samples associated with the personal monitoring. The proposed technique involved the addition of 25 ml of high purity dichloromethane into each borosilicate vial containing recovered XAD-2. The contents of each vial was to be thoroughly vortexed for 10 minutes using a mechanical process. At that time, the extract from each vial was to be decanted into individual, solvent cleaned, borosilicate tubes capable of holding 100 ml of volume. A fresh 25 ml aliquot of dichloromethane was to be added to the original sample vials and the vortex process repeated for another 10 minutes. Recovery of this extract with quantitative transfer would complete the extraction. As of this date, the extraction and subsequent PAH analysis of XAD-2 samples associated from personal monitoring has not been completed by KHS scientists.

PEM Filter Extraction and PAH Sample Preparation

TIGF filters from each PEM were transferred to US EPA laboratories for extraction and PAH analysis. Filters were removed from their individual storage containers and singularly placed within dichloromethane cleaned 4-dram borosilicate vials. A 20 ml aliquot of dichloromethane (DCM) was added to each vial followed by sonication extraction for 10 min (25°C). Extract from each vial was decanted into individual 100 ml borosilicate culture tubes. The above extraction process was repeated a total of 3 times. Quantitative transfer of the final extract was completed by rinsing the filter and extraction vial with 3 X 5 ml volumes of DCM and transferring this to the collection tube.

Extracts were then concentrated down to a volume of approximately 5 ml using nitrogen evaporation (35°C). Concentrates were then quantitatively transferred into borosilicate syringes

equipped with 0.45 micron Teflon filters. Filtrates were collected in 15 ml borosilicate conical centrifuge tubes where they were subsequently placed under nitrogen evaporation (35°C) for concentration/solvent exchange purposes. Concentration was intermittently stopped to permit vortex mixing (1 minute) as volumes approached 5 and 1 ml. Solvent exchange was completed by nitrogen evaporation of the last 1 ml volume of DCM residing in each centrifuge tube with it's immediate replacement with 0.5 ml of HPLC-grade acetonitrile. Vortexing of each solvent-exchanged sample was then performed to ensure displacement/solvation of PAH residues from the interior walls of the vessels. DCM cleaned borosilicate pipets were utilized to transfer 200 µl of each extract prepared for HPLC analysis into individual borosilicate autosampler vials (amber with inserts). Autosampler vials awaiting analysis were stored at -30°C until HPLC was performed.

Indoor/Outdoor Filter Extraction and PAH Sample Preparation

The outside retaining (handling) ring of each Teflo filter was removed using stainless steel scissors because of it's incapability with the extraction solvent (DCM). Each filter was then individually placed into DCM cleaned 4 dram borosilicate vial for extraction and workup as immediately described above for PEM filters.

XRF Elemental Analysis Procedures

Multi-elemental energy dispersive X-ray fluorescence (XRF) analysis was performed by US EPA contractors (ManTech Environmental) using EPA-approved procedures. The instrument utilized was custom designed by Lawrence Berkeley Laboratory and has features specialized for the analysis of environmental pollutants collected upon filter media. The excitation tube is operated in a pulsed mode with a 83 µsec off-time immediately after x-ray detection. A cryogenically cooled lithium-drifted silicon detector allows for optimized collection of x-rays. Four secondary fluorescent targets (Ti, Co, Mo, and Sm) are sequentially excited by the X-ray tube to optimize sensitivity. Both vacuum-deposited metal film as well as polymer film standards are used in the calibration of the instrument. Standard reference materials (NIST#1832 and #1833) are measured before and after each analytical run to validate daily calibration. An accuracy of $\pm$ 10% has been established for the methodology.

PEM and Indoor/Outdoor PAH Analysis Procedures

PAHs were analyzed using analysis high performance liquid chromatography (HPLC) coupled with time-programmable fluorescence detection. The basis behind the techniques have previously been reported (Williams et al, 1994, Watts et al, 1994). In essence, HPLC is utilized to resolve complex environmental extracts containing PAHs into individual peaks where optimized fluorescence excitation and emission wavelengths are utilized to increase both analyte sensitivity and specificity. Duplicate 20 µl aliquots of each solvent exchanged extract were automatically injected into an HPLC configured for PAH analysis. This system consisted of a

Varian Star (v. 4.0) data station connected to a Varian 9095 autosampler, a Waters 680 gradient controller and one Waters 510 pump. A 25 cm X 4.6 mm Supelco LC-PAH column was utilized to achieve chromatographic resolution of the PAHs of interest. A 40°C isocratic solvent composition of helium sparged 90:10 (v/v) acetonitrile:water flowing at 1.5 ml/min eluted extract components into a Perkin Elmer LS40 fluorescence detector. The detector was operated at conditions to achieve acceptable analyte sensitivity and specificity as listed in Table 2.

Multipoint calibration curves for each PAH were established for each 24 hour chromatographic run sequence (3 X 4 concentration levels). Solvent and field filter blanks were run throughout each sequence to document system and method contamination. Raw PAH retention and peak area data was analyzed using the Varian Star (4.0 software) to obtain summarized PAH concentrations. Summarized PAH data was then manually transcribed into spreadsheets (Excel v 5.0) where sample collection information was incorporated to yield individual and total ambient PAH concentration level. Graphic representations of PAH and $PM_{2.5}$ fine particulate mass data from the study were prepared by manipulation of the spreadsheets discussed above (Excel v 5.0).

Biological Sample Processing and Analysis

The analysis of biological specimens will not begin until the spring of 1997. This is due to the desire of Czech and US EPA researchers to define subgroups of those participating in the study for an intense investigation into the variability of biomarkers as they relate to ambient exposure. It is expected that results from the analyses listed below will be completed or initiated in 1997. Details of each, as well as results, will be reported at the conclusion of the biomarker studies at a later time.

<u>Pending Biomarker Study Analyses</u>

Creatinine -Pending reporting by KHS-Ostrava
Metabolic genotyping-Pending analysis and reporting by KHS-Ostrava
1-hydroxypyrene-Pending reporting by KHS-Ostrava
Mutagenicity-Pending reporting by KHS-Ostrava
Cotinine-Pending analysis and reporting by US EPA
Metabolic genotyping-Pending analysis and reporting by US EPA
PAH metabolites-Pending analysis and reporting by US EPA
DNA and albumin adducts-Pending analysis and reporting by US EPA

Section 5
Results and Discussion

PEM and Biomarker Sample Collection

The successful collection of biological and environmental specimens associated with the health study is depicted in Table 3. Nearly 100% of the samples desired in the health study were collected. Two individuals had illness or hospitalizations that temporarily removed them from the project (ID#2,28) but all other subjects completed all required collections (environmental or biological). Collection of biological samples was without complications due to the concerted effort of KHS-Ostrava investigators. Personal monitoring was somewhat more difficult in that while an attempt to collect every sample was exerted some equipment failure was noted. PEM air sampling pump failure was often the result of suspect alkaline batteries. A total of 15% (36/240) of the PEM collections were removed from the data base after US EPA quality assurance procedures because of flow rate fluctuations exceeding 20% of initial set point values or inappropriate flow rate settings during sampling. Missing values observed for data points for individuals in figures discussed throughout this results section ($PM_{2.5}$ mass, PAH, carcinogenic PAH) are the result of these quality assurance procedures.

While an effort to have 50/50 participation of male/female in the study was desired, it was not found possible. The final study population reflected a greater participation by female volunteers at KHS-Ostrava (18 out of 30). Volunteers expressed few complaints about either wearing the PEM or providing blood and urine specimens. This was attributed to the great enthusiasm displayed by Czech investigators leading the study at KHS-Ostrava and the sincere interest of the volunteers in participating. No "drop-outs" from among the volunteers occurred over the course of the 4 week study.

PEM $PM_{2.5}$ Mass Analysis

Individual, average and total exposures to $PM_{2.5}$ from PEM sampling is shown in Figures 2-11. Each of the figures is broken down to specify collection period, volunteer ID (or grouping), respirable particulate matter (RSP), concentration in $\mu g/m^3$, day and nighttime sampling. Note that volunteers 1-15 represent $PM_{2.5}$ Monday-Tuesday sample collections while ID numbers 16-30 represent Thursday-Friday collections. Thus, there may be notable differences in data from the two groups as influenced by ambient weather and pollution episodes changing during each of the 4 weeks. $PM_{2.5}$ mass exposure for the 30 participants is summarized in Table 4. A west-southwest wind pattern dominated weeks 1-3 while week 4 had a weather pattern where winds fluctuated from the southwest/north-northwest. Summarization of daytime and nighttime exposures are presented in Figures 6 and 7.

The summary listed on Table 4, indicates that daytime concentrations of RSP greatly exceeded that of nighttime periods. The overall daytime mean RSP concentration for all

participants was determined to be statistically higher ($P<0.0001$, $\alpha= 0.05$). This was somewhat expected due to the fact that daytime sampling was centered around KHS-Ostrava which is located near operating coke oven and steel work facilities (Sverma and Vitkovice) while nighttime sampling was influenced by a wide distribution of homes throughout Ostrava. Daytime sampling ranged from 14.5-474.6 $\mu g/m^3$ over the course of 4 weeks with an average of 90.3 $\mu g/m^3$ observed. This average was highly influenced by volunteers like #2, 14, 16, 29 and 30 who often had daytime exposures 2-5 fold higher in comparison to other KHS-Ostrava staffers. Personal survey information was reviewed to determined what conditions were prevalent that separated these and similar individuals in terms of their RSP exposures. A cursory investigation determined that exposure to pollutants from passive cigarettes, cooking aerosols, machinery, or in the case of volunteer #30, fine wood dust might account for the elevated exposures. A more sophisticated analysis will have to be performed to fully investigate the findings. RSP concentrations were found to fluctuate during the four weeks with week 4 having an appreciably lower average concentration than that encountered during weeks 1-3 (35 $\mu g/m^3$). This was probably the result of changing wind conditions discussed above.

Results from nighttime RSP collections revealed that while concentrations fluctuated between the 30 volunteers, they were not of the same magnitude as that observed in the daytime central site data (KHS-Ostrava). Rarely was a 2 fold difference observed during a given week between individual exposures regardless of where they lived within the city. Nighttime concentrations ranged from 5.1-281.8 $\mu g/m^3$ during the entire study with an overall average of 43.2 $\mu g/m^3$. Averages from individual weeks ranged from 22.3 $\mu g/m^3$ (week 4) to 58.9 $\mu g/m^3$ (week 3).

Calculations were performed that summarized each individual's total 24 hour RSP exposure (Figures 8-11). Pooling all 30 individuals/week resulted in a range of 27.6-77.8 $\mu g/m^3$ weekly. The overall 4 week average was 57.3 $\mu g/m^3$. Week 4 was found to have 24 hour ambient RSP concentrations that would be typical of one relatively free from commonly encountered industrial/residential emission sources (27.6 $\mu g/m^3$) . It should be kept in mind that northern wind patterns dominated meteorological conditions during the first half of week 4 as reported by CHMI platform monitoring not detailed in this report. This in effect would drastically alter the normal industrial-influenced RSP fallout in Ostrava.

PEM $PM_{2.5}$ PAH Analysis

PAH analysis from the individual PEMs indicated detectable levels of carcinogenic PAHs were present in most of the collected samples, especially those collected at KHS-Ostrava. Measurements were performed for the IARC listed animal carcinogenic PAHs detailed in Table 2. Pyrene was measured but is not a listed carcinogen and was not included in total carcinogenic PAH levels described here. Benz(a)anthracene, benz(a)pyrene, benzo(ghi)perylene, and indeno(cd)pyrene were often found to be the dominant species (by concentration) of those investigated. Overall detectability of PAHs was hindered by having two sampling periods for

each 24 hours (8- hour daytime, 16- hour nighttime). This division reduced the total sample available for analyte determination as compared to normal 24 hour integration, nevertheless, quantification was possible within quality assurance margins.

Benz(a)pyrene concentrations determined from PEM analysis are presented in Figures 12-15. Daytime versus nighttime sample collection periods are depicted in the figures for each week of the study. A summary of this data is shown in Table 5. Daytime B(a)P concentrations were found to range from 0.7-22.0 ng/m^3 during the study with a 4-week average of 4.7 ng/m^3. There were some individual variation in B(a)P concentrations observed for daytime sample collections, generally within 2-5 fold of the overall high-low extremes. Monday-Tuesday versus Thursday-Friday sample collections also revealed observable daytime B(a)P concentration variations.

Daytime B(a)P concentration patterns followed those observed with RSP determinations with the exception of measurements during week 2 (ie, daytime having higher concentrations than nights). During this week, average nighttime B(a)P concentrations were nearly twice the daytime values (6.5 vs 3.6 ng/m^3) respectively. Nighttime values represent exposures during non-work hours and would typically reflect travel and home indoor conditions. An explanation for this atypical finding has not been proposed at this time. Nighttime B(a)P concentrations were found to range from 0.3-22.0 ng/m^3 during the 4 weeks. Average weekly concentrations ranged from 1.1-6.5 ng/m^3 with an overall monthly average of 3.5 ng/m^3. The overall daytime mean B(a)P concentration for all participants was determined to be statistically higher in comparison to nighttime exposures ($P<0.0229$, $\alpha= 0.05$).

Total B(a)P exposure during the 24 hour sample collection period was calculated for each participant as the sum of daytime and nighttime exposures. Weather conditions were probably responsible for the low 24 hour average exposure concentration observed for week 4 (2.5 ng/m^3). This week also had low RSP values (overall average <30 μg/m^3) suggesting that PAH exposures observed during this week are probably background levels contributed by mobile source or similar urban emissions with only minor influences from industrial sources (e.g., coke oven batteries). An overall 4 week 24 hour average of 3.9 ng/m^3 of B(a)P was observed from summarizing exposure from all individuals. Week 2 collections were found to have the highest 24 hour totals (6.0 ng/m^3), again heavily influenced by nighttime exposures.

Individual carcinogenic PAH concentrations, the sum of 8 IARC listed animal carcinogens, were utilized to obtain a value of total carcinogenic PAH exposure. Graphic depiction of this data is shown in Figures 16-19. Summary of the individual exposures is presented in Table 6. Variability was observed between given individuals and collection periods which followed the pattern observed in both the fine particulate matter and B(a)P measurements. An exposure range of 0.4-393.2 ng/m^3 for daytime sample collections occurred over the 4 week period. Week 1 had the highest overall daytime average of 68.6 ng/m^3 and week 4 exposures had the lowest overall daytime average of only 18.8 ng/m^3. The standard deviation calculated between individual total carcinogen exposures within each week of sampling revealed a high

degree of fluctuation (overall 4 week standard deviation average of 21.9 ng/m^3). The 4 week overall daytime average for total carcinogenic PAH exposure was calculated to be 36.6 ng/m^3.

Nighttime total carcinogen exposures for week 2 followed the pattern established in analysis of the B(a)P data, i.e., higher nighttime than daytime exposures (average of 46.7 ng/m^3). A range of 0.5-226.6 ng/m^3 was revealed over all nightime personal monitoring during the 4 weeks with an overall average of 25.8 ng/m^3 calculated. Review of the average weekly exposures indicated that weeks 2-3 had approximately 3-4 fold higher ambient nighttime concentrations in comparison to weeks 1 and 4 . Cumulative total carcinogen (24 hour) exposures were calculated for each individual and averaged for each week. The average 24 hour exposure ranged from 17.4 ng/m^3 (week 4) to 44.7 ng/m^3 (week 2) with an overall average of 29.0 ng/m^3. The overall daytime mean total carcinogenic PAH concentration for all participants was determined to be statistically higher in comparison to nighttime exposures ($P<0.0489$, $\alpha= 0.05$).

Comparison of exposure data collected from all 4 weeks of the personal monitoring revealed B(a)P correlations of $R^2=0.7706$ in relation to total carcinogenic PAH concentrations. This is graphically depicted in Figure 20. This correlation is important in that B(a)P levels may be used as a significant indicator of overall PAH exposures in future studies when conditions similar to those encountered here are present. Cumulative RSP and B(a)P concentrations from the entire study failed to correlate as graphically depicted in Figure 21. This result would indicate that RSP determinations alone would not be an acceptable indicator of personal ambient exposure to PAHs, including those that are carcinogenic in this study. This finding is consistent with the "personal cloud" concept. RSP data from personal monitoring often fails to correlate well with stationary monitoring because of the human interaction with dust and dust-laden surfaces that stationary monitoring does not take into account. A more thorough statistical evaluation of individual as well as total carcinogenic PAH concentrations with respect to RSP findings will be necessary to fully understand their relationship.

Because the 30 volunteers involved in the personal monitoring lived throughout different parts of Ostrava, data from their nighttime collections were investigated as to RSP and B(a)P concentrations and either Monday-Tuesday or Thursday-Friday collection periods.. Ostrava was geographically broken down into three sections based approximately upon distribution of benzene soluble organic (BSO) concentration data determined in 1993-95 by KHS-Ostrava and other Czech Republic Ministries (Report No 5-Silesia Environmental Health Report, 1995). This distribution basically divides the western half of the city into one part (group#1) with the remaining eastern side divided horizontically into two portions at approximately the center of Ostrava (northeastern distribution was labeled group #2, southeastern distribution labeled group #3). Groups 1,2,3 were broken down into participants numbering 10,11, and 9 respectively. Pollutant concentrations of all individuals living within the specified group were averaged. Average pollutant concentrations, including the location of individual homes, dominant wind patterns (seen as arrows within the maps), coke oven and monitoring sites are shown in Figures 22-31.

Review of this spatial distribution of ambient nighttime RSP and PAH concentrations would indicate that when west/southwest or westerly winds dominate meteorological conditions, individuals living within group #1 experienced the lowest average B(a)P exposure in relation to the other groups. Averages from all 4 weeks revealed that group #1 had overall B(a)P concentrations ranging from 2.60-3.01 ng/m^3 (Monday and Thursday, respectively) with group #2 and #3 experiencing average monthly concentrations of 3.94-4.84 and 3.63-2.79 ng/m^3 B(a)P (Monday and Thursday, respectively). Review of this same data would support the concept presented in the 1995 Czech report on BSO data that residents living within the geographical area represented by Group #2 (central to east-north/northeastern Ostrava) are exposed to higher overall B(a)P concentrations in comparison to other locations (Vit et al, 1995). Statistical analysis conducted on all nighttime exposure measurements relative to the three groups indicated that group#3 participants experienced the highest overall RSP exposures for the 30 day study (93.2 μg/m^3) but that there was not a significant difference between any of the group means ($P>0.6699$, $\alpha= 0.05$). Comparison of overall B(a)P exposures between the groups for all nighttime measurements failed to detect differences in mean values ($P>0.1360$, $\alpha= 0.05$) with group#2 observed to average 4.46 ng/m^3. It should be noted that locations of major industrial pollution sources, like coke ovens, are positioned so that the dominant wind pattern could potentially carry PAH-rich emissions into the upper right half of Ostrava (Group #2 in this study).

Indoor/Outdoor $PM_{2.5}$ Mass and PAH Analysis

Sample collection information from indoor/outdoor monitoring at the KHS-Ostrava is presented in Table 7. Indoor RSP concentrations were calculated to average 56.2 % of those determined from outdoor measurements after samples voided for quality assurance reasons (filter or equipment failure) were removed from the data set. Indoor concentrations ranged from 8.9-54.4 μg/m^3 with outdoors collections ranging from 18.4-146.1 μg/m^3. Graphic presentation of the daily indoor/outdoor variation is presented in Figure 32. Indoor RSP concentrations (μg/m^3) were found to correlate with the outdoor air mass concentration ($R=0.8861$) during the collection period.

Concentrations of B(a)P and total carcinogenic PAH observed in outdoor samples collected at KHS-Ostrava were observed to be in good agreement with the three primary stationary monitoring site samples analyzed by the Czech firm ECOCHEM. B(a)P concentrations from the continuous outdoor monitoring platforms are listed in Table 8 for comparison purposes. Outdoor concentrations of B(a)P ranged from 1.3-20.2 ng/m^3 at KHS-Ostrava.

Graphic representation of B(a)P and total carcinogenic PAH from the indoor and outdoor samples collected at KHS-Ostrava is depicted in Figure 33. Indoor B(a)P concentrations were found to be in general agreement with those observed for daytime PEM measurements. Indoor-

Outdoor B(a)P concentrations were determined to have a correlation of R=0.9254. The use of open windows to affect human comfort, as well as the fact that there were no reported PAH emission sources within the facility, certainly influenced the degree to which outdoor and indoor B(a)P levels were correlated.

Indoor/Outdoor $PM_{2.5}$ XRF Analysis

Data from elemental analysis performed upon indoor and outdoor samples collected at KHS-Ostrava is presented in Table 9-10. Appreciable concentrations of sulfur, silicon, chlorine, potassium, magnesium, iron, copper, zinc, bromine, barium, and lead were detected by the XRF procedures. These concentrations in some respects are not dissimilar to those reported for other areas of the Czech Republic noted as having high particulate levels (Czech Hydrometerological Institute, 1992). It is notable that suspect carcinogenic elements (chromium, nickel and arsenic) are present in concentrations exceeding those usually found in urban areas of major US cities. While source apportionment is currently not present on this data set, it is reasonable to conclude that the concentration of S,V, Zn, As, and Se species among other elements, reflect the impact of industrial emission sources (e.g.., coke ovens, steel manufacturing). Residential heating emissions (oil+coal furnaces) may also influence ambient metal concentrations in Ostrava.

Indoor-outdoor fine particle mass was determined to correlate (R^2=0.8861). This data is presented in Table 11. Similar comparisons revealed that ambient indoor and outdoor concentrations of S, K, Ti ,Fe, Cu, Br, and Pb correlated (R^2 generally exceeding 0.6) between paired species. Calculation of elemental indoor/outdoor mass ratios and enrichment factors was performed as detailed in Table 12. Enrichment is the process where the indoor mass fraction of a given specie deviates from the ambient mass fraction due to a lack of equilibration or clearance at the measurement point. Chlorinated species collected indoors were determined to be depleted with respect to those outdoors (0.5 ratio). Enrichment factors for species representing crustal matter (Si, K, Ca, Ti, and Fe) exceed 1.0, and may be indicative of track-in by KHS-Ostrava entrees.

The ratio of ambient B(a)P to Pb concentration is a useful determinant of PAH emission sources. This ratio is typically around 0.01 when mobile sources are the dominant PAH source in ambient air. Values exceeding 0.03 and higher will generally indicate that other sources, such as coke oven emissions, have a greater influence upon the urban air shed. As can be seen in Figure 34, B(a)P/Pb ratios indicate that starting around October 29th, industrial sources probably contributed significantly to the fine particulate matter (ratios >0.03). Fluctuations in the ratios give an excellent indication of changing weather patterns (wind, precipitation). This short 14 day study provides evidence that mobile source emissions rarely were the source of the majority of the fine particulate matter in Ostrava during the time period under surveillance. Coke ovens, along with other major industrial point sources and possibly residential coal heating in the Ostrava area are presumed to be the origin of much of the fine particulate matter detected in this study based upon elemental analysis of ambient air particulate. Residential heating using various coal mixtures has been espoused to be a significant contributor to ambient air pollution in the Ostrava

area (J. Novak and Tom Hartlage, personal communication). Temperatures were transitional during the time of the study and residential heating probably was a minor contributor to overall ambient $PM_{2.5}$ mass and PAH levels. Source apportionment analysis upon the data presented from indoor/outdoor monitoring at the KHS-Ostrava site will need to be conducted to more fully estimate local and point source contribution to ambient particulate concentrations.

References

Binkova, B., J. Lewtas , I. Miskova, J. Lenicek and R. Sram, "DNA adducts and personal air monitoring of carcinogenic polycyclic aromatic hydrocarbons in an environmentally exposed population", *Carcinogenesis,* 16, 1037-1046 (1995).

CHMI, "Air pollution in the Czech Republic in 1992", Czech Hydrometeorological Institute, Air Quality Protection Department, Prague (1994).

Lewtas, J., D. Walsh, R. Williams and L. Dobias, "Air pollution exposure-DNA adduct dosimetry in humans and rodents: Evidence for nonlinearity at high doses", *Mutation Research* (in press).

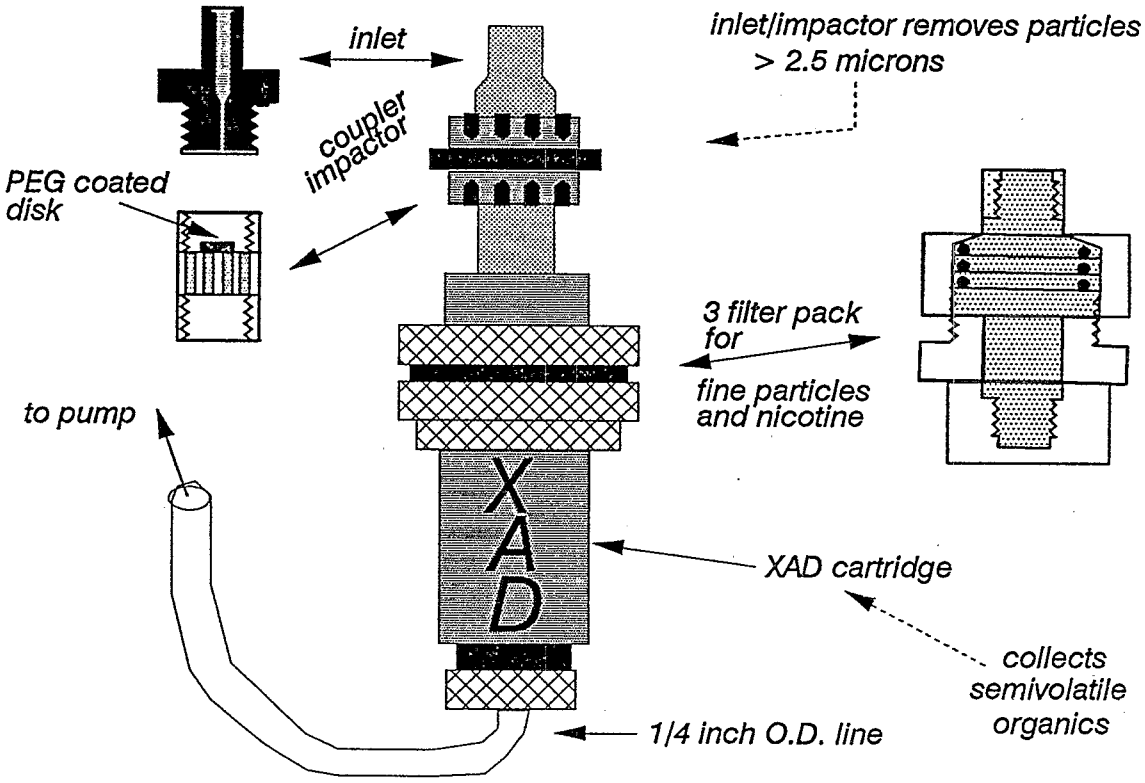
Vit, M., C. Kantor, I. Tomasek and J. Volf, "Report No. 5-Silesia Environmental Health Report", (1995).

Watts, R., J. Lewtas, R. Stevens, T. Hartlage, J. Pinto, J. Miskova, I. Benes, F. Kotesovec, K. Hattaway and R. Williams, "Czech-US EPA Health Study: Assessment of personal and ambient air exposures to PAH and organic mutagens in the Teplice district of Northern Bohemia", *Int. J. Environ. Anal. Chem.*, 56:271-287 (1994).

Williams, R., L. Brooks, R. Stevens, V. Marple and J. Lewtas, "Field test and laboratory evaluation of a lightweight, modular designed, personal sampler for human biomarker studies", AWMA Symposium on Toxic and Related Air Pollutants, EPA/600/R-92/131, pp. 998-1003 (1992).

Williams, R., J. Meares, L Brooks, R. Watts and P. Lemieux, "Priority pollutant PAH analysis of incinerator emission particles using HPLC and optimized fluorescence detection", *Int. J. Environ. Anal. Chem.*, 54:299-314 (1994).

Willis, R., Ellenson, W., Pinto, J., Hartlage, T., Novak, J., Dosdalek, H., L. Cernikovsky and V. Bures, draft report entitled "Ostrava Air Quality Monitoring and Receptor Modeling Study", US EPA, RTP, NC. (January 1997).



Total length of sampler is 21.5 cm.

Figure 1. Personal exposure monitor (in sampling orientation).

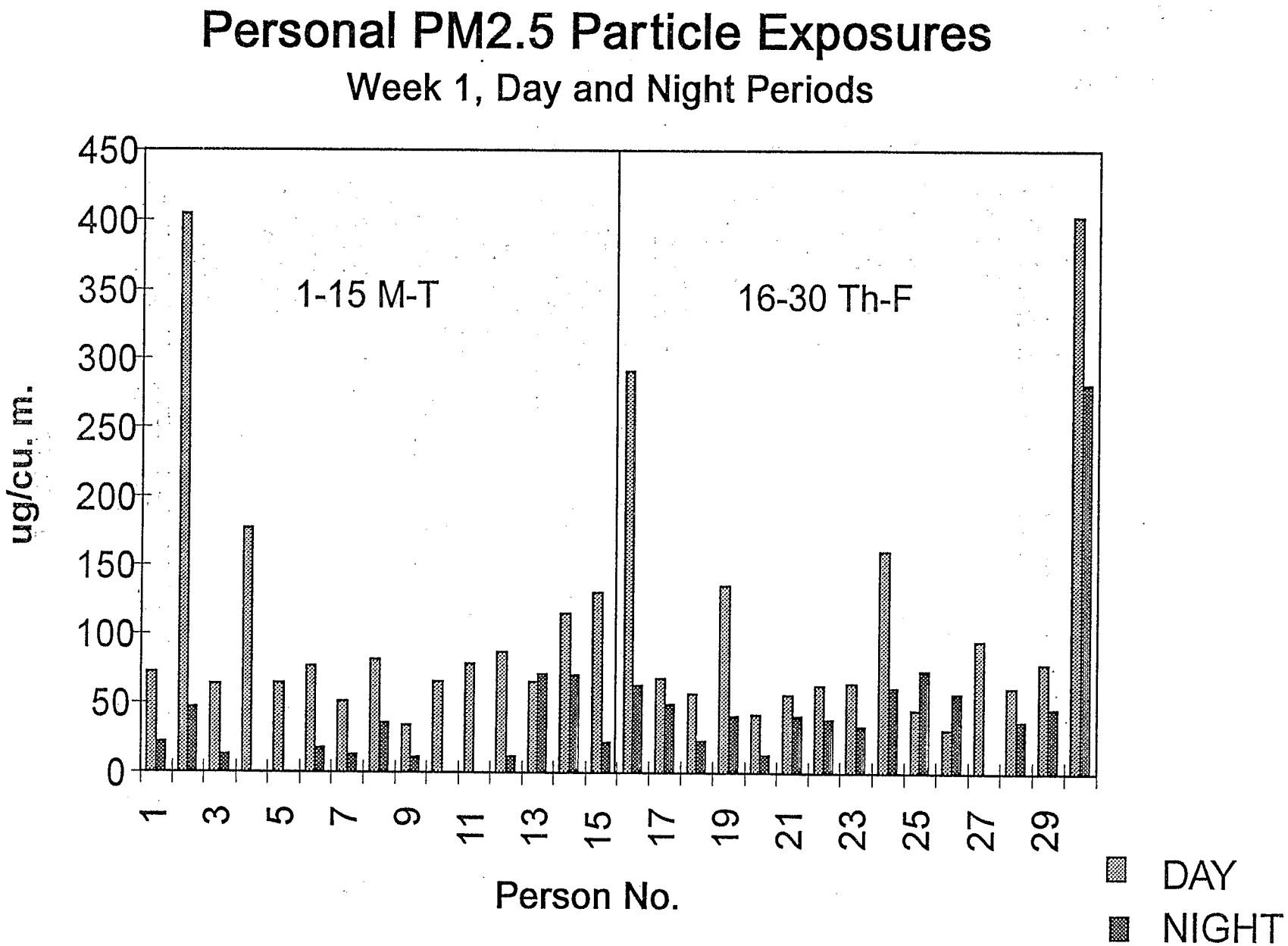


Figure 2. Individual PM(2.5) particle exposures from Week 1 personal monitoring.

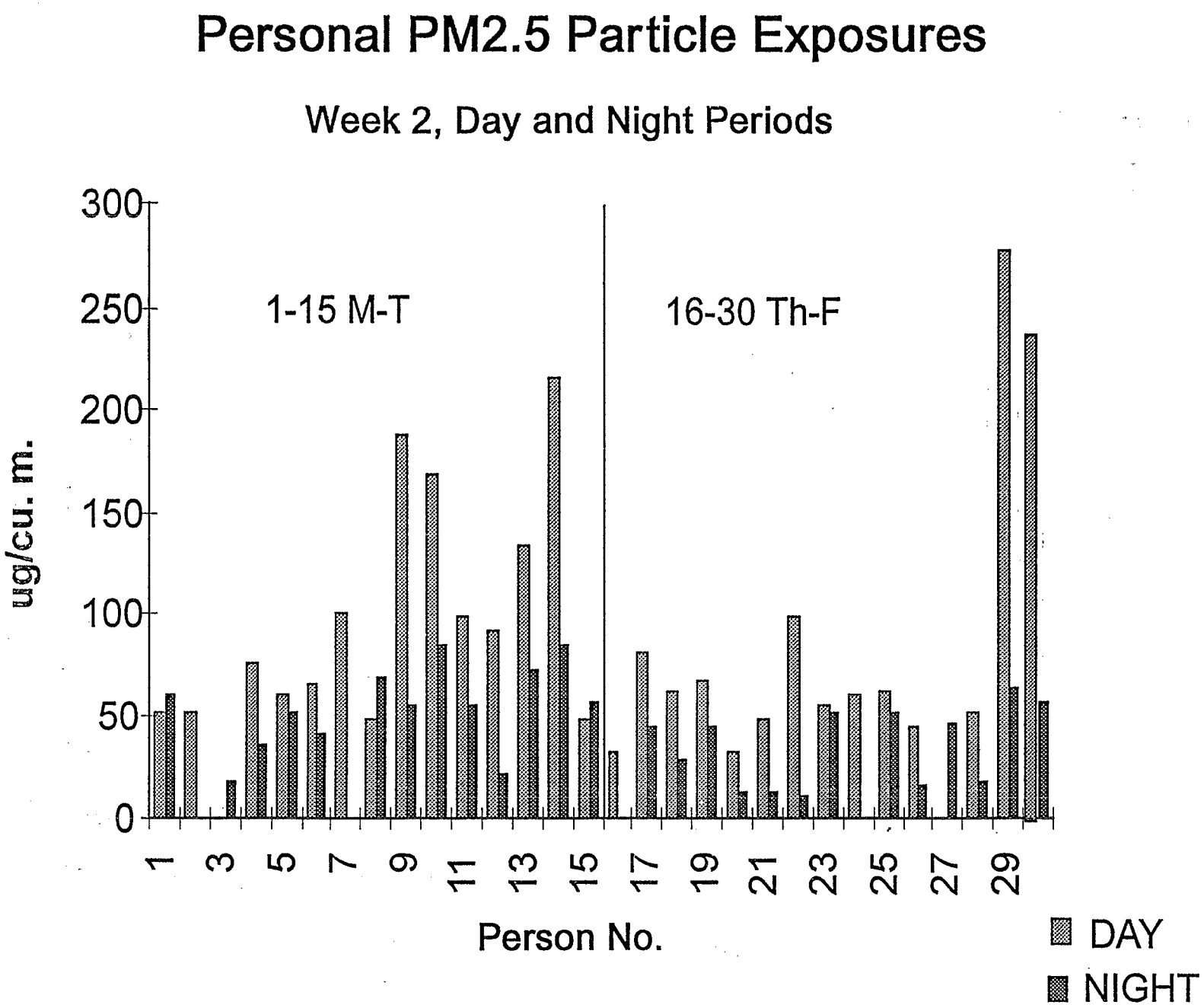


Figure 3. Individual PM(2.5) particle exposures from Week 2 personal monitoring.

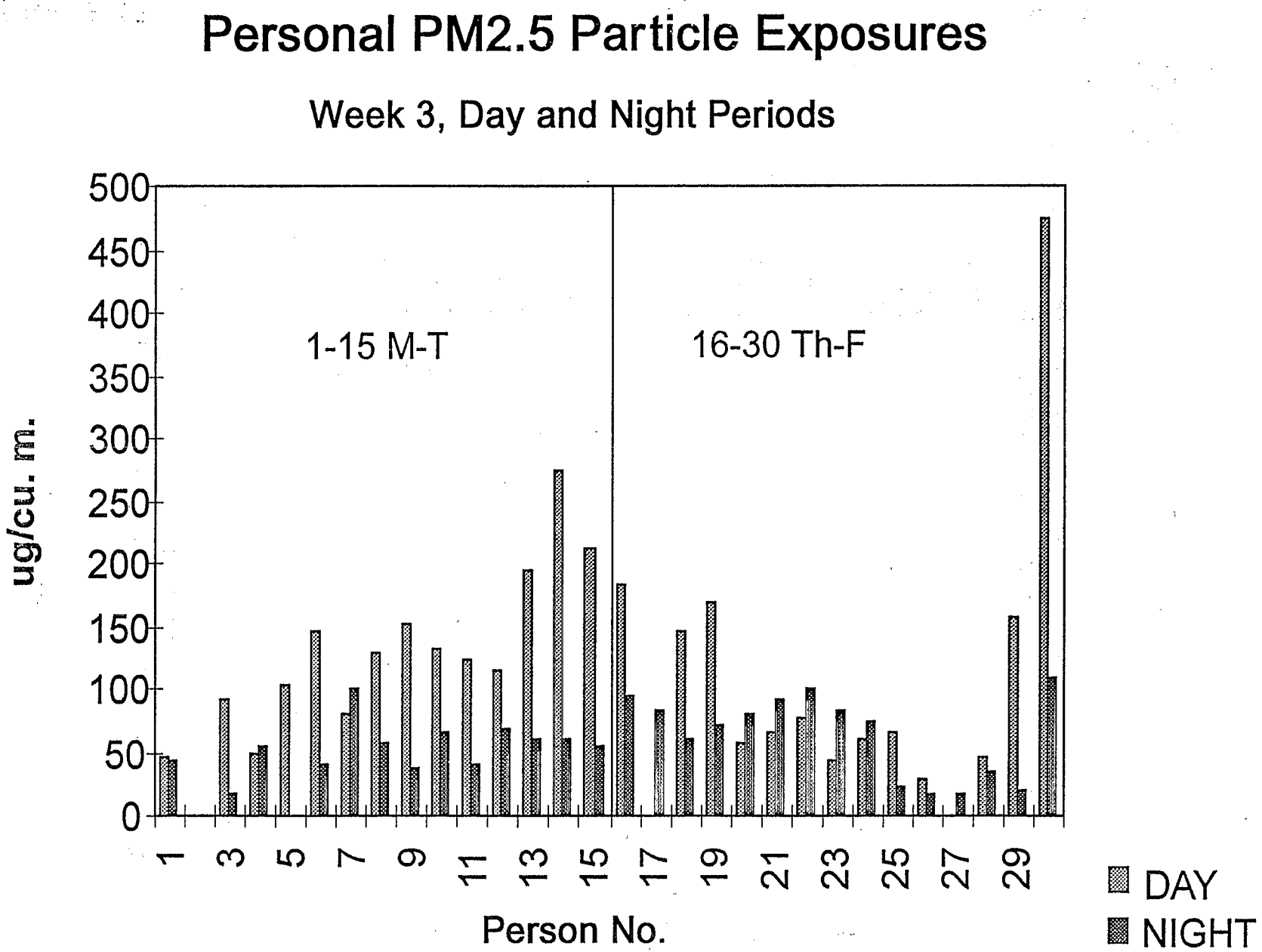


Figure 4. Individual PM(2.5) particle exposures from Week 3 personal monitoring.

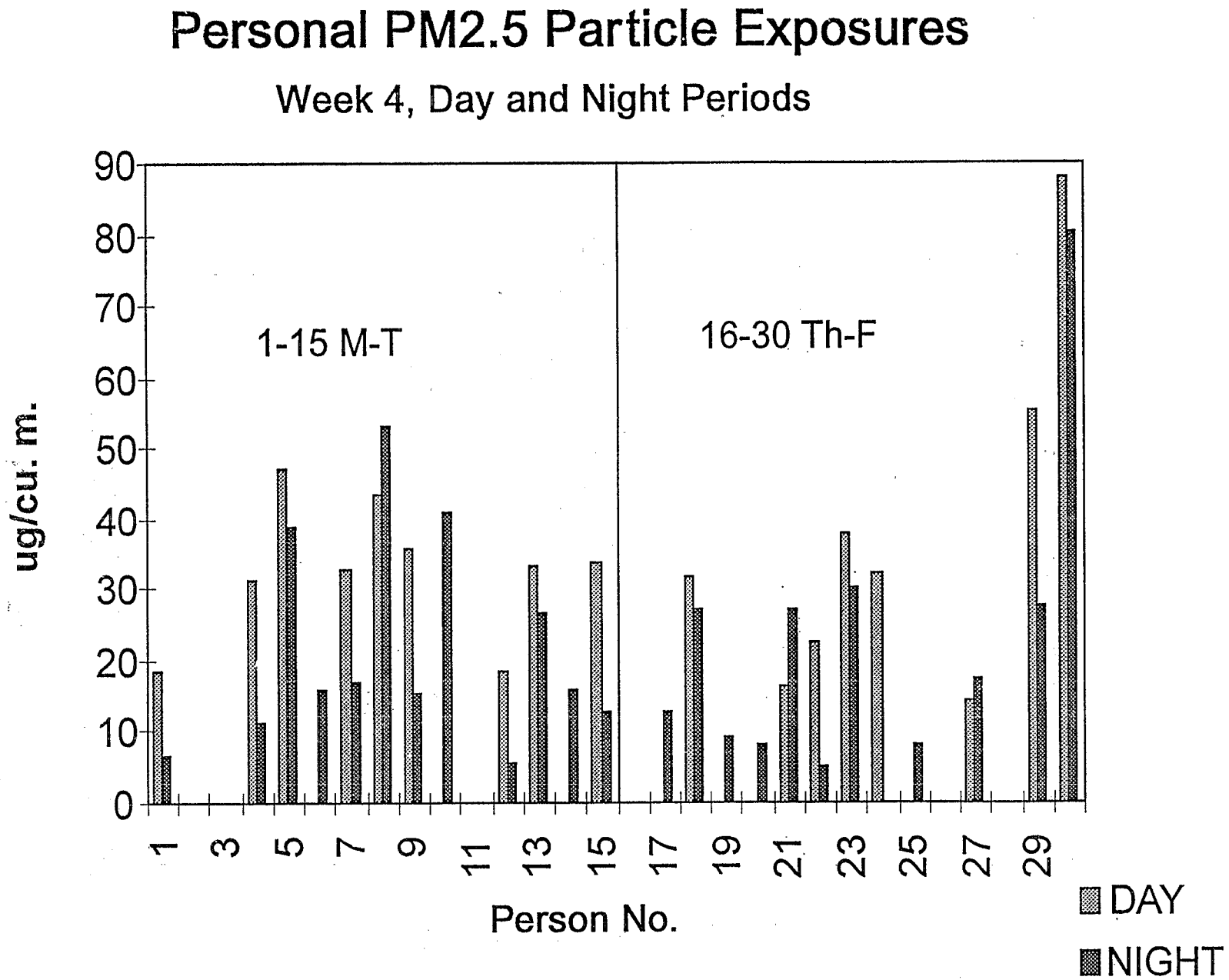


Figure 5. Individual PM(2.5) particle exposures from Week 4 personal monitoring.

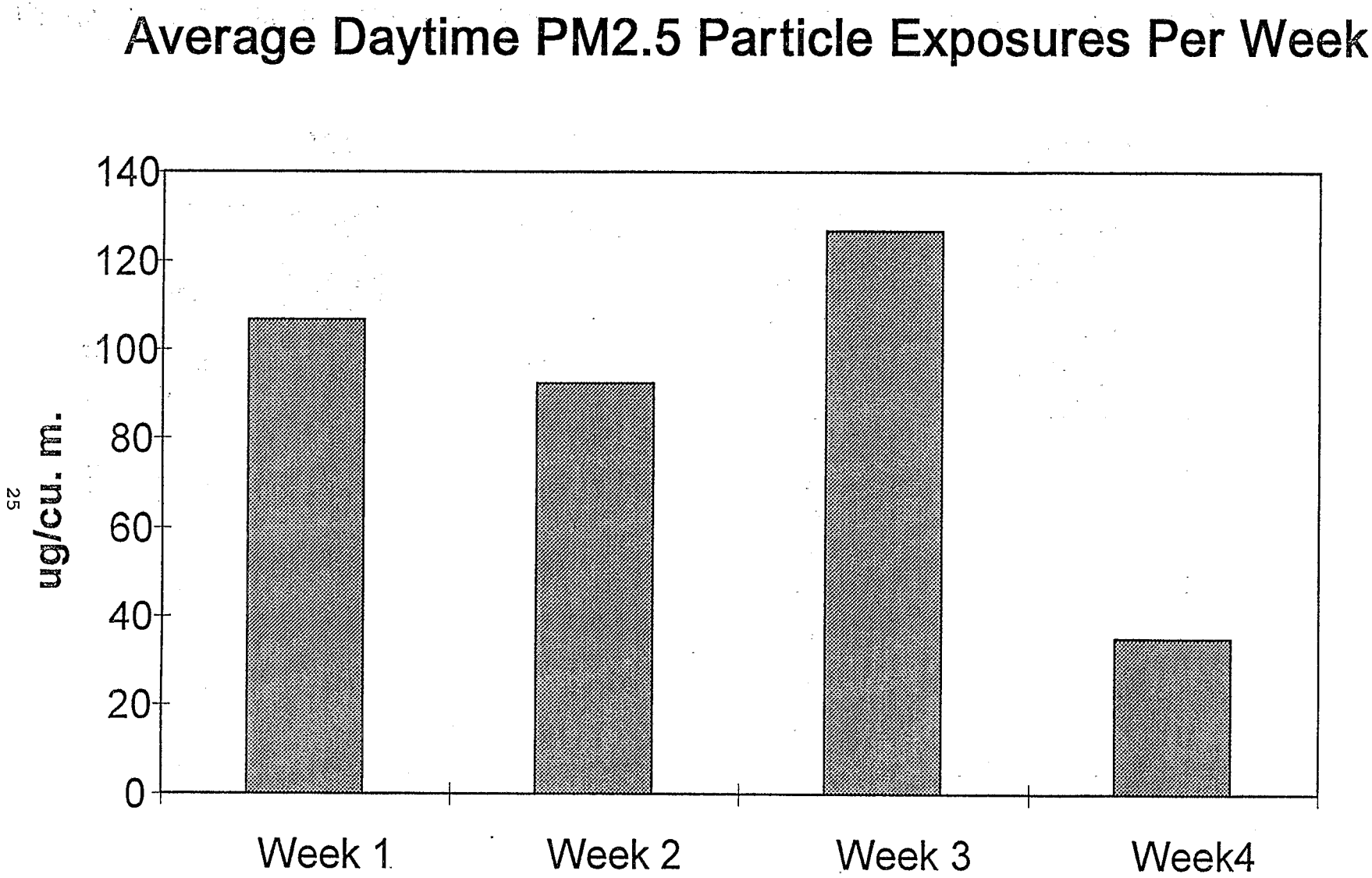


Figure 6. Average daytime PM(2.5) particle exposures by week for all 30 individuals.

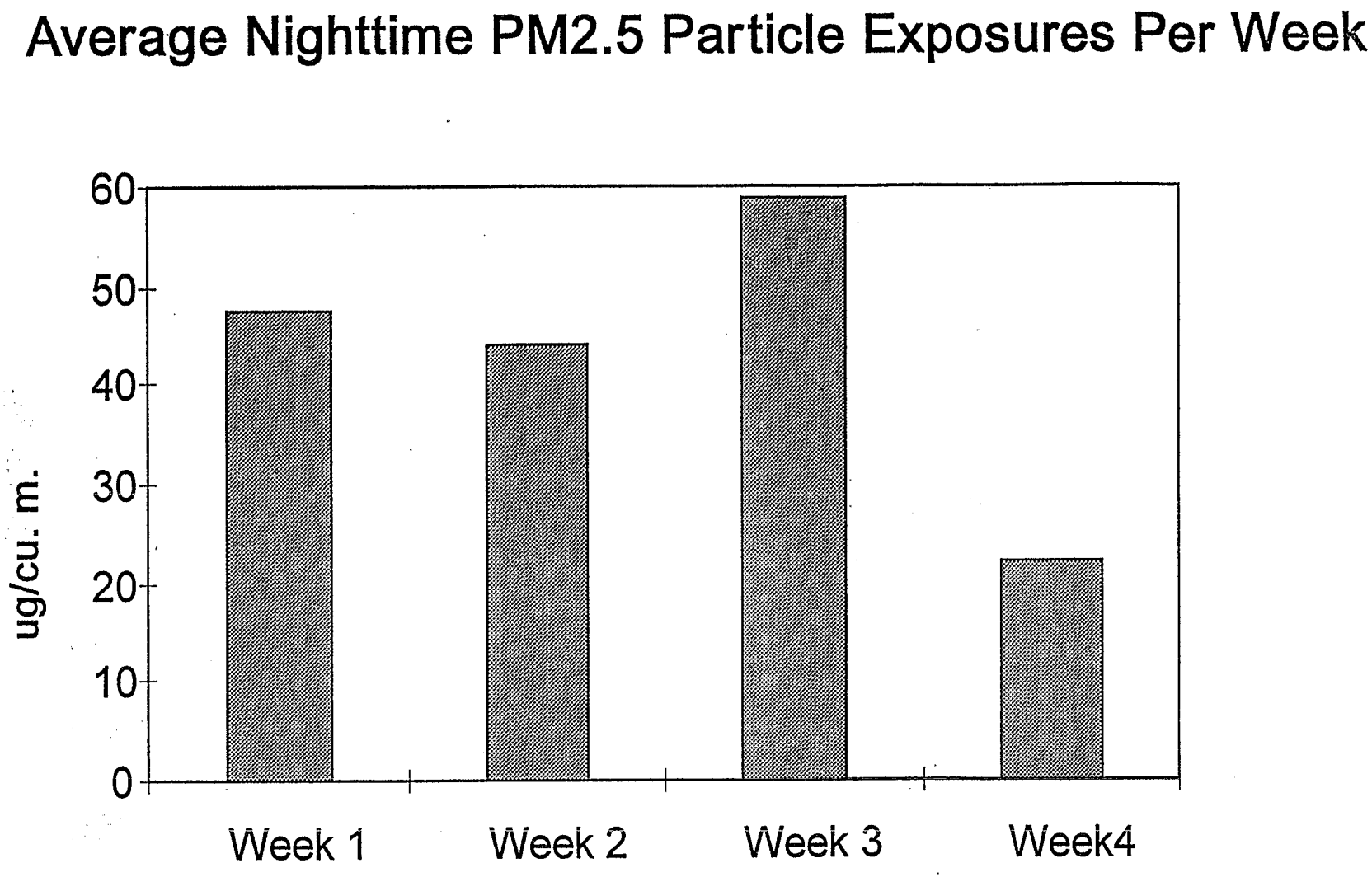


Figure 7. Average nighttime PM(2.5) particle exposures for all 30 individuals.

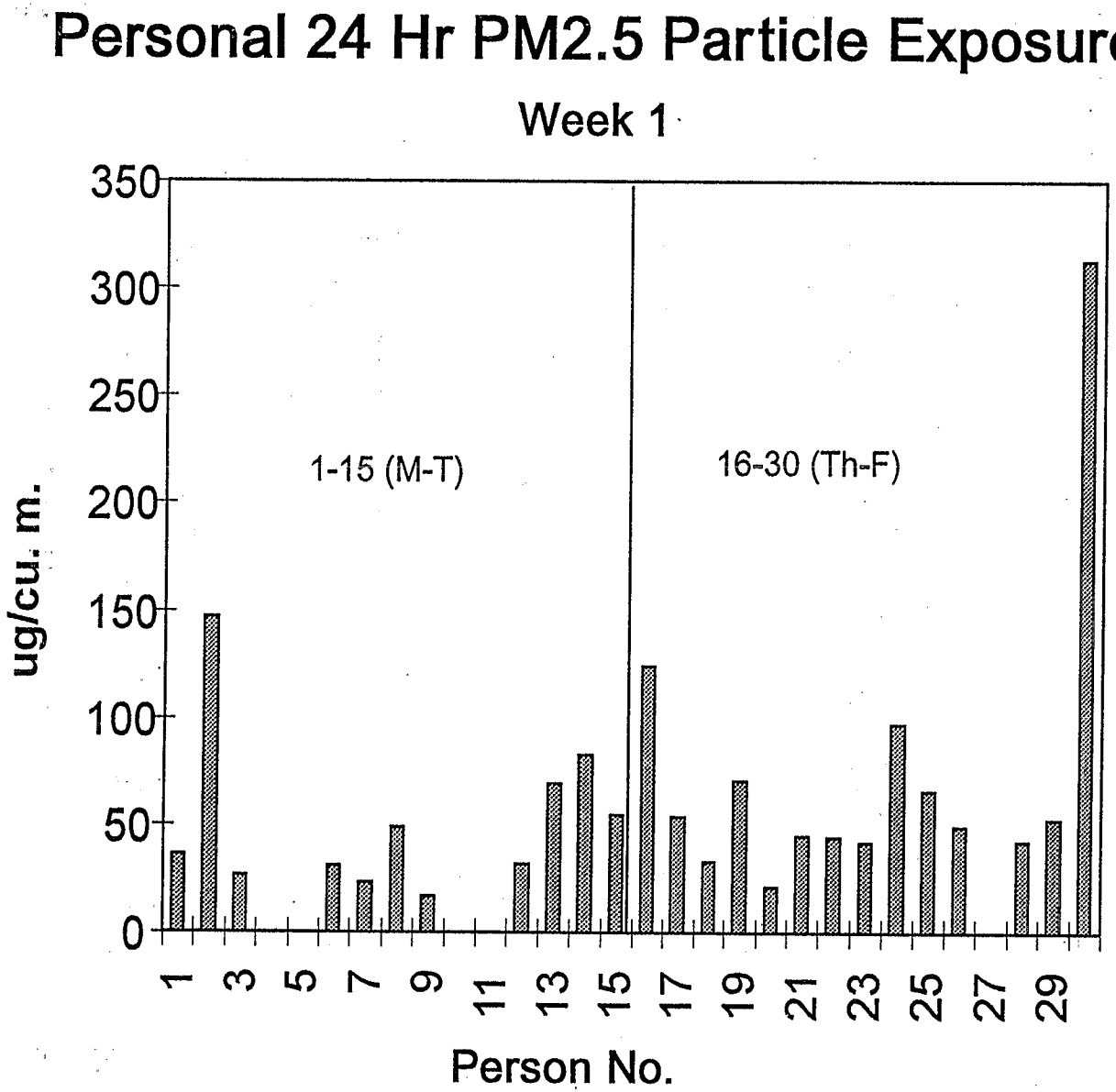


Figure 8. Individual 24 hour PM(2.5) particle exposures for Week 1 sampling.

Personal 24 Hr PM2.5 Particle Exposures

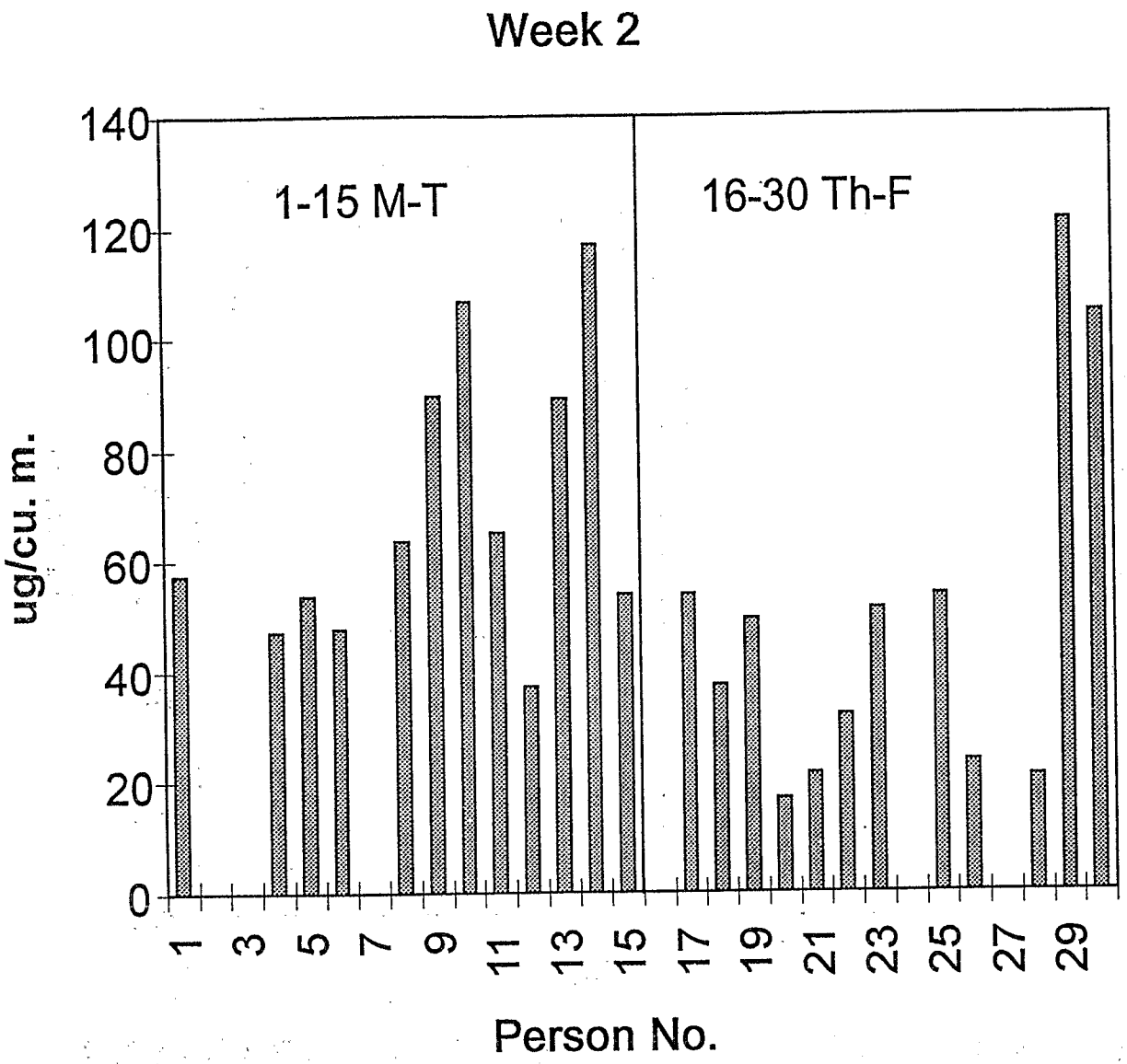


Figure 9. Individual 24 hour PM(2.5) particle exposures for Week 2 sampling.

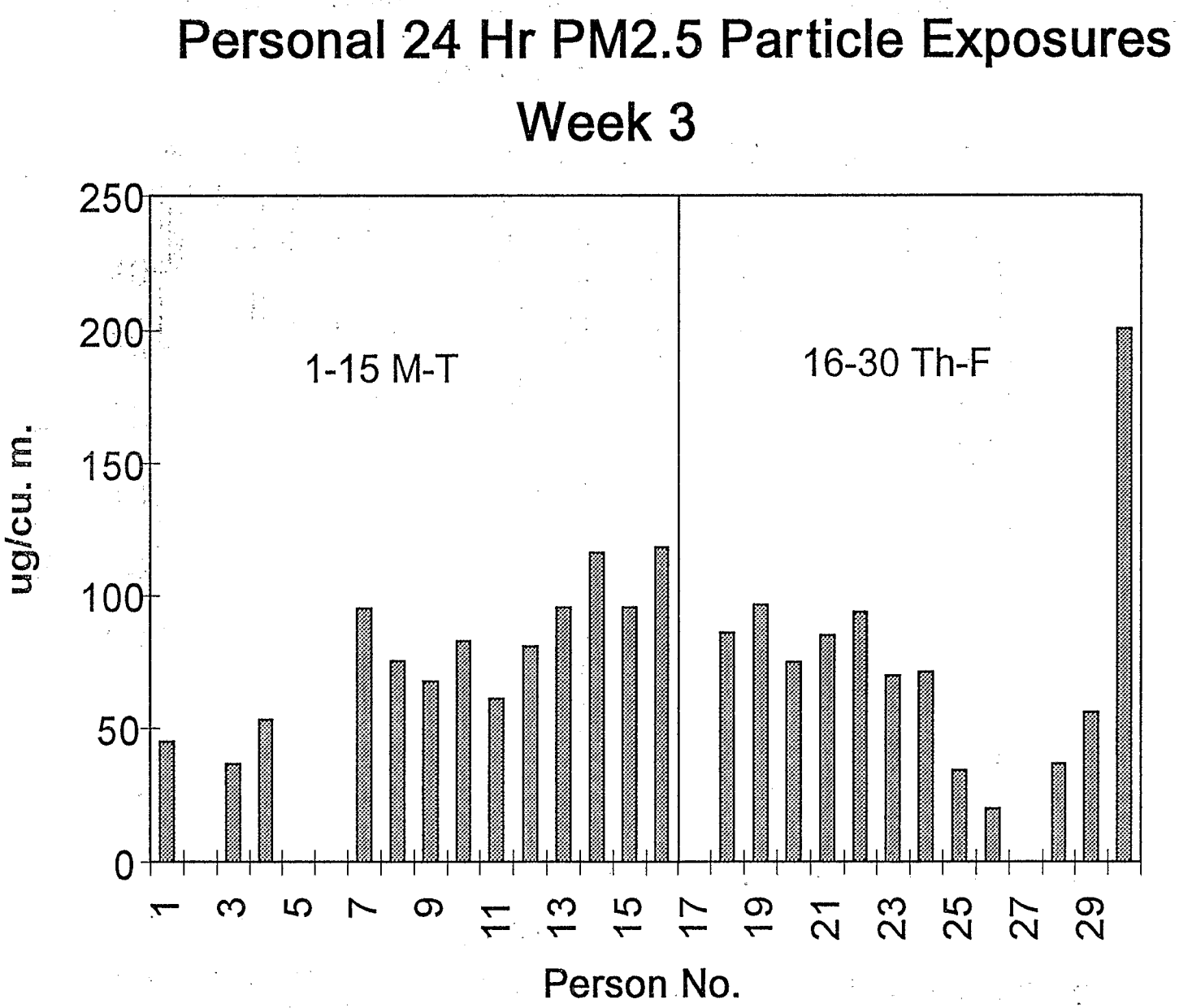


Figure 10. Individual 24 hour PM(2.5) particle exposures for Week 3 sampling.

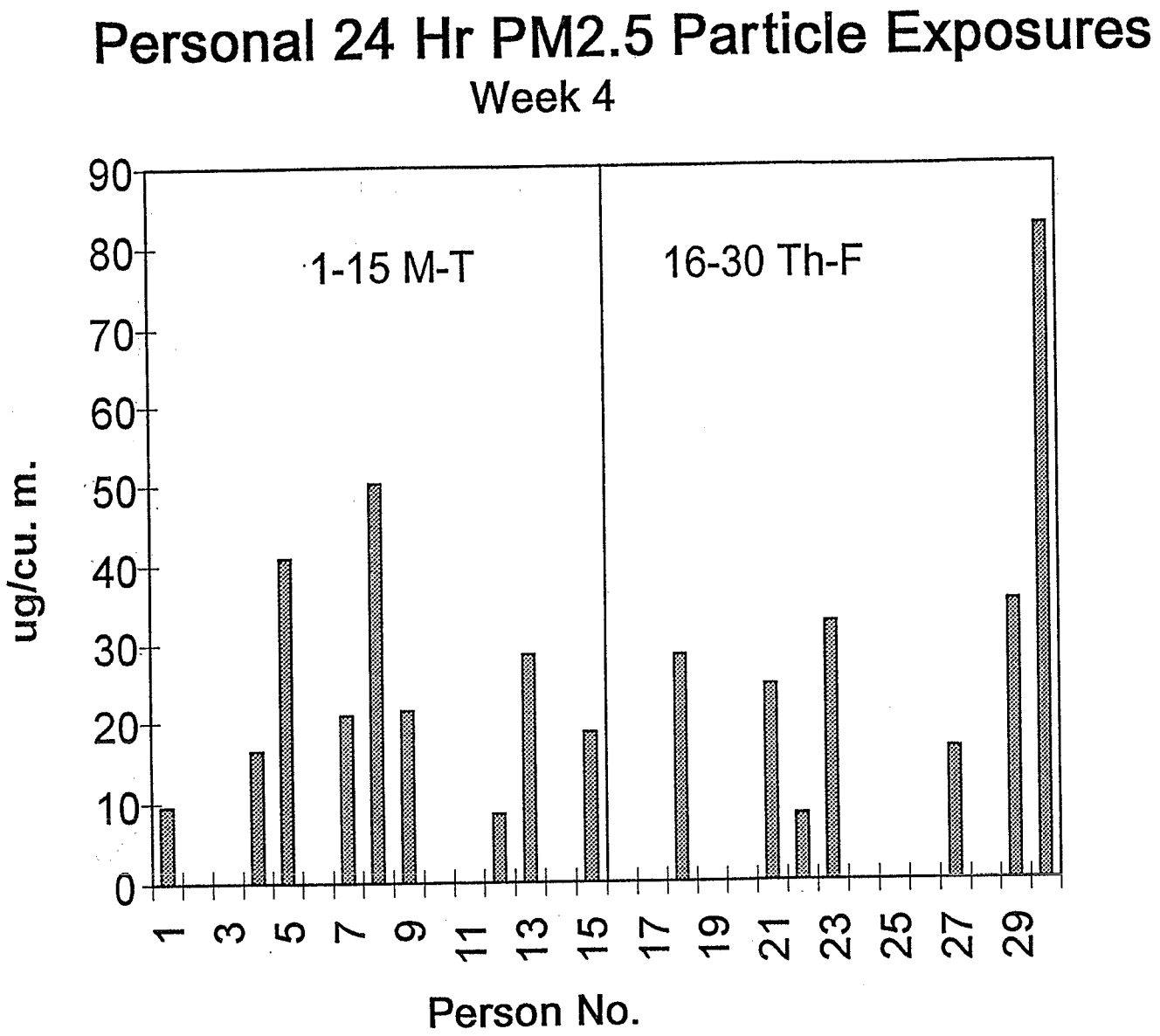


Figure 11. Individual 24 hour PM(2.5) particle exposures for Week 4 sampling.

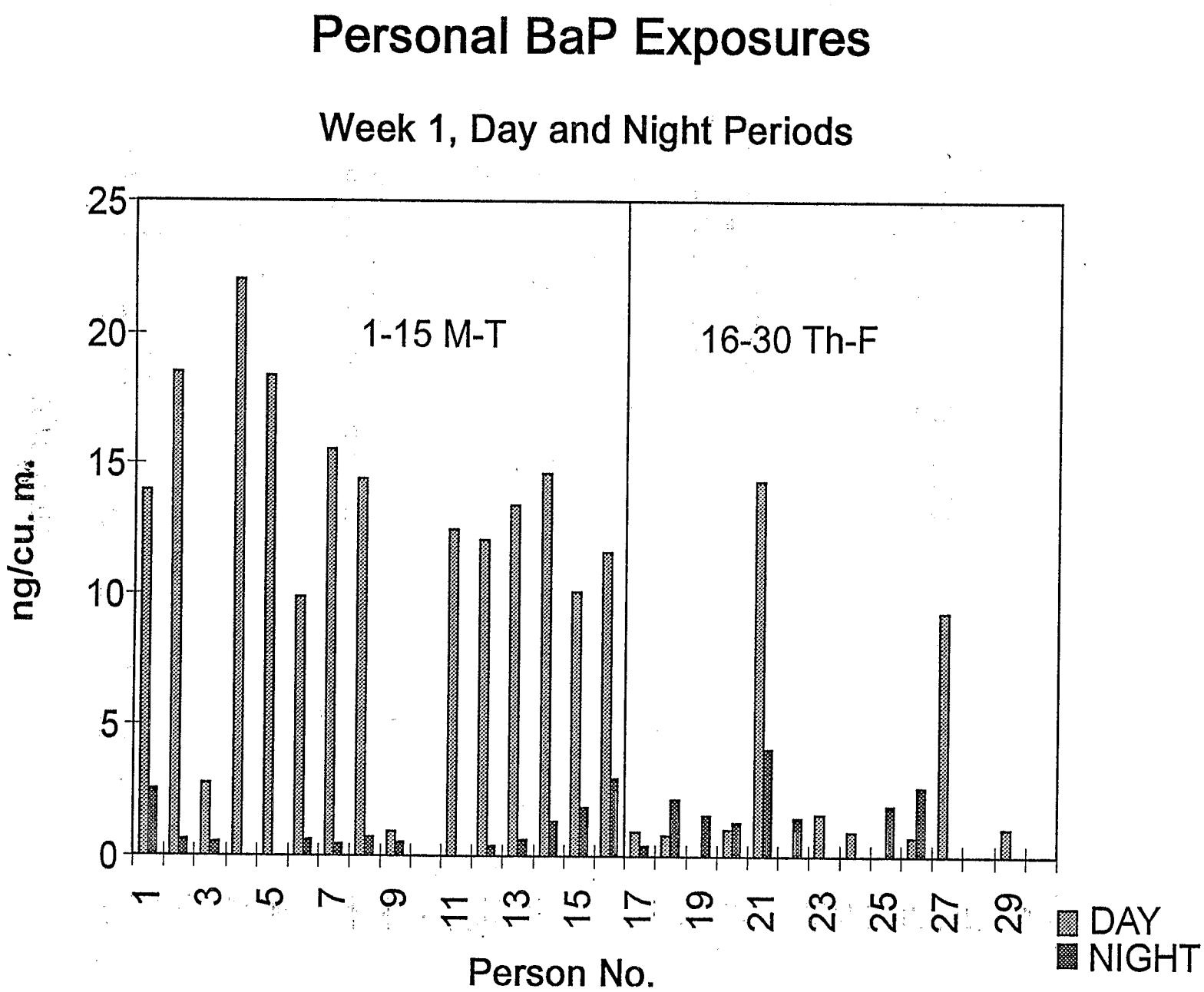


Figure 12. Individual PM(2.5) B(a)P from Week 1 personal monitoring.

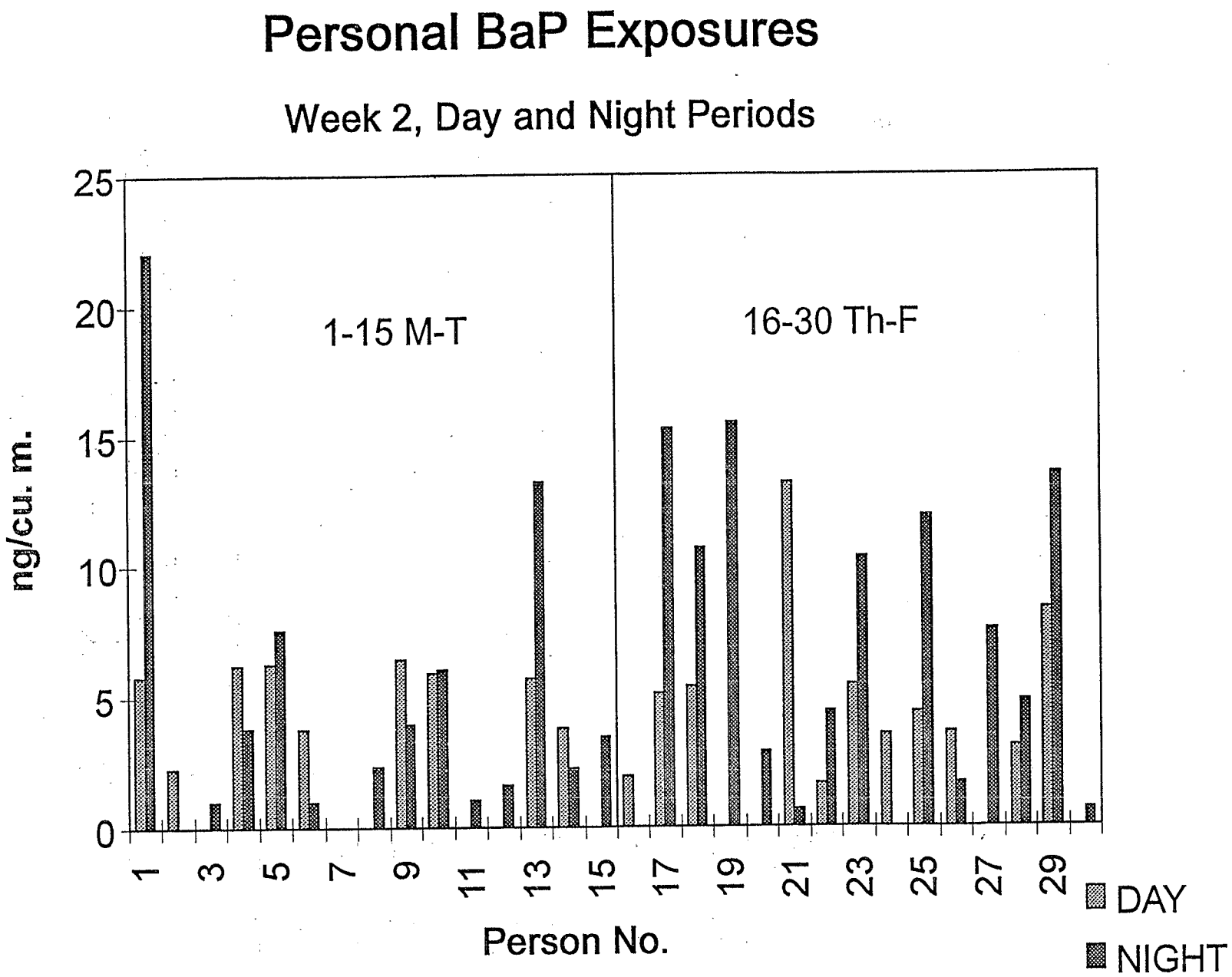


Figure 13. Individual PM(2.5) B(a)P from Week 2 personal monitoring.

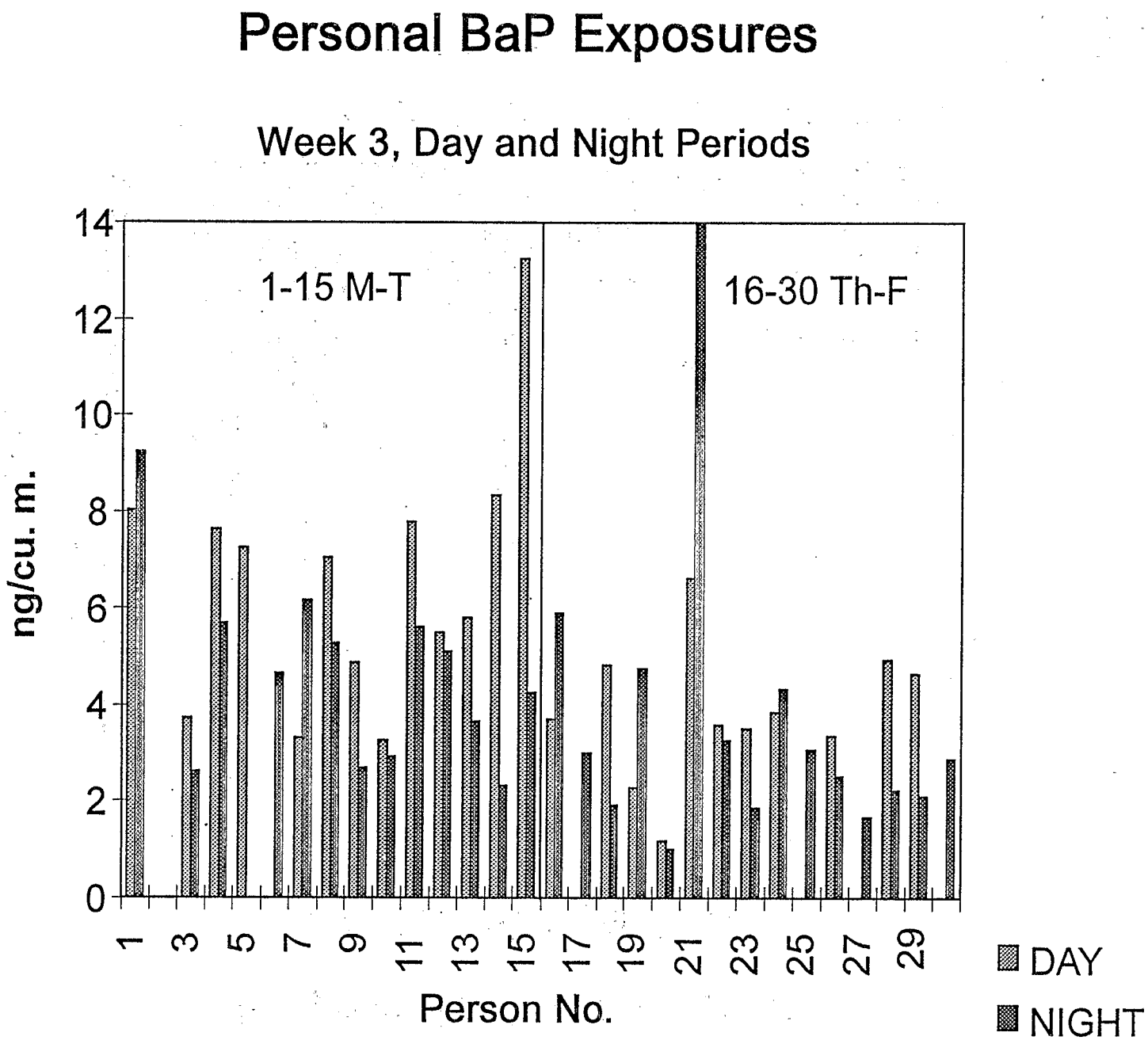


Figure 14. Individual PM(2.5) B(a)P from Week 3 personal monitoring.

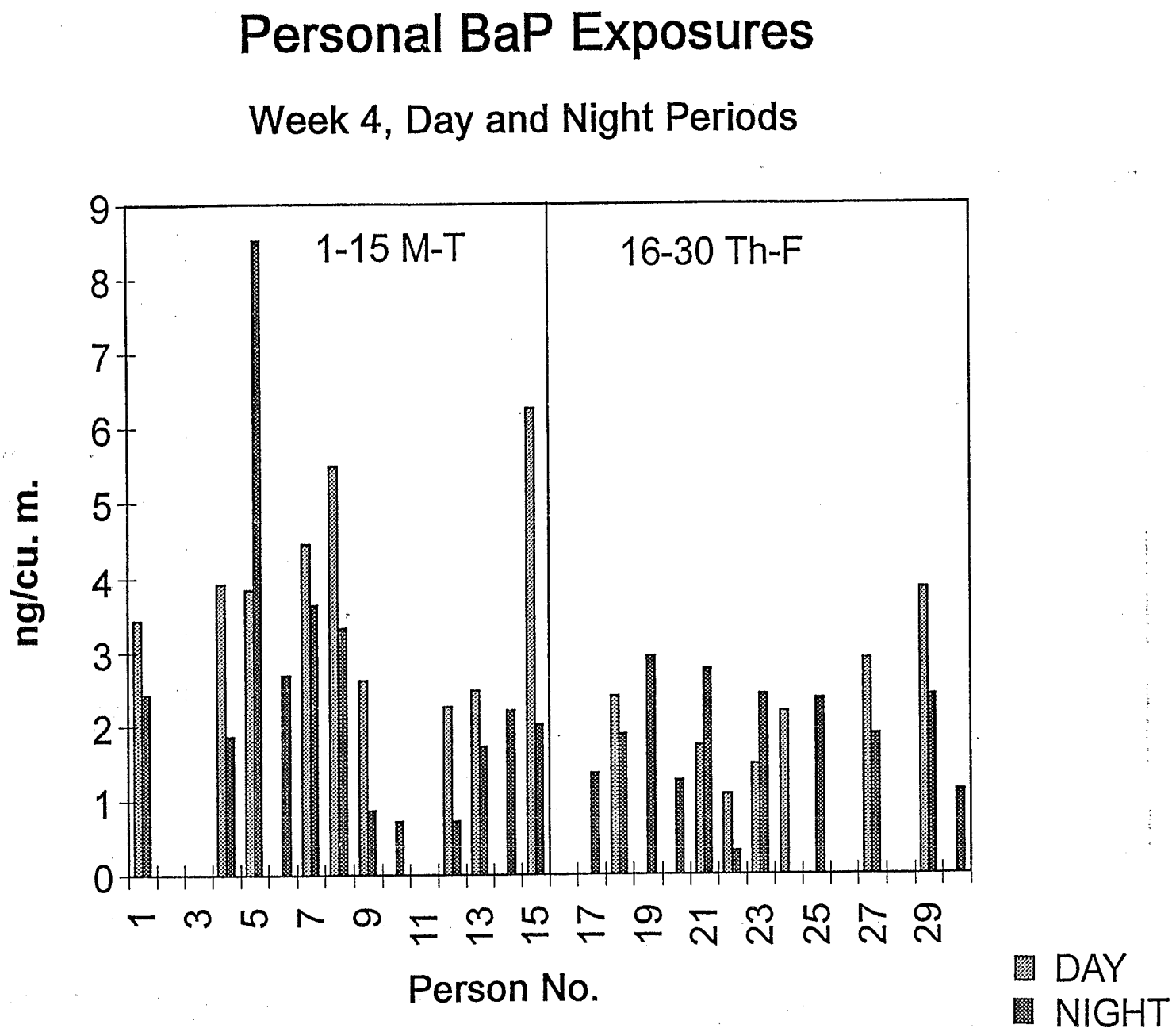


Figure 15. Individual PM(2.5) B(a)P from Week 4 personal monitoring.

Personal Carcinogenic PAH Exposures

Week 1, Day and Night Periods

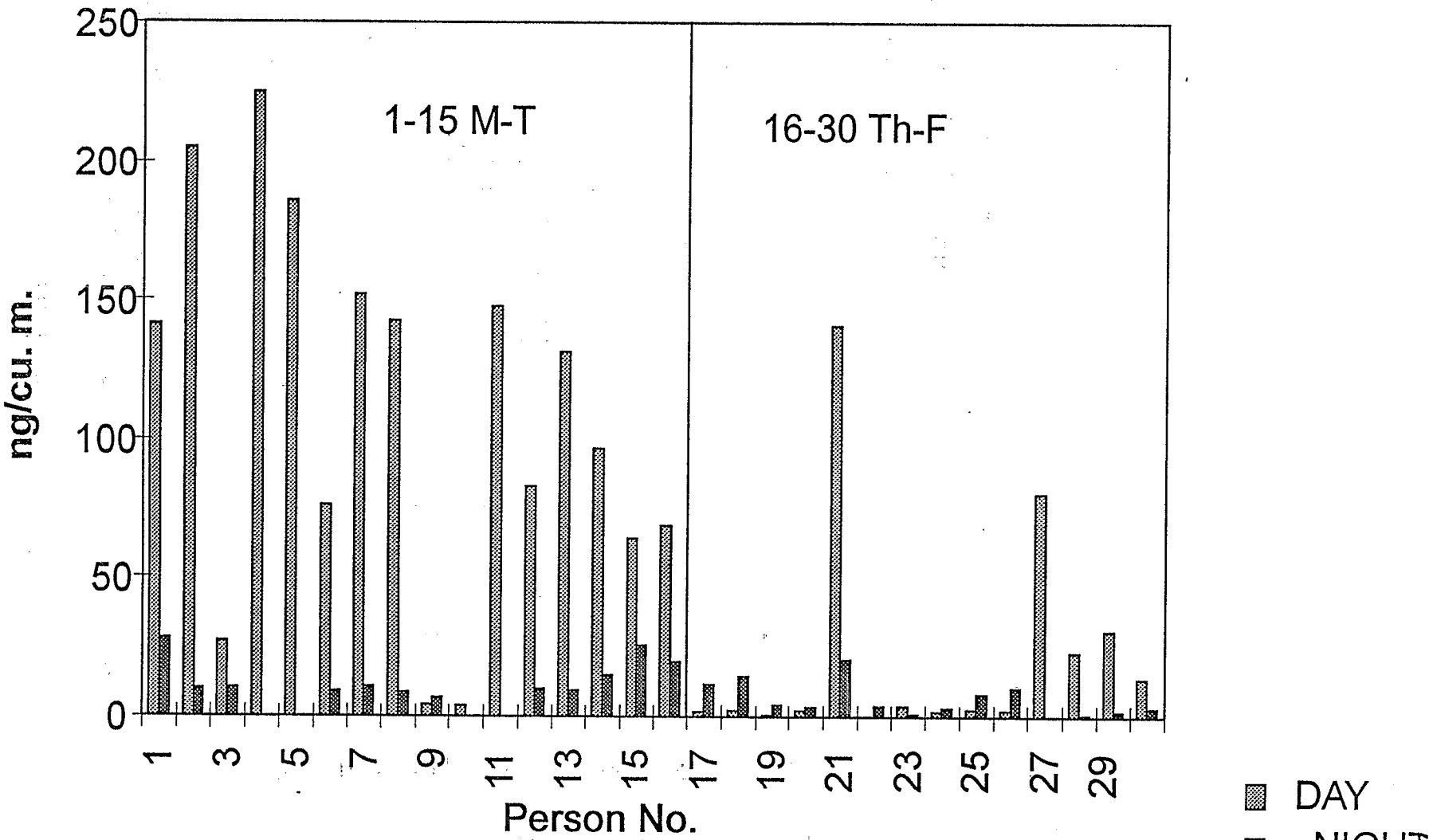


Figure 16. Individual PM(2.5) total carcinogenic PAH's from Week 1 personal monitoring.

Personal Carcinogenic PAH Exposures

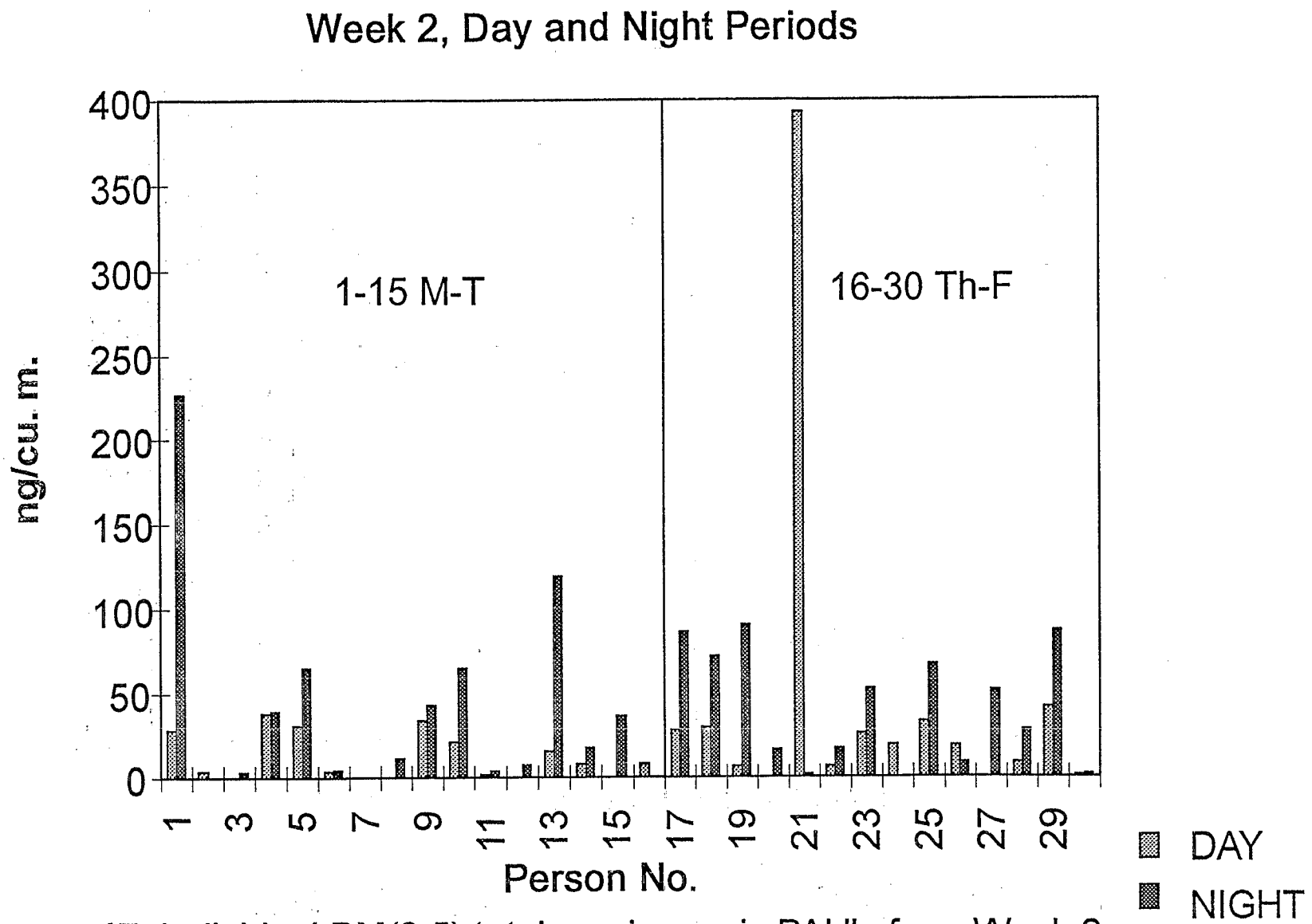


Figure 17. Individual PM(2.5) total carcinogenic PAH's from Week 2 personal monitoring.

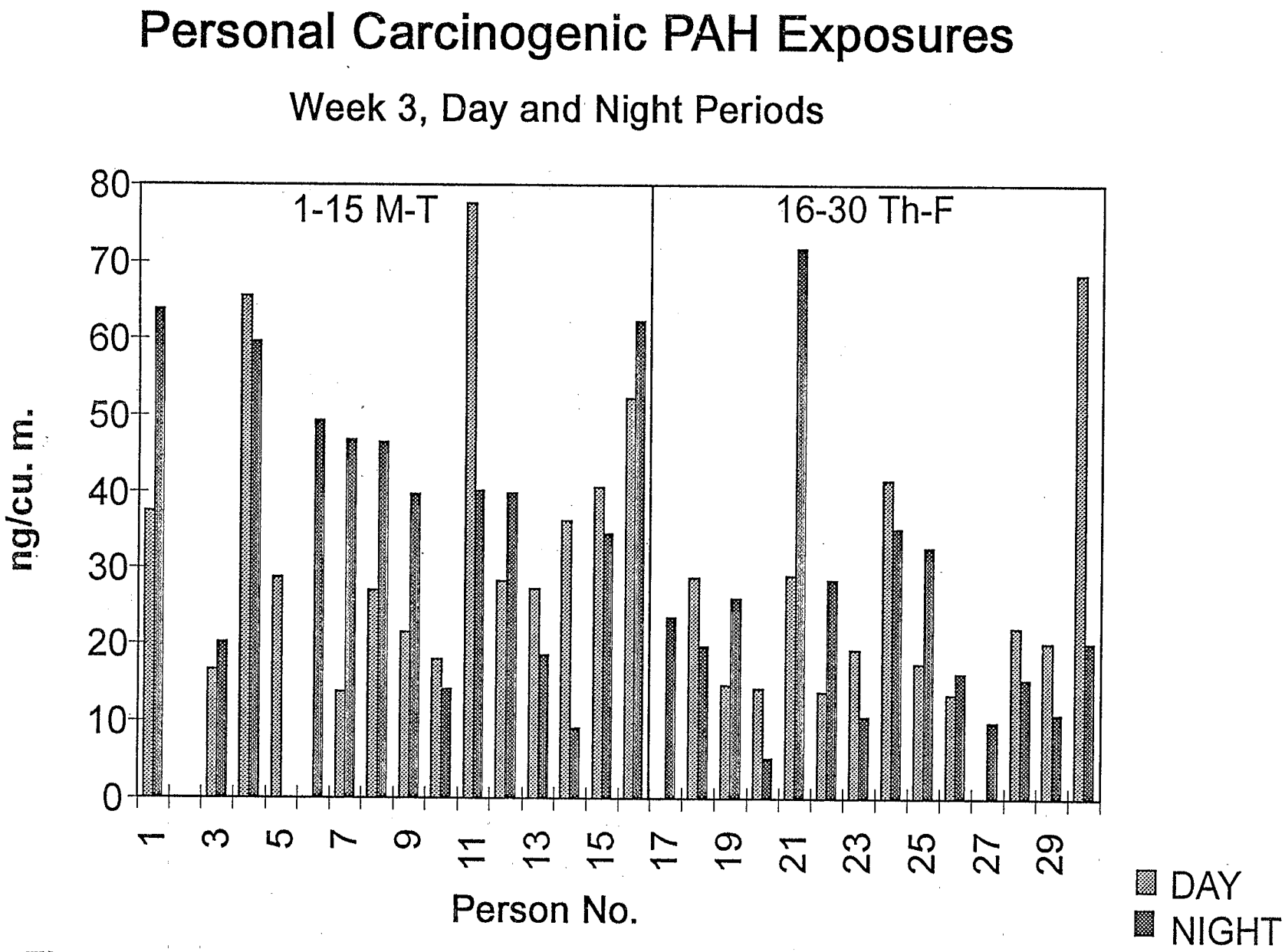


Figure 18. Individual PM(2.5) total carcinogenic PAH's from Week 3 personal monitoring.

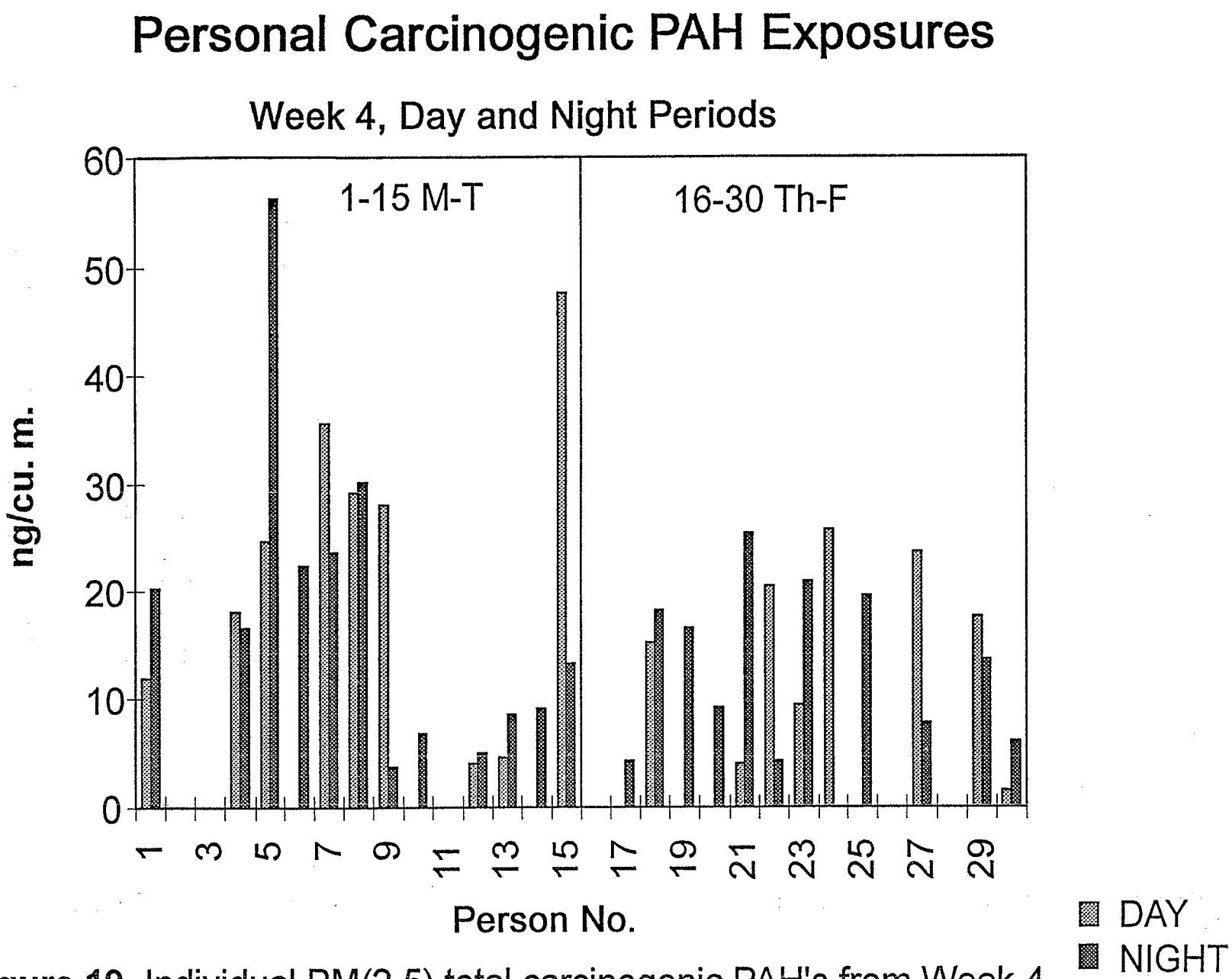


Figure 19. Individual PM(2.5) total carcinogenic PAH's from Week 4 personal monitoring.

Comparison of Personal BaP and Carcinogenic PAH Exposures

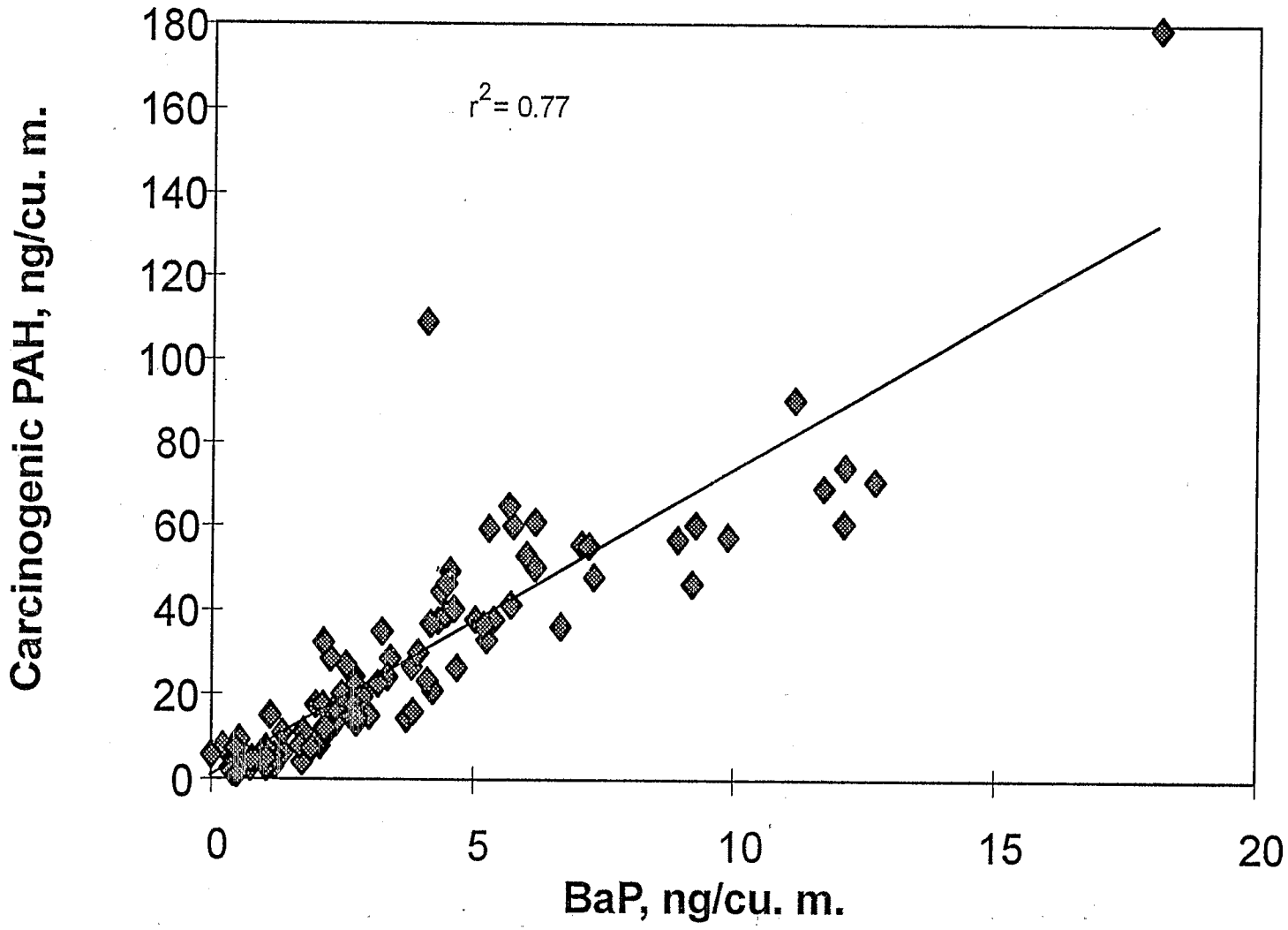


Figure 20. Comparison of personal monitoring B(a)P and total carcinogenic PAH exposures for the 30 day study.

Comparison of 30 Day Personal Particle and BaP Exposures

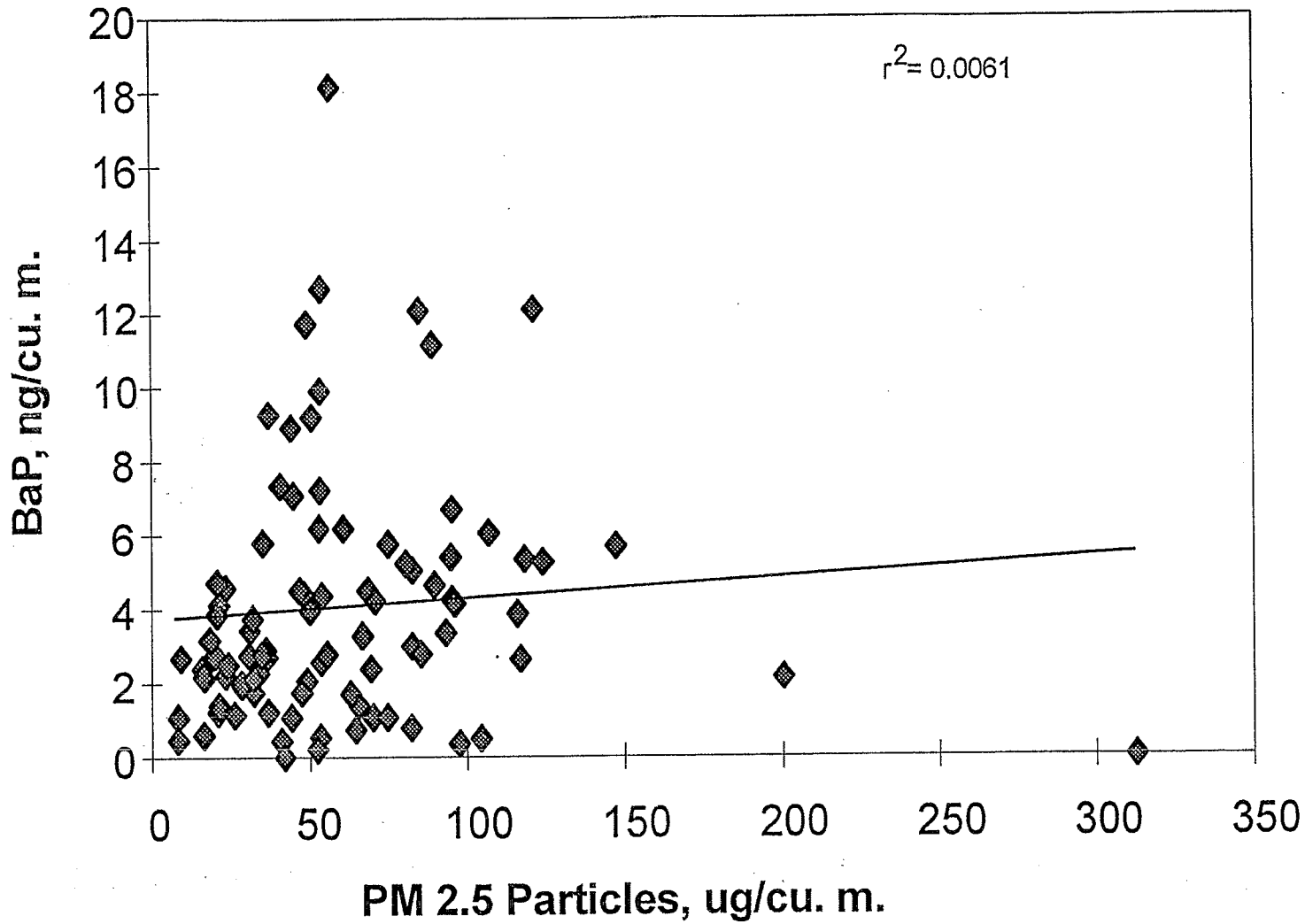


Figure 21. Comparison of personal exposures to PM(2.5) particles and BaP

Week 1 Average Nighttime PM2.5 Particle and BaP Exposures

Monday-Tuesday

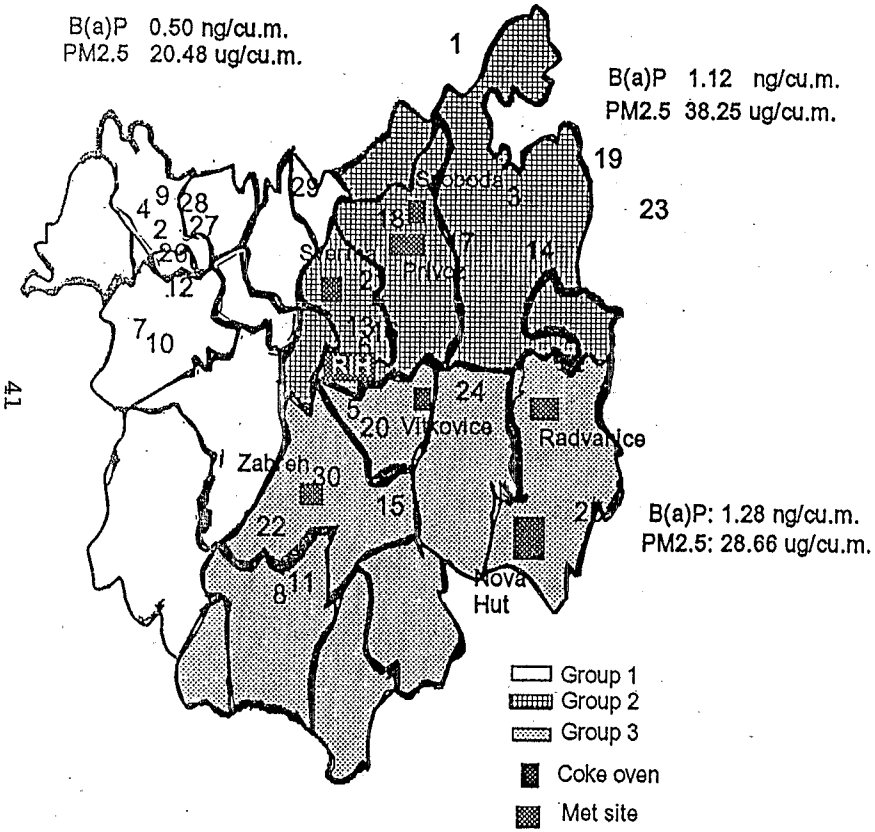


Figure 22. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent individuals and where they live. The location of stationary monitoring platforms and coke ovens are indicated by the key.

Thursday-Friday

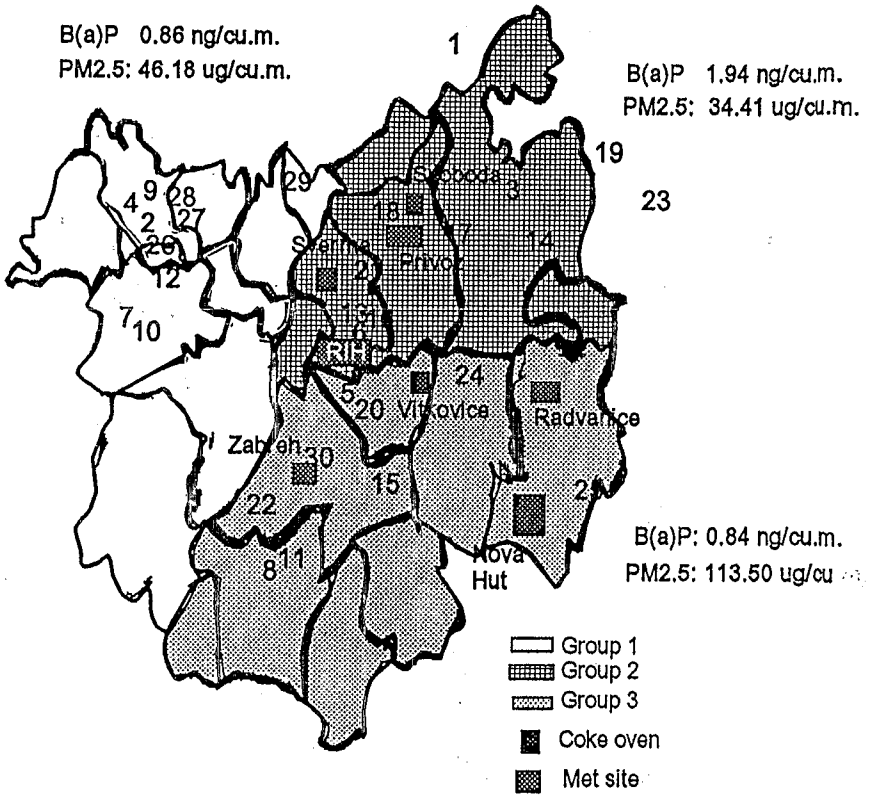


Figure 23. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent individuals and where they live. The location of stationary monitoring platforms and coke ovens are indicated by the key.

Week 2 Average Nighttime PM2.5 Particle and BaP Exposures

Monday-Tuesday

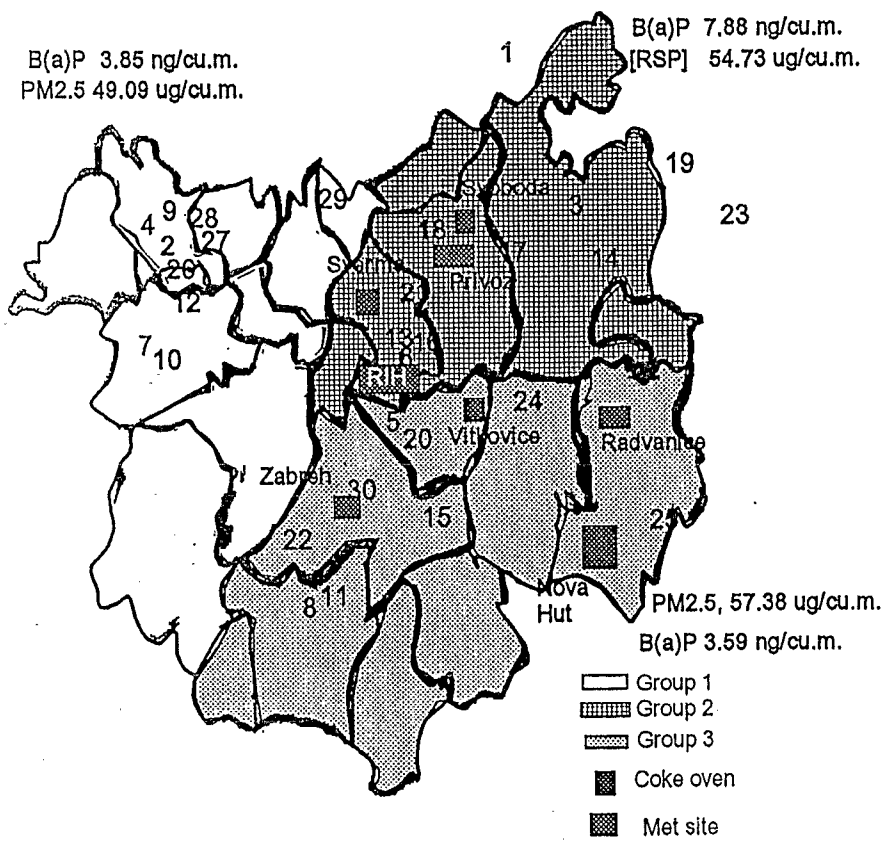


Figure 24. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent individuals and where they live. The location of stationary monitoring platforms and coke ovens are indicated by the key.

Thursday-Friday

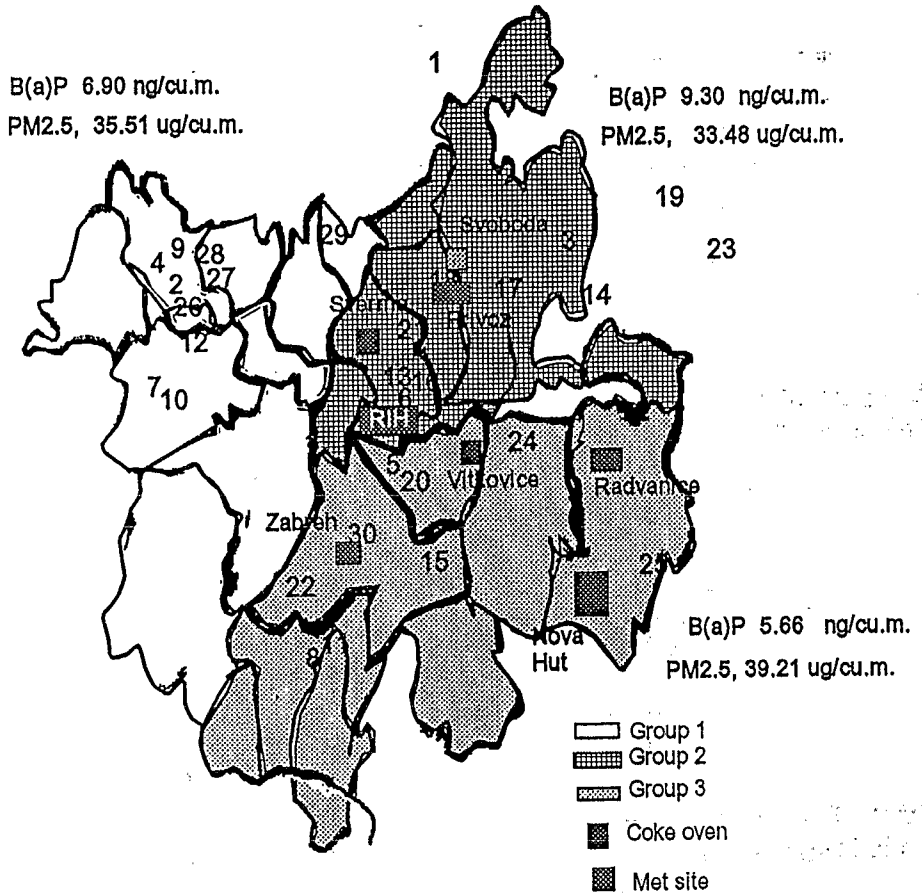


Figure 25. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent individuals and where they live. The location of stationary monitoring platforms and coke ovens are indicated by the key.

Week 3 Average Nighttime PM2.5 Particle and BaP Exposoures

Monday-Tuesday

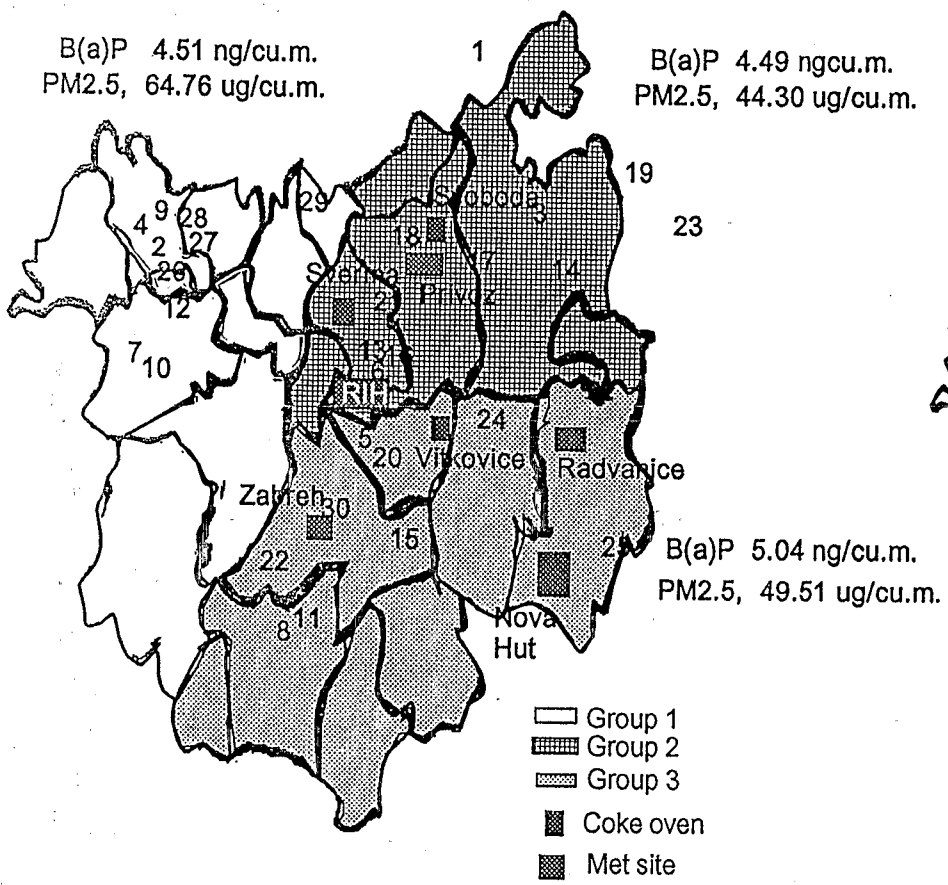


Figure 26. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent individuals and where they live. The location of stationary monitoring platforms and coke ovens are indicated by the key.

Thursday-Friday

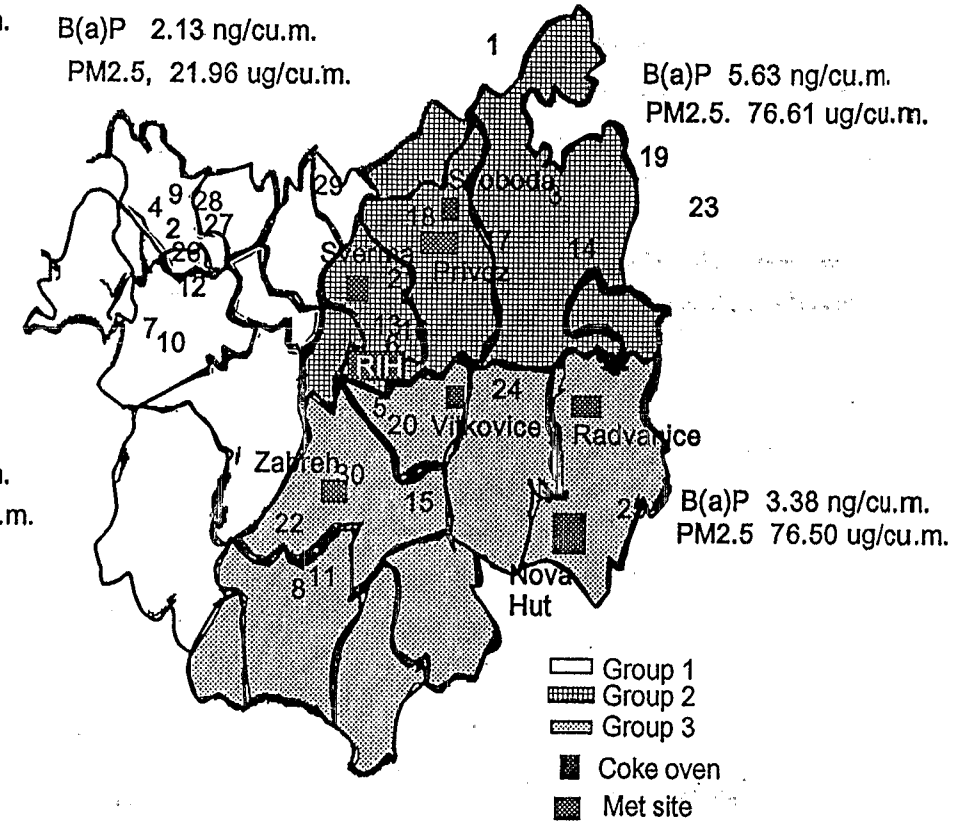


Figure 27. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent individuals and where they live. The location of stationary monitoring platforms and coke ovens are indicated by the key.

Week 4 Average Nighttime PM2.5 Particle and BaP Exposures

Monday-Tuesday

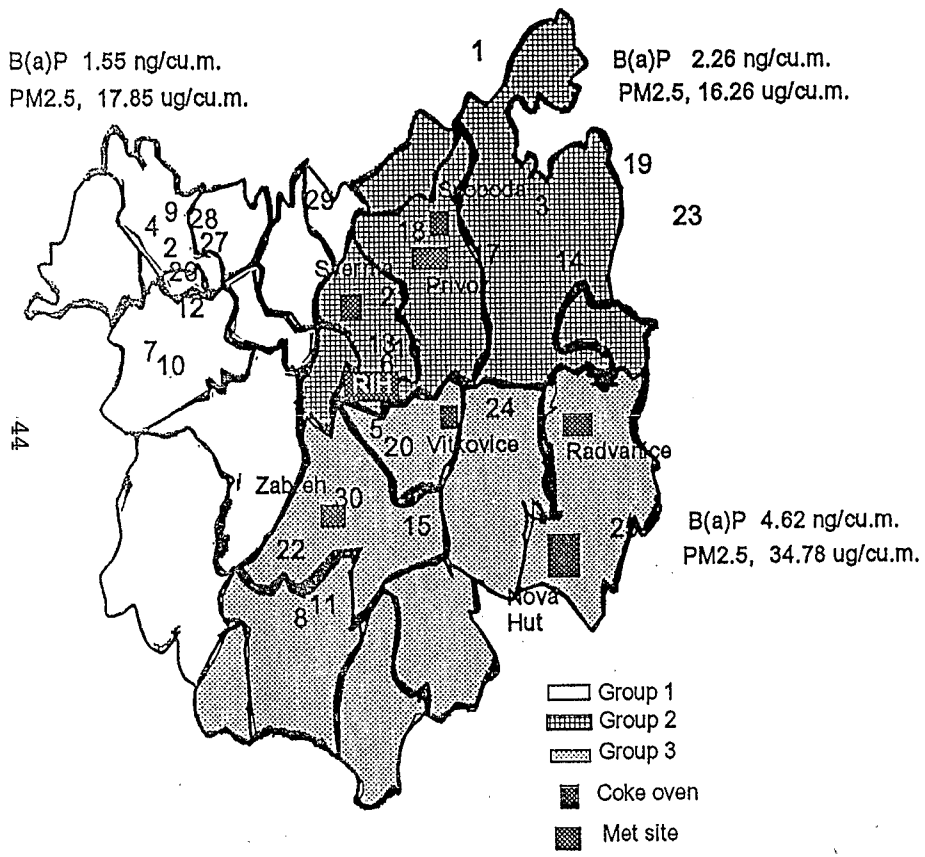


Figure 28. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal
monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent
individuals and where they live. The location of stationary monitoring platforms and coke ovens
are indicated by the key.

Thursday-Friday

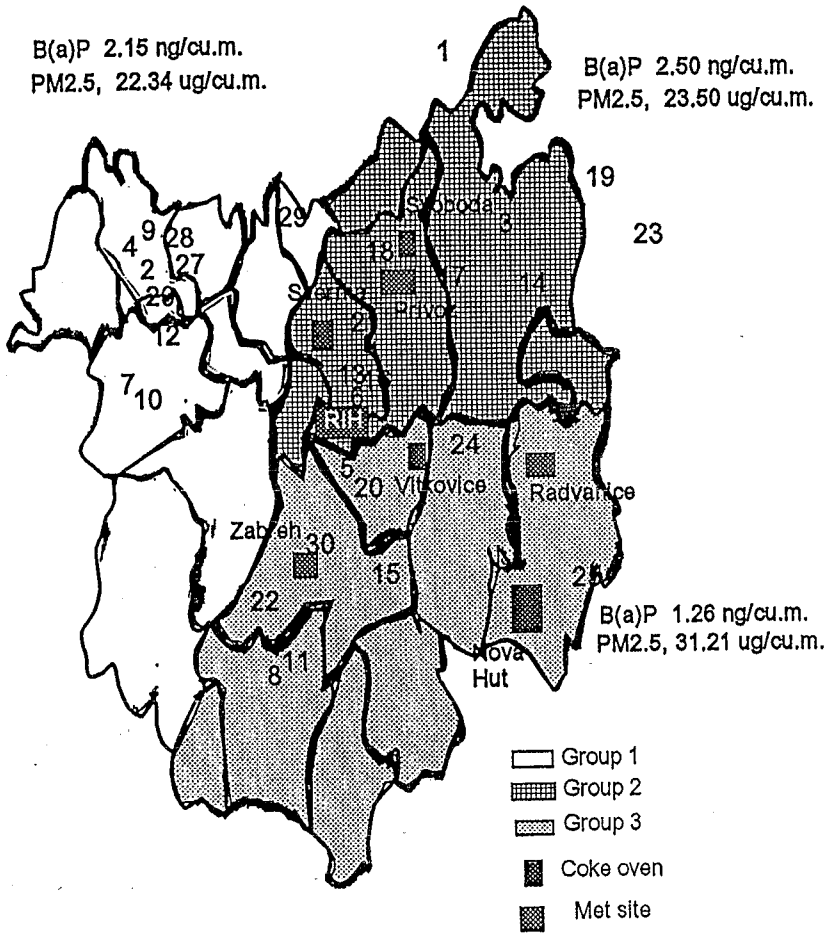


Figure 29. Average PM(2.5) mass and B(a)P concentrations from, individual nighttime personal
monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent
individuals and where they live. The location of stationary monitoring platforms and coke ovens
are indicated by the key.

Average Nighttime PM2.5 and BaP Exposures for 30 Day Study

Monday-Tuesday

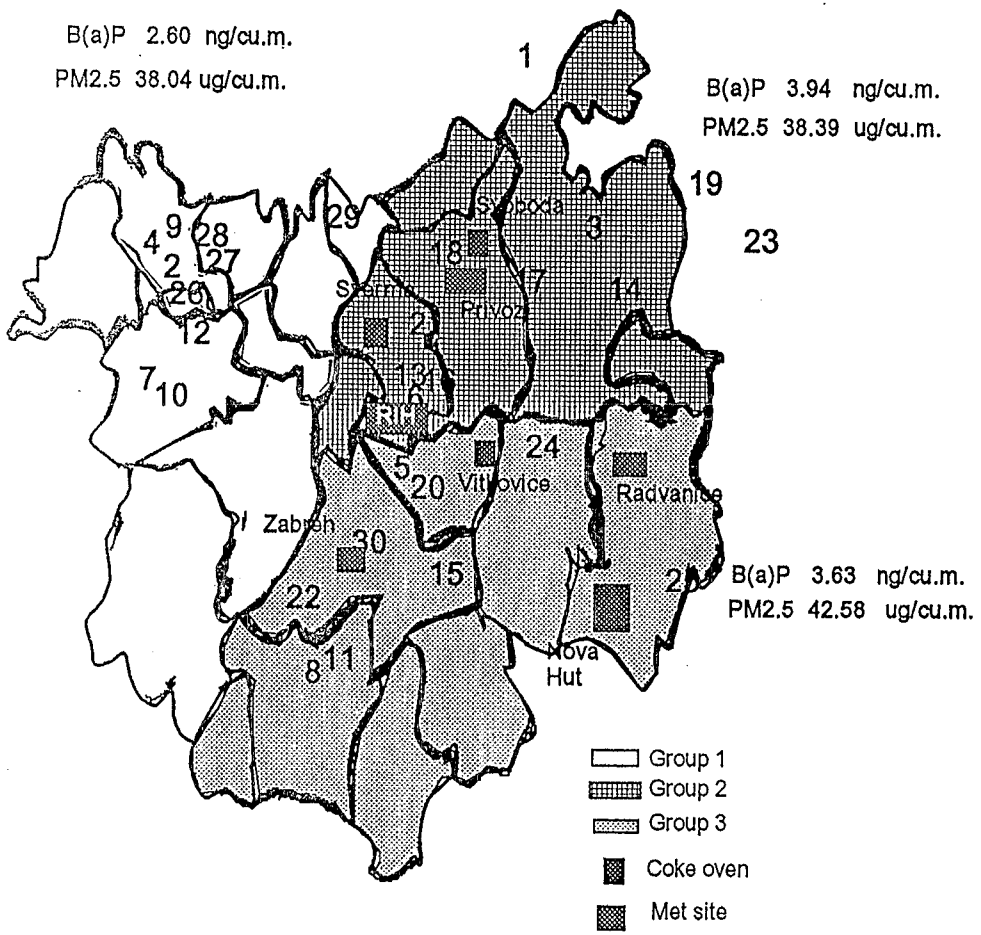


Figure 30. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent individuals and where they live. The location of stationary monitoring platforms and coke ovens are indicated by the key.

Thursday-Friday

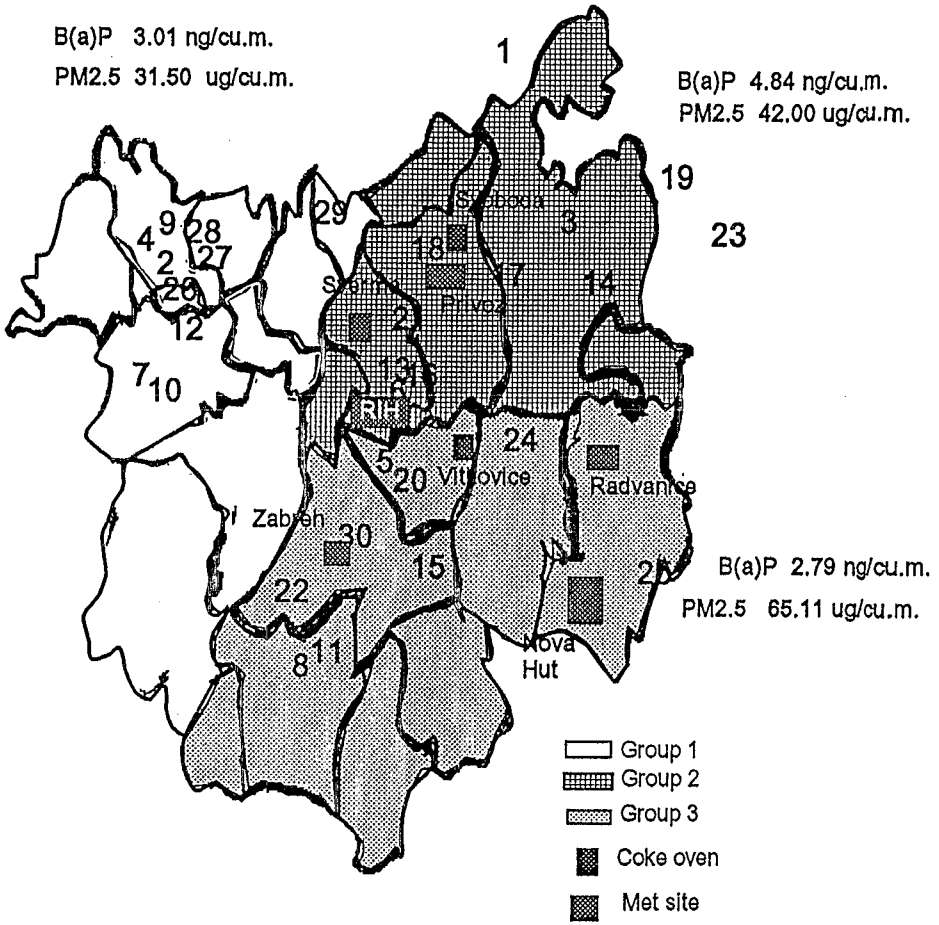


Figure 31. Average PM(2.5) mass and B(a)P concentrations from individual nighttime personal monitoring of volunteers residing within defined shaded areas(groups 1-3). Numbers represent individuals and where they live. The location of stationary monitoring platforms and coke ovens are indicated by the key.

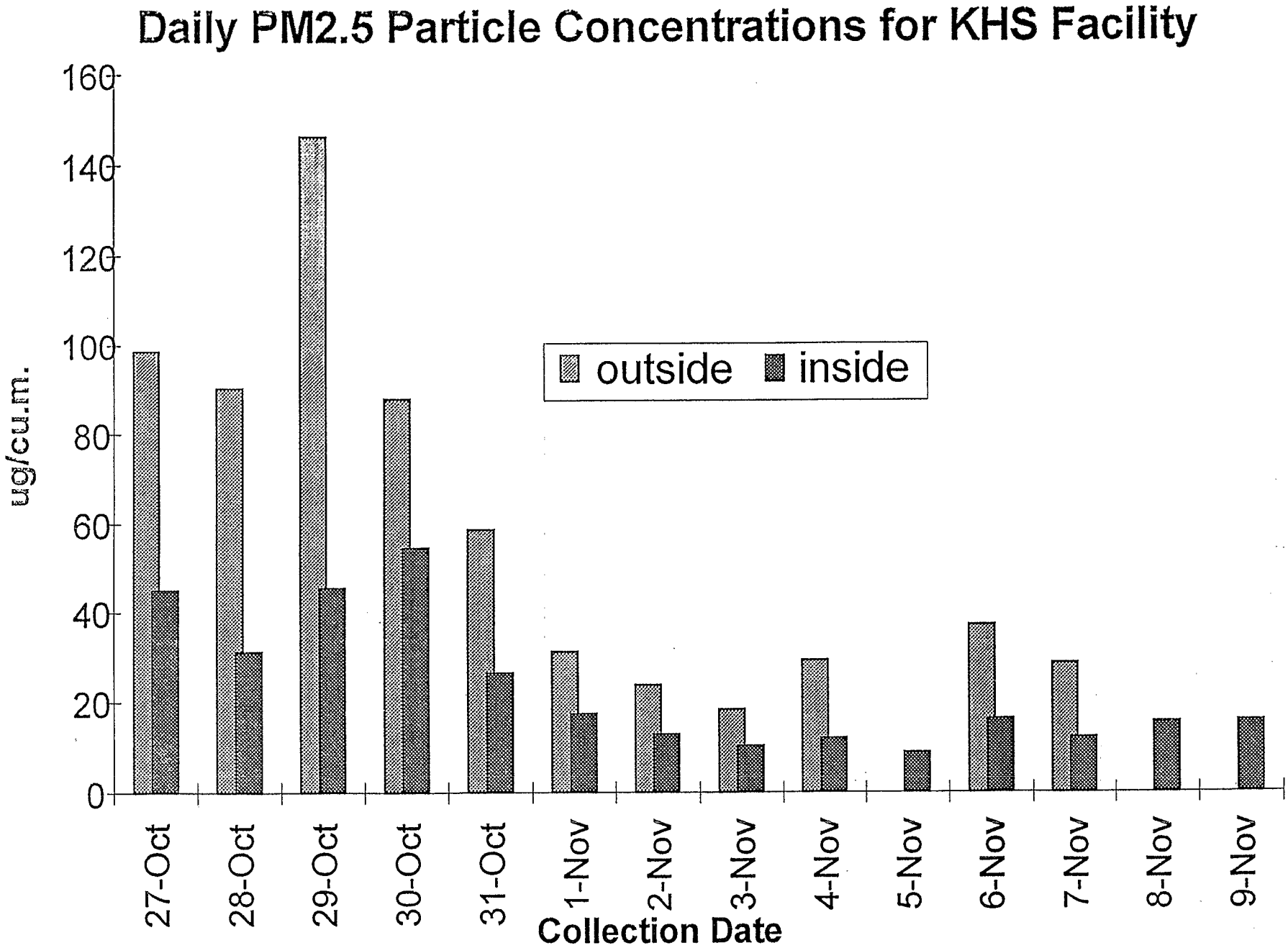


Figure 32. Comparison of PM(2.5) mass concentration from matched indoor and outdoor samplers at KHS-Ostrava.

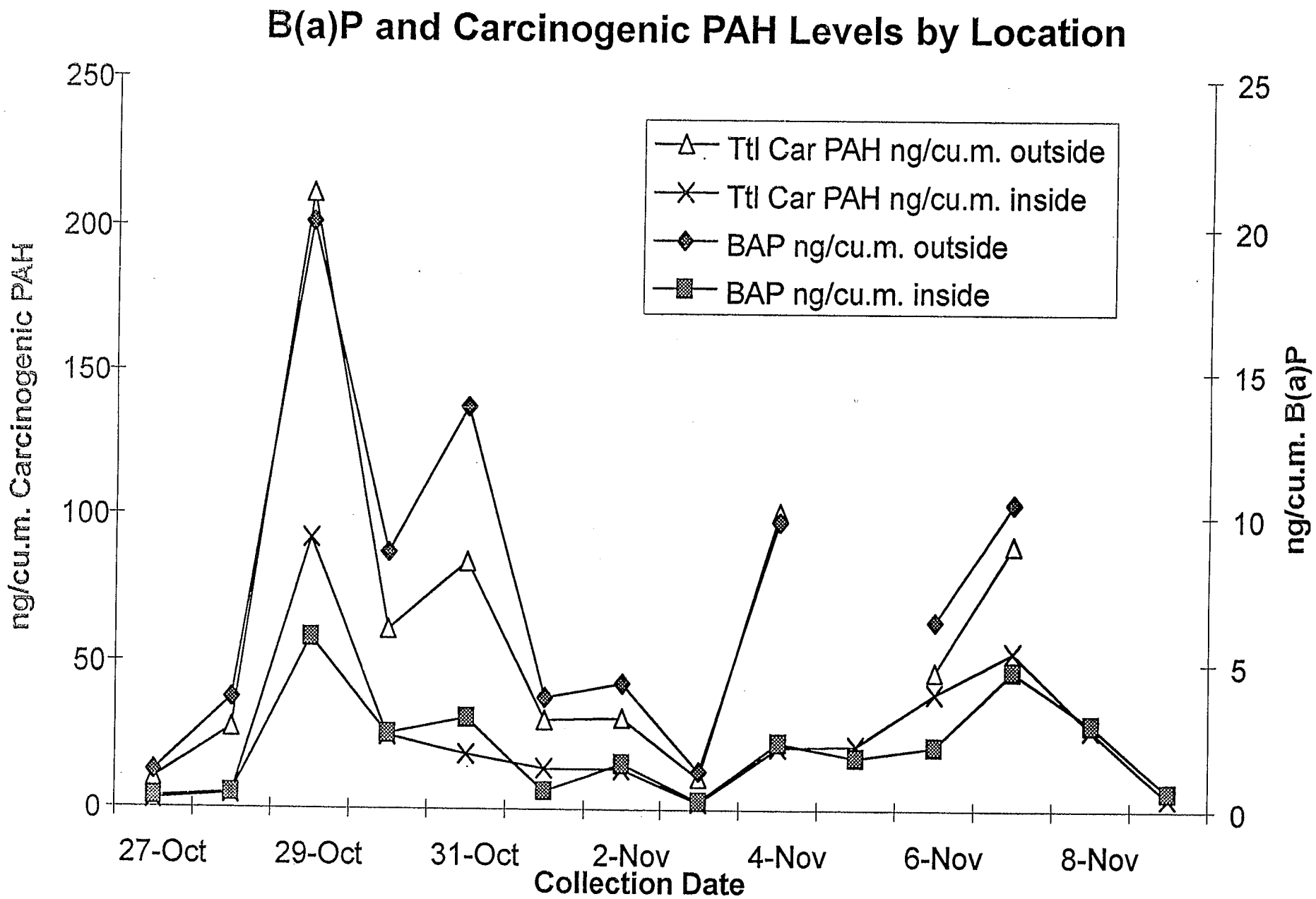


Figure 33. Comparison of PM(2.5), B(a)P, and total carcinogenic PAH's from matched indoor and outdoor samplers located at KHS-Ostrava.

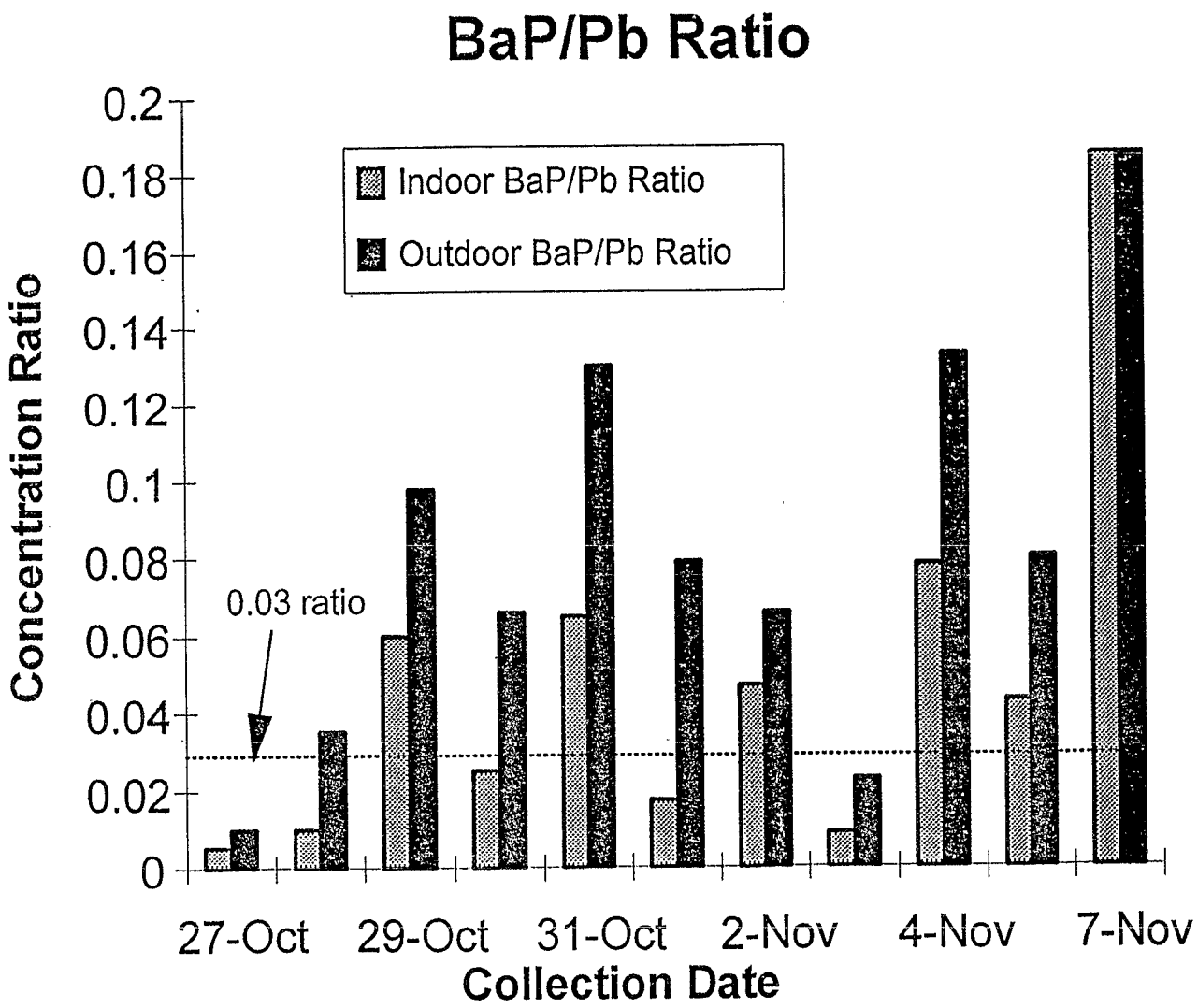


Figure 34. PM(2.5) B(a)P to lead ratio of matched samplers from KHS-Ostrava. Note: Ratios > 0.03 are generally indicative of fine particulate matter sources other than automotive.

Table 1. Ostrava Health Study Testing Regimen						
ACTIVITY	Monday 8:00 am Group 1-Day 1	Monday 4:00 pm Group 1-Day 1	Tuesday 8:00 am Group 1-Day 2	Thursday 8:00 am Group 2-Day 1	Thursday 4:00 pm Group 2-Day 1	Friday 8:00 am Group 2-Day 2
Issue daytime PEM[1]	X[2]			X		
Collect 1st urine	X			X		
Collect daytime PEM and issue nighttime PEM		X			X	
Recover nighttime PEM			X			X
Recover 2nd urine			X			X
Administer survey instrument			X			X
Collect blood specimen			X			X
Process PEM samples		X	X		X	X
Process biological samples			X			X

[1]PEM: Personal exposure monitor.

[2]X's indicate the planned collection of environmental and biomarker samples from each study participant as defined by grouping.

Table 2. HPLC Detection Parameters and Quantitation Limits				
PAH*	Excitation (nm)	Emission (nm)	ILOD**(pg/µl)	QL***(ng/m^3)
Pyrene	276	391	1.4	0.5
Benza(a)anthracene	265	380	3.6	1.2
Chrysene	265	380	0.3	0.1
Benz(b)fluoranthene	290	430	7.6	2.6
Benz(k)fluoranthene	290	430	0.3	0.1
Benzo(a)pyrene	290	430	0.5	0.2
diBenz(ah)anthracene	298	440	5.8	2.0
Benz(ghi)perylene	302	500	32.9	11.4
Indeno(cd)pyrene	302	500	0.4	0.2

*Listed PAHs are IARC registered animal carcinogens with the exception of pyrene.
**Instrument Limit of Detection, based upon a 10 µl standard injection.
***Quantifiable Limit based upon ILOD as well as air volume collected, values represent a 16 hour collection at 1.5 l/min.

Table 3. Inventory of Environmental and Biological Specimens						
ID Number/Period	Male	Female	Week 1	Week 2	Week 3	Week 4
1/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
1 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
2/ Day		X	U,PEM	U,PEM		
2 /Night		X	U,PEM,B,S	U,PEM,B,S		
3/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
3 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
4/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
4 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
5/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
5 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
6/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
6 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
7/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
7 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
8/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
8 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
9/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
9 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,S
10/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
10 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
11/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
11 /Night		X	U,PEM,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
12/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
12 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
13/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
13 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
14/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
14 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
15/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
15 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
16/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
16 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S

1-30 represent volunteer ID numbers, Day-Night represents when PEM exposure started. X=Gender, U=Urine collection, PEM=Personal Exposure Monitoring, B=Blood collection, S=Survey collected.

Table 3. Inventory of Environmental and Biological Specimens (continued)						
ID Number/Period	Male	Female	Week 1	Week 2	Week 3	Week 4
17/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
17 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
18/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
18 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
19/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
19 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
20/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
20 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
21/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
21 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
22/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
22 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
23/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
23 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
24/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
24 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
25/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
25 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
26/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
27 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
27/ Day		X	U,PEM	U,PEM	U,PEM	U,PEM
27 /Night		X	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
28/ Day	X		U,PEM	U,PEM	U,PEM	
28 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	
29/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
29 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S
30/ Day	X		U,PEM	U,PEM	U,PEM	U,PEM
30 /Night	X		U,PEM,B,S	U,PEM,B,S	U,PEM,B,S	U,PEM,B,S

1-30 represent volunteer ID numbers, Day-Night represents when PEM exposure started. X=Gender, U=Urine collection, PEM=Personal Exposure Monitoring, B=Blood collection, S=Survey collected.

Table 4. Summary of Personal Exposure Monitoring $PM_{2.5}$ Particle Concentrations (ug/m^3)					
Study Week	Day		Night		Average Total 24 Hour Exposure ± S.D.
	Range	Average RSP ± S.D.	Range	Average RSP ± S.D.	
Week 1	30.5-404.0	107.0 ± 95.7	12.0-281.8	47.4 ± 52.83	64.7 ± 60.5
Week 2	31.0-277.8	92.8 ± 65.6	10.5-83.0	44.2 ± 22.0	58.9 ± 30.7
Week 3	29.5-474.6	126.7 ± 92.1	16.4-107.4	58.9 ± 27.5	77.8 ± 36.1
Week 4	14.5-87.7	34.9 ± 17.5	5.09-80.1	22.3 ± 17.8	27.6 ± 18.7
4 Week Average		90.3 ± 39.5		43.2 ± 15.3	57.3 ± 21.3

Values represent summation of all 30 participants each week. S.D.=Standard deviation in μg/m^3.

Table 5. Summary of Personal Exposure Monitoring B(a)P Concentrations (ng/m^3)					
Study Week	Day		Night		Average Total 24 Hour Exposure ± S.D.
	Range	Average B(a)P ± S.D.	Range	Average B(a)P ± S.D.	
Week 1	0.7-22.0	7.4 ± 7.2	0.4-4.1	1.1 ± 1.1	2.6 ± 2.2
Week 2	1.6-13.2	3.6 ± 3.2	0.7-22.0	6.5 ± 5.8	6.0 ± 4.7
Week 3	1.2-13.3	4.9 ± 2.9	1.0-14.0	4.1 ± 2.6	4.4 ± 2.4
Week 4	1.1-6.3	3.0 ± 1.6	0.3-8.5	2.2 ± 1.6	2.5 ± 1.6
4 Week Average		4.7 ± 1.9		3.5 ± 2.3	3.9 ± 1.7

Values represent summation of all 30 participants each week. S.D.=Standard deviation in ng/m^3.

Table 6. Summary of Personal Exposure Monitoring 24 Hour Total Carcinogenic PAH Exposure (ng/m^3)					
Study Week	Day		Night		Average Total 24 Hour Exposure ± S.D.
	Range	Average Carcinogenic PAH's ± S.D.	Range	Average Carcinogenic PAH's ± S.D.	
Week 1	0.5-224.9	68.6 ± 71.4	0.5-27.9	9.9 ± 7.4	22.8 ± 20.9
Week 2	0.4-393.2	28.6 ± 72.7	1.1-226.6	46.7 ± 49.6	44.7 ± 41.6
Week 3	13.5-77.6	30.5 ± 17.8	5.3-71.7	31.0 ± 18.6	31.2 ± 16.4
Week 4	1.5-47.6	18.8 ± 12.5	3.6-56.3	15.6 ± 11.8	17.4 ± 17.4
4 Week Average		36.6 ± 21.9		25.8 ± 16.5	29.0 ± 11.9

Values represent summation of all 30 participants each week. S.D.=Standard deviation in ng/m^3.

Table 7. Indoor and Outdoor Ostrava Sample Collection Data

Start Date	Filter No. Inside	Filter No. Outside	Particle mass (mg) Inside	Particle mass (mg) Outside	m^3 Collected Inside	m^3 Collected Outside	Min. Collected Inside	Min. Collected Outside	Particle (ug/m3) Inside	Particle (ug/m3) Outside	Particle Concentration In/Out (%)
10/27/95	TM615	TM614	0.67	1.42	15.0	14.4	1500	1500	45.0	98.7	45.6
10/28/95	TM612	TM613	0.41	1.35	13.2	15.0	1411	1426	31.2	90.0	34.7
10/29/95	TM579	TM577	0.64	1.79	14.1	12.2	1418	1400	45.4	146.1	31.1
10/30/95	TM578	TM576	0.78	1.26	14.4	14.4	1429	1440	54.4	87.6	62.1
10/31/95	TM555	TM554	0.38	0.80	14.5	13.8	1449	1435	26.4	58.4	45.3
11/01/95	TM556	TM539	0.25	0.45	14.3	14.4	1430	1440	17.2	31.3	55.2
11/02/95	TM540	TM542	0.18	0.32	14.3	13.5	1431	1417	12.8	23.7	54.0
11/03/95	TM666	TM667	0.15	0.26	14.7	14.1	1424	1444	10.3	18.4	55.8
11/04/95	TM665	TM664	0.17	0.40	14.4	13.8	1443	1425	12.0	29.3	40.9
11/05/95	TM663	TM662	0.13		14.5		1441		8.9		
11/06/95	TM661	TM659	0.23	0.51	14.1	13.9	1437	1413	16.0	37.1	43.2
11/07/95	TM561	TM660	0.17	0.43	14.2	14.9	1420	1452	12.2	28.6	42.8
11/08/95	TM560	TM559	0.22		14.2		1456		15.4		
11/09/95	TM558		0.23		14.5		1436		15.7		

Table 8. Outdoor B(a)P Concentrations (ng/m^3)				
Date	KHS-Ostrava	Zabreh	Radvanice	Privoz
October 27	1.3		3.4	3.0
October 28	3.8		5.7	8.5
October 29	20.16		15	13.2
October 30	8.73		11	11.2
October 31	13.76	5.4		9.1
November 1	3.84	1.8		4.2
November 2	4.3	3.3		5.1
November 3	1.33	0.9		2.0
November 4	9.82	4.0		3.0
November 6	6.43	2.4		3.8
November 7	10.45	3.5		3.7

Values from Zabreh, Radvanice, and Privoz were determined during the continuous 30 day monitoring study running concurrent with the Ostrava Health Study. These values were provided by the Czech firm ECOCHEM.

Table 9. Indoor Fine Particle Concentrations (ng/m^3)														
	10/27	10/28	10/29	10/30	10/31	11/1	11/2	11/3	11/4	11/5	11/6	11/7	11/8	11/9
Fine Mass	44978	31243	45432	54414	26432	17243	12788	10258.0	11989.0	8867.0	16048.0	12226.0	15427.0	15676.0
AL	151.9			157.2	173.3	163.0		110.5	128.9	160.8		118.0	155.8	
SI	230.0	106.2	172.1	319.3	247.6	193.9	191.8	124.5	143.9	41.5	196.6	90.6	200.4	246.0
P			48.7				39.6	30.6				53.6		
S	3618.0	2606.0	3453.5	5121.4	2850.6	1306.9	775.7	661.6	1052.4	920.8	1329.0	999.5	1023.4	838.2
CL	239.7	188.3	259.2	337.7	235.0	380.7	187.7	313.5	129.0	90.7	250.4	205.0	226.8	271.6
K	686.2	568.7	604.0	676.2	267.6	164.5	100.9	119.0	142.2	84.9	136.0	93.6	167.5	177.4
CA	193.1	71	177.9	229.4	316.0	226.2	162.2	216.0	171.1	45.9	208.8	136.6	227.5	238.5
TI	18.9		23.3	18.5	16.0	13.0		12.8		21.1				14.3
V	8.4		5.6	8.0						5.5				
CR	3.0		2.5			2.4		2.1		4.8				
MN	24.1	13.9	11.5	9.8	11.8	8.9	5.9	18.7	2.2		5.5			
FE	526.1	216.8	247.6	255.5	194.5	164.9	142.3	258.9	61.3	64.3	110.0	45.5	86.6	377.6
NI														3.6
CU	11.4		10.0	8.8	4.0	3.4	4.3				5.8		17.2	7.7
ZN	316.8	109.2	178.3	408.2	151.7	339.4	147.7	248.0	38.6	65.0	133.2	40.5	66.2	164.9
AS	8.6	8.4		9.9	7.4								10.2	15.4
SE				2.1									1.7	1.9
BR	13.1	9.9	14.2	18.1	7.5		4.3	3.9	3.2	2.4	6.8	6.0	6.5	5.0
RB		2.6	4.1		4.0				1.9					2.2
SR		3.4		2.4									2.4	
I			22.7											
BA		38.9	31.6	38.7					33.4	29.3	31.2	30.2		
PB	68.9	50.9	96.3	100.7	48.1	35.4	33.5	28.9	29.6	18.3	50.1	25.7	43.1	42.1

Values determined by XRF analysis of $PM_{2.5}$ collected ambient air particulate at KHS-Ostrava. Sampler located in an unused office area. Values have been blank corrected. Only data greater than 2 X sigma(analytical uncertainty) is presented.

Table 10. Outdoor Fine Particle Concentration (ng/m^3)											
	10/27	10/28	10/29	10/30	10/31	11/1	11/2	11/3	11/4	11/6	11/7
Fine Mass	98724.0	90029.0	146148.0	87639	58413.0	31250.0	23697.0	18396.0	29341.0	37109.0	28556.0
AL	204.3		511.0						140.4		
SI	406.4	239.2	790.9	234.8	188.6	163.9	101.3	119.0	55.6	66.4	46.7
S	6416.3	4785.9	7168.3	5341.5	4572.4	2075.6	1544.1	1146.4	2389.3	2453.6	2017.7
CL	834.3	1192.9	5336.4	1962.2	1780.5	1020.8	840.1	502.8	1395.4	1711.6	1453.1
K	1361.3	1043.3	1296.0	675.1	456.2	194.4	171.5	129.9	222.8	168.4	139.3
CA	261.9	153.6	219.4	87.6	145.2	64.7	114.7	65.2	41.0	38.3	65.3
TI	28.1	29.6	38.6	19.1	17.7	14.5	15.0				
V	14.6			8.0	6.3	5.3		4.7			
CR	5.1	2.9	3.5	3.9	5.0		2.3	3.8			
MN	60.1	21.4	29.9	11.4	43.2	10.8	26.7	30.0		7.8	2.3
FE	1248.6	480.8	936.6	334.5	492.2	215.9	412.8	321.4	44.0	171.9	50.4
NI	4.3	8.8						3.5			
CU	15.8	11.4	25.9	12.7	10.5	10.5	7.6	11.8		8.7	3.2
ZN	560.8	233.5	437.4	633.7	430.5	579.8	531.8	350.5	74.2	284.3	74.2
AS	22.9	12.9	14.1	15.1	6.5	8.6	9.3			13.8	
SE	3.2	3.0		3.2		1.7	2.0		1.7		
BR	22.1	23.2	50.1	27.1	23.6	7.4	9.1	4.5	12.6	22.5	11.4
RB	4.5	3.7	7.7				3.3	2.6	1.8		2.3
SR			4.2			2.3			3.2		
I	26.8	17.0	35.5	25.8							
BA		47.5	133.6						41.1	42.8	
PB	123.2	107.6	205.6	130.7	105.4	48.5	64.8	56.2	73.6	79.6	56.2

Values determined by XRF analysis of $PM_{2.5}$ collected ambient air particulate at KHS-Ostrava. Sampler located on an outdoor monitoring platform already operating. Values have been blank corrected. Only data greater than 2 X sigma(analytical uncertainty) is presented.

Table 11. Correlation of Select Ambient Air Metal Concentrations

	Mass	Si	S	Cl	K	Ca	Ti	Mn	Fe	Cu	Zn	Br	Pb
Mass	0.886	0.285	0.812	0.065	0.904	-0.113	0.996	0.431	0.569	0.847	0.261	0.842	0.87
Si	0.721	0.177	0.604	0.159	0.72	-0.029	0.911	0.445	0.548	0.709	0.266	0.667	0.755
S	0.92	0.42	0.882	0.039	0.923	0.03	0.949	0.473	0.635	0.85	0.3	0.858	0.861
Cl	0.491	0.103	0.431	0.032	0.402	0.028	0.824	-0.117	-0.012	0.407	-0.068	0.488	0.659
K	0.835	0.204	0.746	-0.033	0.922	-0.215	0.9	0.617	0.74	0.913	0.266	0.756	0.735
Ca	0.675	0.199	0.581	-0.081	0.743	-0.069	0.752	0.679	0.782	0.707	0.22	0.558	0.549
Ti	0.578	-0.419	0.41	-0.305	0.71	-0.462	0.929	0.479	0.431	0.792	-0.272	0.431	0.583
Mn	0.341	0.24	0.302	-0.205	0.409	0.264	0.242	0.81	0.809	0.429	0.194	0.12	0.19
Fe	0.678	0.286	0.572	0.05	0.732	0.031	0.703	0.771	0.878	0.782	0.363	0.566	0.583
Cu	0.679	0.216	0.563	0.197	0.678	0.067	0.871	0.496	0.567	0.72	0.33	0.614	0.746
Zn	0.548	0.77	0.521	0.66	0.438	0.465	0.138	0.47	0.599	0.178	0.867	0.62	0.532
Br	0.753	0.294	0.707	-0.006	0.706	0.012	0.962	0.154	0.29	0.653	0.066	0.735	0.844
Pb	0.836	0.336	0.775	0.018	0.808	0.01	0.989	0.321	0.464	0.765	0.19	0.797	0.886

Comparison of select PM2.5 indoor and outdoor metal concentrations from sampling at KHS-Ostrava. Correlations indicate agreement between paired elements. Shading indicates highly correlated species.

Table 12. KHS-Ostrava Indoor/Outdoor Correlations, Ratios, and Enrichment Factors			
	Correlation	I/O Ratio	Enrichment Factor
Mass	0.886	0.56	
Si	0.177	1.41	3.0
S	0.882	0.58	1.2
Cl	0.032	0.22	0.5
K	0.922	0.69	1.5
Ca	-0.069	2.43	5.2
Ti	0.929	0.81	1.7
Mn	0.810	0.59	1.3
Fe	0.878	0.65	1.4
Cu	0.720	0.53	1.2
Zn	0.867	0.50	1.1
Br	0.735	0.47	1.0
Pb	0.886	0.54	1.2

For a given elemental species, the enrichment factor is calculated as the ratio of the indoor mass fraction to the outdoor mass fraction where the mass fraction is the mass concentration of the species divided by the $PM_{2.5}$ mass concentration.