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Background Levels of Polycyclic Aromatic Hydrocarbons (PAH) and Selected Metals in New England Urban Soils

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ABSTRACT: Polycyclic aromatic hydrocarbons (PAH) are byproducts of combustion and are ubiquitous in the urban environment. They are also present in industrial chemical wastes, such as coal tar, petroleum refinery sludges, waste oils and fuels, and wood-treating residues. Thus, PAHs are chemicals of concern at many waste sites. Risk assessment methods will yield risk-based cleanup levels for PAHs that range from 0.1 to 0.7 mg/kg. Given their universal presence in the urban environment, it is important to compare risk-based cleanup levels with typical urban background levels before utilizing unrealistically low cleanup targets. However, little data exist on PAH levels in urban, nonindustrial soils. In this study, 60 samples of surficial soils from urban locations in three New England cities were analyzed for PAH compounds. In addition, all samples were analyzed for total petroleum hydrocarbons (TPH) and seven metals. The upper 95% confidence interval on the mean was 3 mg/kg for benzo(*a*)pyrene toxic equivalents, 12 mg/kg for total potentially carcinogenic PAH, and 25 mg/kg for total PAH. The upper 95% confidence interval was 373 mg/kg for TPH, which exceeds the target level of 100 mg/kg used by many state regulatory agencies. Metal concentrations were similar to published background levels for all metals except lead. The upper 95% confidence interval for lead was 737 mg/kg in Boston, 463 mg/kg in Providence, and 378 mg/kg in Springfield.

KEY WORDS: background, PAH, metals, urban, anthropogenic, soil.

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are byproducts of combustion and are naturally occurring chemicals in the environment. Forest fires and volcanoes are major natural sources of PAHs, but there are anthropogenic sources as well due to burning of fossil fuels, including automobile and industrial emissions. PAHs are chemicals of concern in many waste site investigations that are undertaken pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the Resource Conservation and Recovery Act (RCRA), and state hazardous waste programs. Risk assessments performed according to federal guidance for former manufactured gas plant sites, wood treating facilities, petroleum refineries, and other sites generally conclude that PAHs pose unreasonable risks to human health and that remedial actions must be taken to reduce risks to acceptable levels. The majority of the risk posed by PAHs is generally due to benzo(*a*)pyrene and the other PAHs that have been shown to cause cancer in laboratory animals after repeated dosings. The U.S. EPA (1993a) currently identifies seven PAHs as "probable human (B2) carcinogens": benzo(*a*)pyrene, benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, chrysene, dibenz(*a*,*h*)anthracene, and indeno(1,2,3-c,d)pyrene.

Because of the very health-protective assumptions used in regulatory risk assessments, very low risk-based clean-up levels for PAHs are derived for such sites. In Michigan, residential soil cleanup levels of 0.33 mg/kg for each carcinogenic PAH have been set (MDNR, 1993). In New Jersey, proposed residential soil cleanup levels are 0.66 mg/kg for benzo(*a*)pyrene (New Jersey *Register*, 1992). The use of standard CERCLA risk assessment guidance (U.S. EPA, 1993b) results in the derivation of a risk-based cleanup level for benzo(*a*)pyrene of 0.1 mg/kg.

All of these risk-based soil cleanup levels are below the urban, nonindustrial background soil concentrations presently reported in the literature. However, the availability of such data is very limited. Blumer (1961) reports that benzo(*a*)pyrene concentrations in Cape Cod, MA, soils range from 0.04 to 1.3 mg/kg. Menzie et al. (1992) report that urban background soil levels of total carcinogenic PAH range from 0.06 to 5.8 mg/kg. Butler et al. (1984) report that total PAH levels in soils alongside roadways in England range from 4 to 20 mg/kg, and potentially carcinogenic PAH range from 0.8 to 11.5 mg/kg. Blumer et al. (1977) report that total PAH levels in soils in a Swiss town range from 6 to 300 mg/kg.

It is very difficult to compare the data from these studies to the results of site risk assessments due to the limited dataset and the nonuniformity of the PAH compounds evaluated. Clearly, more data are required from nonindustrial urban locations to define the urban background level for PAH and to critically evaluate the role of risk assessment in setting remedial goals for PAH in soils. Accordingly, we have collected 60 samples of surficial soils from urban locations in three New England cities and analyzed them for all 17 PAH compounds present on the EPA's Target Compound List, which is used in the Superfund program. In addition, all samples were analyzed for total petroleum hydrocarbons (TPH) and for seven metals: arsenic, barium, cadmium, chromium, lead, mercury, and selenium.

II. METHODS

A. Sample Collection

Samples of surficial soils from urban locations in three New England cities were collected: Boston, MA; Providence, RI; and Springfield, MA. Twenty independent samples and duplicates of two samples were collected in each city. The samples were collected on July 21, 22, and 23, 1992, respectively. The samples were taken at a depth of 0 to 6 in. in areas considered to be not directly affected by industrial sites. Generally, the locations were along roads and sidewalks, and in parks and open lots. Each location was characterized in writing, including a soil description, and photographically documented. The samples were collected following standard environmental sampling protocols (U.S. EPA, 1986).

B. **Sample Analysis**

Chemical analysis of the samples was performed by AnalytiKEM, Inc. (Cherry Hill, NJ). The samples were analyzed by GC-MS for the 17 PAH compounds present on the EPA's Target Compound List using the methods required by EPA Method 8270 for the analysis of semivolatile compounds. In addition, the samples were analyzed for the eight RCRA metals, total petroleum hydrocarbons (TPH; EPA Method 418.1), and total solids. The complete analyte list is given in Table 1.

C. **Data Validation**

Validation of the data received from AnalytiKEM was performed according to U.S. EPA (1991) guidelines. The data were reviewed for completeness, holding times, GC-MS tuning and system performance, initial and continuing calibrations, laboratory method blank analysis, surrogate recoveries, matrix spike and matrix spike duplicate analysis, field duplication precision, and compound quantitation and detection limits.

D. **Data Analysis**

The analytical data were summarized in accordance with U.S. EPA (1989) risk assessment guidance. If a compound was detected at least once in surface soil, one half the sample quantitation limit (SQL) was used as a proxy concentration for all samples reported as "below detection limit" in the estimation of exposure point concentrations. However, if a compound was not detected in any sample, that compound was omitted from further consideration. In addition, when a proxy concentration (i.e., one half the detection limit) was greater than the highest actual detected value for a compound in any sample, that concentration was considered to be an aberration and was omitted from the database. This is consistent with U.S. EPA (1989) guidance, which recognizes that high sample quantitation limits can lead to unrealistic concentration estimates.

TABLE 1
Chemical Analyses of Urban Soils

Semivolatile Organics, EPA Target Compound List
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo(*a*)anthracene
Chrysene
Benzo(*b*)fluoranthene
Benzo(*k*)fluoranthene
Benzo(*a*)pyrene
Indeno(1,2,3-cd)pyrene
Dibenzo(*a,h*)anthracene
Benzo(*g,h,i*)perylene
2-Methylnaphthalene
Metals
Arsenic, total
Barium, total
Cadmium, total
Chromium, total
Lead, total
Mercury, total
Selenium, total
Silver, total
Other
Total petroleum hydrocarbons
Solids

A slightly different method of analysis was used to evaluate PAH. Because PAH are generally found in groups, it was conservatively assumed that if one PAH was detected in a sample, other compounds in that class might also be present in that sample. Therefore, if one PAH was detected in a sample, all undetected PAH were assigned a proxy concentration equal to one half the SQL. If a sample had no detected PAH, no PAH were assumed to be present in the sample, and a concentration of zero was used for all nondetects.

Summary statistics (minimum, maximum, arithmetic mean, upper 95% confidence limit on the arithmetic mean, and frequency of detection) were generated for each compound for each city and for all three cities combined.

The data for PAH were summarized in several different ways. Of the 17 PAH analyzed in each sample, seven are considered to be probable human carcinogens (Group B2) by the U.S. EPA (1993a). The U.S. EPA has derived a cancer slope factor, which is a measure of the carcinogenic potency of a compound, only for benzo(*a*)pyrene (B(*a*)P) (U.S. EPA, 1993a). Review of the literature indicates that not all PAH are equally potent with respect to tumor induction. Several researchers have proposed toxic equivalency schemes that relate the tumorigenic potency of each PAH to that of B(*a*)P (ICF-Clement Associates, 1988; Woo, 1989). B(*a*)P toxic equivalency factors (B(*a*)P-TEFs) can be used to adjust either the B(*a*)P dose-response value to provide a compound-specific dose-response value, or the concentration of each PAH in a sample to be expressed in terms of B(*a*)P toxic equivalents (B(*a*)P-TE). The latter method was used here. B(*a*)P-TE were calculated using the B(*a*)P toxic equivalency factors recommended for use by the U.S. EPA (1993c), as shown in Table 2. For each sample, PAH concentrations were reported for each of the 17 PAH on the analyte list, for total PAH (tPAH), for total carcinogenic PAH (cPAH), and for B(*a*)P-TE, and these values were used to generate the summary statistics for each group of samples.

III. RESULTS

Analysis of the laboratory results for the PAH indicates that quality control criteria were acceptable. The data were analyzed to determine if any statistically significant differences existed between the datasets for the three cities. A Hartley test for homogeneity of variances (Mendenhall, 1979) and a one-factor analysis of variance to test for equality of the means (Mendenhall, 1979) indicated no statistically significant differences. The results indicate that the PAH data can be pooled and treated as one dataset for further statistical analyses.

TABLE 2
Benzo(*a*)Pyrene Toxic Equivalent Factors (BAP-TEF)

Compound	EPA TEF
Benzo(*a*)pyrene	1.0
Benz(*a*)anthracene	0.1
Benzo(*b*)fluoranthene	0.1
Benzo(*k*)fluoranthene	0.1
Chrysene	0.001
Dibenzo(*a,h*)anthracene	1.0
Indeno(1,2,3-c,d)pyrene	0.1

The results of the PAH analyses are presented in Table 3 for all cities combined. A summary of the PAH results by city and for all cities combined is presented in Table 4, which reports for each: tPAH, total cPAH, and total B(*a*)P-TE. The arithmetic mean and the upper 95% confidence limit concentration are reported for each. Table 4 provides a summary of the data by city, and the results are graphically presented in Figure 1.

Table 5 presents a summary of the metals, TPH, and solids data by city. A Hartley test for homogeneity of variances and a one-factor analysis of variance to test for equality of the means indicated that the metals and TPH data from the three cities cannot be combined. This is due to the fact that the concentrations in each city are not normally distributed and did not have equal variances. The concentrations of the metals are compared to the arithmetic mean concentrations in the eastern U.S. (ATSDR, 1992) in Table 5. Most notably, lead concentrations are much higher than background concentrations. This is most likely due to the effects of automobile exhaust.

In order to determine if sample location significantly affected PAH concentration results, individual samples were classified based on the sample location's

TABLE 3
Summary Statistics for PAH — All Areas Combined

Compound	Minimum detect (mg/kg)	Maximum detect (mg/kg)	Arithmetic mean	Upper 95% interval (mg/kg)	Frequency of detection[a]	
2-Methylnaphthalene	0.017	0.64	0.151	0.173	19	62
Acenaphthene	0.024	0.34	0.201	0.306	30	62
Acenaphthylene	0.018	1.10	0.173	0.208	24	62
Anthracene	0.029	5.70	0.351	0.535	54	62
Benzo(*a*)anthracene	0.048	15.00	1.319	1.858	58	62
Benzo(*a*)pyrene	0.040	13.00	1.323	1.816	57	62
Benzo(*b*)fluoranthene	0.049	12.00	1.435	1.973	55	62
Benzo(*g,h,i*)perylene	0.200	5.90	0.891	1.195	36	62
Benzo(*k*)fluoranthene	0.043	25.00	1.681	2.522	59	62
Chrysene	0.038	21.00	1.841	2.693	60	62
Dibenzo(*a,h*)anthracene	0.020	2.90	0.388	0.521	32	62
Fluoranthene	0.110	39.00	3.047	4.444	60	62
Fluorene	0.022	3.30	0.214	0.317	35	62
Indeno(1,2,3-c,d)pyrene	0.093	6.00	0.987	1.293	43	62
Naphthalene	0.018	0.66	0.125	0.149	35	62
Phenanthrene	0.071	36.00	1.838	2.982	61	62
Pyrene	0.082	11.00	2.398	2.945	61	62
Total BAP-TE	0.257	21.31	2.437	3.324	62	62
Total carcinogenic PAH	0.680	77.70	8.973	12.423	62	62
Total PAH	2.292	166.65	18.361	24.819	62	62

[a] Frequency of detection = number detected: number samples.

TABLE 4
Background PAH Concentrations in Urban Surface Soils[a]

	Boston (n = 20)		Providence (n = 20)		Springfield (n = 20)		All cities (n = 60)	
Compound	**Arithmetic mean (ppm)**	**Upper 95% CI (ppm)**	**Arithmetic mean (ppm)**	**Upper 95% CI (ppm)**	**Arithmetic mean (ppm)**	**Upper 95% CI (ppm)**	**Arithmetic mean (ppm)**	**Upper 95% CI (ppm)**
Total B(*a*)P-TE	2.4	4.6	2.1	2.9	2.8	4.5	2.4	3.3
Total cPAH	8.4	16.0	7.8	11.0	10.6	18.3	9.0	12.4
Total PAH	18.7	35.9	16.8	23.5	19.1	29.9	18.4	24.8
TPH	474.9	652.6	267.4	338.2	184.4	233.3	306.2	372.8

[a] 0 to 6 in.

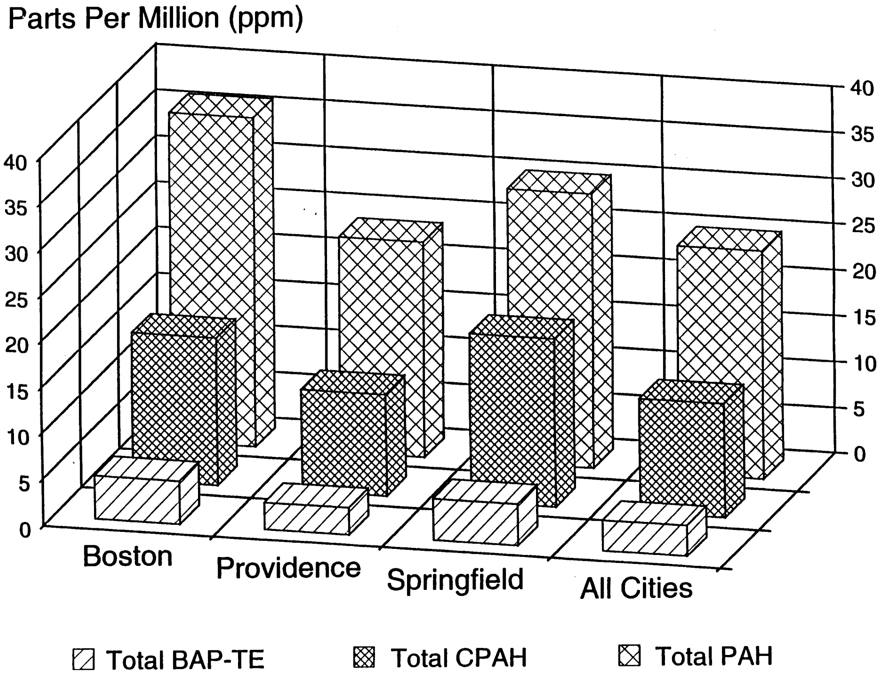

FIGURE 1. Background concentrations of PAH in urban soils. Data presented are the upper 95% confidence interval on the arithmetic mean. Data are presented numerically in Table 4.

proximity to asphalt pavement, based on both written and photographic documentation of sample location. Generally, samples collected within 4 to 6 ft of a road were considered to be near pavement. Of the 60 separate locations, 42 were considered to be near pavement and 18 were not. When tested for equality of variance and means as above, the two populations were determined to be significantly different. The mean total PAH concentration near pavement was 22 ppm compared to 8 ppm not near pavement. These results are shown in Table 6.

Similar analyses were performed to see if TPH or total organic carbon concentrations could be used as surrogates for PAH concentrations. The results showed that there is no correlation between PAH and TPH concentrations, nor between PAH and total organic carbon concentrations (data not shown).

The highest total PAH concentration detected was 166 mg/kg, taken from a street corner in Boston. The next highest PAH concentration was 109 mg/kg, taken at the base of a telephone pole. Four of the 60 samples were taken at the bases of telephone poles, with widely varying results. The total PAH concentrations in the other three locations were 62, 4, and 45 mg/kg.

TABLE 5

Summary Statistics for Metals, TPH, and Soils by City

	Boston (n = 20)		Providence (n = 20)		Springfield (n = 20)		
Compound	**Arithmetic mean (mg/kg)**	**Upper 95% interval (mg/kg)**	**Arithmetic mean (mg/kg)**	**Upper 95% interval (mg/kg)**	**Arithmetic mean (mg/kg)**	**Upper 95% interval (mg/kg)**	**Arithmetic mean in U.S. soils[a] (mg/kg)**
Arsenic, total	4.20	5.59	3.53	4.27	5.63	9.23	7.4
Barium, total	53.95	66.25	45.29	59.43	45.17	51.03	420
Cadmium, total	1.55	2.79	ND	ND	ND	ND	0.25[b]
Chromium, total	23.00	27.69	12.08	14.35	12.62	14.45	52
Lead, total	398.70	737.44	305.76	462.98	261.69	377.76	17
Mercury, total	0.29	0.39	0.19	0.24	0.20	0.25	0.12
Selenium, total	0.51	0.57	0.39	0.48	0.53	0.55	0.45
Total petroleum hydrocarbons	474.90	652.62	267.43	338.19	184.38	233.27	—
Total solids	90%	93%	93%	95%	90%	92%	—

[a] ATSDR. 1992. *Public Health Assessment Guidance Manual.* PB92-147164. U.S. Department of Health and Human Services.

[b] ATSDR. 1991. *Toxicological Profile for Cadmium.* PB92-147164. Draft. U.S. Department of Health and Human Services.

TABLE 6

Comparison of Background PAH Concentrations in Urban Soils: The Effects of Proximity to Pavement

					Results of statistical analysis					
					Test for homogeneity of variances			**Test of equality of means**		
	Near pavement		**Not near pavement**							
Compound	**Arithmetic mean (ppm)**	**Standard deviation**	**Arithmetic mean (ppm)**	**Standard deviation**	**Sample F-statistics**	**Associated degrees of freedom**	**Statistically significant at 0.05 level of significance**	**Sample Student's *t***	**Associated degrees of freedom**	**Statistically significant at 0.05 level of significance**
Total B(*a*)P-TE	2.9	4.2	1.1	0.92	21.3	41, 17	Yes	2.69	50	Yes
Total PAH	21.9	30.7	8.3	7.2	18.4	41, 17	Yes	2.69	50	Yes

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IV. **CONCLUSION**

In this study, 20 surface soil samples were collected from each of three New England cities and analyzed for PAH, TPH, and metals. The results of the statistical analyses described in the previous section show that, with respect to PAH, the three datasets are not significantly different and can be considered as one dataset representative of urban environments. The samples were taken in typical urban areas but not near known industrial sites. Therefore, these data are considered to be representative of the generalized effects of urban activities.

It is clear from the results presented here that common regulatory target cleanup levels for cPAH and B(*a*)P-TE (0.1 to 0.66 mg/kg) are much below the background concentrations of these compounds in urban surface soils (upper 95% confidence interval of 3.3 and 12.4 mg/kg for total B(*a*)P-TE and total cPAH, respectively). Figure 2 graphically compares the "bright line" target cleanup level for B(*a*)P of 0.1 mg/kg with the total B(*a*)P-TE (upper 95% confidence interval on the arithmetic mean) measured in urban environments.

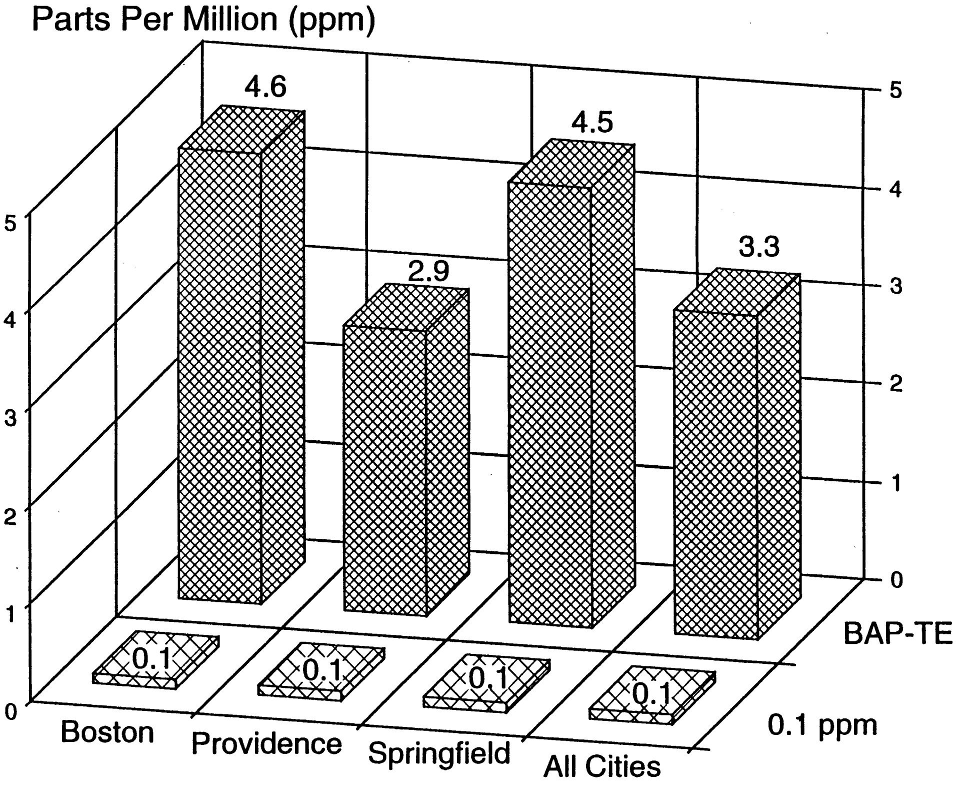

FIGURE 2. Comparison of B(*a*)P-TE with U.S. EPA Region III[4] risk-based concentration for B(*a*)P. B(*a*)P data presented are the upper 95% confidence interval on the arithmetic mean.

Upper 95% confidence intervals are compared because this is the statistic preferred by EPA and many states for risk assessment. Moreover, the State of Massachusetts defines its background concentrations of metals based on the upper 95% confidence limit on the arithmetic mean concentration (Massachusetts Department of Environmental Protection, 1992). For all cities combined, the background level of B(*a*)P-TE of 3.3 mg/kg is approximately ten times greater than the target cleanup level of 0.33 mg/kg and approximately 30 times higher than the target cleanup level of 0.1 mg/kg. For those regulatory situations in which the use of B(*a*)P-TEFs in determining site risk is not allowed, the background level of cPAH is approximately 40 to 100 times greater than these target cleanup levels.

An analysis of the data comparing samples taken near pavement with those determined to be not near pavement indicated that those samples designated near pavement had significantly higher, approximately threefold higher, PAH concentrations for both total PAH and total B(*a*)P-TE. This is most likely due to the presence of diesel and automobile exhaust particles, perhaps influenced by the presence of asphalt and runoff of vehicular oil from the roads.

Total petroleum hydrocarbons (TPH) were also found at consistently high levels in each city. The commonly applied regulatory cleanup level for TPH is 100 mg/kg. This cleanup level is not risk based and is three times lower than the background concentration of TPH found in this study (arithmetic mean of 306 mg/kg and upper 95% confidence interval on the mean of 373 mg/kg).

It is incumbent upon the regulatory agencies to recognize that substantial background levels of PAH and TPH exist in our urban environments and to acknowledge this information in the development of realistic target cleanup levels. The use of these background data in setting more realistic target cleanup levels may result in better allocation of remedial and regulatory dollars in site investigations.

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