Concentrations of Six Metals in the Air of Eight Cities

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■ During 1968–1971, 8763 samples were collected at 59 sites in U.S. cities for a study of particulate lead concentrations in air. Each site was sampled continuously for a full year. These samples have been analyzed for total suspended particulate matter and for cadmium, chromium, lead, manganese, nickel, and zinc. Results of over 42 000 analyses are summarized in convenient graphical form, showing geometric means, geometric standard deviations, maxima, and minima. Supplementary tables present these data and cumulative frequency distributions. This historical data base should be a useful reference to determine effects of changes in fuel consumption patterns and trends. It presents a uniquely extensive cross-sectional picture of trace metal concentrations determined by a single highly experienced laboratory. Results were compared with available recent data for 17 identical sites. Recent lead concentrations averaged 35% of the older values, and some reductions occurred in concentrations of other metals.

During the past decade a substantial change has occurred in the world energy picture. Changes in fuel composition and consumption have altered air pollution patterns. The hazards from lead emissions from automobiles have remained a long standing controversial subject. Two extensive lead studies were reported. From June 1961 through May 1962, 3400 samples of particulate lead from the atmosphere were obtained at 20 sites in three cities (1). From Dec 1968 through Feb 1971, 8763 samples of particulate matter were collected at 59 sites in eight cities in widely different sections of the country, including the cities in the previous study for purposes of comparison, and were analyzed for lead (2). Since these samples were suitable for other analyses, they also were analyzed for cadmium, chromium, manganese, nickel, zinc, and total particulate because the effects of these substances were believed to be of biological and economic importance.

The environmental significance of most trace metals in air is not yet fully understood, and data on their concentrations are essentially for archival purposes for future interpretation. There are no current air quality standards for metals except for lead. Comparisons are difficult because most data are for only a few sites in each city for relatively few samples per year, and frequently for only a few metals. Analyses have been conducted by laboratories of variable qualifications using a variety of methods, none of which have been collaboratively tested. Thus, one can expect substantial interlaboratory variations, and some data confirm this. This comprehensive study was conducted at numerous sites in each of eight cities, continuously for a full year at each location, and all samples were analyzed by a single highly experienced laboratory. Thus, these data present a uniquely extensive cross-sectional picture permitting relative comparisons of different sites. They also should be valuable as historical background levels for future studies of trends and changes.

Collection of Samples

The cities sampled were selected to reflect a wide range of geographic and climatological characteristics. Cincinnati, Philadelphia, and Los Angeles were included for

comparisons with an earlier lead study (1). New York City, Chicago, and Houston represented large northern, midwestern, and southern cities. Washington, DC, represented a large city without industrialization. Los Alamos and Okeana, OH, represented background areas with low pollution. Table I provides a summary of the sampling sites and analytical data. Figure 1 presents map outlines of the seven major cities and shows the positions of all sites. More detailed information on the sites is presented in the tables of the supplementary material (see paragraph at end of paper regarding supplementary material.)

The sampling equipment consisted of a filter holder, a 106-mm mixed cellulose ester membrane filter of 3-μm pore diameter, efficiency >99% (Millipore, type WS), a vane pump and motor unit drawing a nominal free air flow of 0.17 m^3/min, a cooling fan, and suitable electrical and air connections. A plywood housing with a gable roof permitted the necessary ventilation and noise attenuation. Initial and final air flows through each filter were determined from calibrated orifice meter measurements. The units were operated continuously for 12 months at each site. Filters were changed at most locations on Monday, Wednesday, and Friday. However, at high traffic sites in Los Angeles, it was necessary in order to avoid filter obstruction to install tandem automatic switch-over units which collected 24-h samples. In low traffic and rural sites the filters were changed weekly.

Analytical Methods

Before use, the filters were conditioned in a controlled atmosphere and weighed in Cincinnati. Each was then shipped in a numbered plastic Petri dish to the sampling site. The monitors returned the filters in the same dishes with the necessary sampling information. The filters were again conditioned and weighed to determine the total particulate weights by difference.

Half of each filter was cut off and placed in a 100-mL beaker. The filters collected during 1968–1969 (in Cincinnati, Los Alamos, Los Angeles, Okeana, and Philadelphia) were combined so that one sample was analyzed for each week for each site. These samples were not analyzed for manganese and nickel. The filters collected during 1970–1971 were analyzed individually. Each composite or individual sample was wetted with 2–3 mL of concentrated nitric acid. It was then heated to dryness on a hot plate and ashed in a muffle furnace at 500 °C. The ash was dissolved in 10% (v/v) nitric acid and transferred into a 10-mL glass-stoppered cylinder. After the final volume was adjusted to 10 mL, the solution or an appropriate dilution was aspirated directly into the burner of a Perkin-Elmer Model 403 atomic absorption spectrophotometer with a three-slot Boling burner. The instrument settings and resonance lines used were those recommended in the manufacturer's analytical methods manual (3).

In analyses for Cd, Cr, Ni, and Mn, portions of the original solution were aspirated into the burner, whereas for Pb and Zn an aliquot of the original solution diluted 1:9 with 10% v/v nitric acid was employed. For a similar preparation with the volumes and dilutions employed, studies indicated that analysis of half of a filter representing an air volume of approximately 100 m^3 could detect

† Deceased.

Table I. Summary of Sampling Sites and Results

| area	no. of sites	dates of sampling, from–thru	total no. of samples	geometric mean concentration, $\mu g/m^3$						
				PM	Cd	Cr	Pb	Mn	Ni	Zn
Chicago	9	3/70–2/71	1298	80	0.005	0.012	1.44	0.075	0.018	0.47
Cincinnati	4	12/68–11/69	384	62	0.005	0.011	1.45			0.61
Houston	7	3/70–2/71	1070	56	0.001	0.009	1.14	0.044	0.015	0.17
Los Alamos	2	12/68–11/69	91	10	0.001	0.005	0.17			0.02
Los Angeles	8	12/68–11/69	1841	70	0.002	0.012	3.40			0.26
New York	9	3/70–2/71	998	67	0.007	0.013	1.40	0.031	0.042	0.36
Okeana, OH	2	12/68–11/69	125	44	0.002	0.005	0.30			0.16
Philadelphia	10	12/68–11/69	1744	69	0.006	0.009	1.53			0.62
Washington, DC	8	10/70–9/71	1213	53	0.003	0.010	1.36	0.033	0.023	0.17
totals	59		8763							
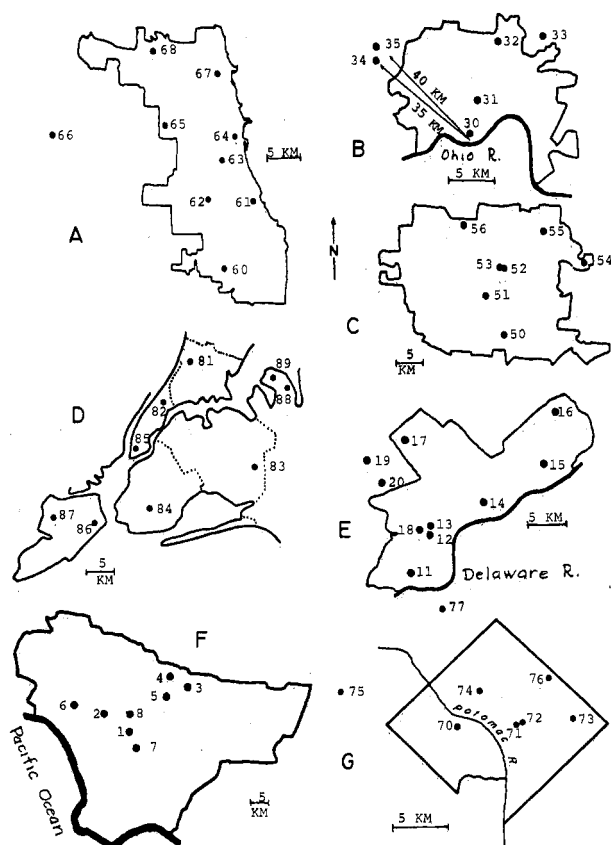
Figure 1. Maps of cities showing locations of sampling sites: A, Chicago; B, Cincinnati and Okeana; C, Houston; D, New York City; E, Philadelphia; F, Los Angeles; G, Washington, DC.

as little as 0.1 μg of Pb/m^3, 0.01 $\mu g/m^3$ each of Zn, Cr, Ni, and Mn, and 0.001 μg of Cd/m^3. The sensitivities of detection for samples of course improved in proportion to the ratio of the actual sample air volume to that assumed. However, nils or values below the detectable limits indicated above were recorded merely as less than the detectable limit for the specific metal. In the case of particulate matter, the limit of significance by weight was 10 $\mu g/m^3$. Studies with known quantities of the metals added to filters carried through the preparatory procedure yielded recoveries of approximately 95% for Pb, Zn, Cr, Ni, and Mn and approximately 85% for cadmium. However, the values reported here do not include any corrections for recoveries.

Results

The sampling periods, numbers of sites, numbers of samples collected, and geometric mean concentrations in each city for this study are given in Table I. Plots were made of the data for each sampling site of frequencies for

each concentration interval (each covering $^1/_{50}$ of the range). In the statistical calculations each sample was weighted according to its sampling period. Although practical considerations in running a large scale sampling program required different periods for some samples, as explained below the statistical effects were expected to be minor. Even though these plots each represented over 150 samples, the curves were not smooth. The bumps in the frequency curves at the high concentration ends suggested that these frequencies might be substantially underestimated from a log-normal concentration model. Cumulative distributions also were plotted. From these curves the concentrations for each tenth percentile were interpolated. A summary of the mass of data obtained for this 1968–1971 study is presented graphically in Figure 2, in a form to permit ready comparisons. These represent for each site the minimum, maximum, geometric mean, and geometric standard deviation for the concentrations of each metal. For the calculations of geometric mean, values below the detection limits were assigned values of 50% of the limit, in order to calculate the necessary logarithms. Since usually only a small fraction of the samples were in this category, this approximation involved little error. More exact calculations are complex (4).

Discussion

The zinc concentrations showed the greatest range of geometric mean concentrations and geometric standard deviations, whereas the particulate concentrations showed one of the smallest ranges for both of these variables. As expected, commercial and industrial sites usually showed higher concentrations of particulate pollutants. Although the sampling time does not affect the observed arithmetic mean, it does slightly affect the geometric standard deviation. A study (5) of continuous monitoring data for sulfur dioxide during 1962–1964 showed empirically that the geometric standard deviation varied with the sampling time raised to an exponent which was –0.02 for Chicago, –0.04 for Los Angeles, –0.05 for Washington, DC, –0.07 for Philadelphia, and –0.10 for both Cincinnati and San Francisco. This study theoretically explained some of the complexities of the effects of sampling times on resulting data. Although the figures cited are only for sulfur dioxide, in the absence of better information, they may be applied for estimating effects for particulate matter. In the data reported here, samples for Cincinnati, Los Alamos, Los Angeles, Okeana, and Philadelphia were weekly composites, whereas those for the other cities, generally two 2-day samples and one 3-day sample each week, were analyzed individually. If a worst case estimate of an exponent of –0.1 is used, the differences in geometric standard deviations between 3-day and 2-day samples would be only 4% and between 7-day and 2-day samples 13%. For the latter case if the exponent were –0.02, the difference would be
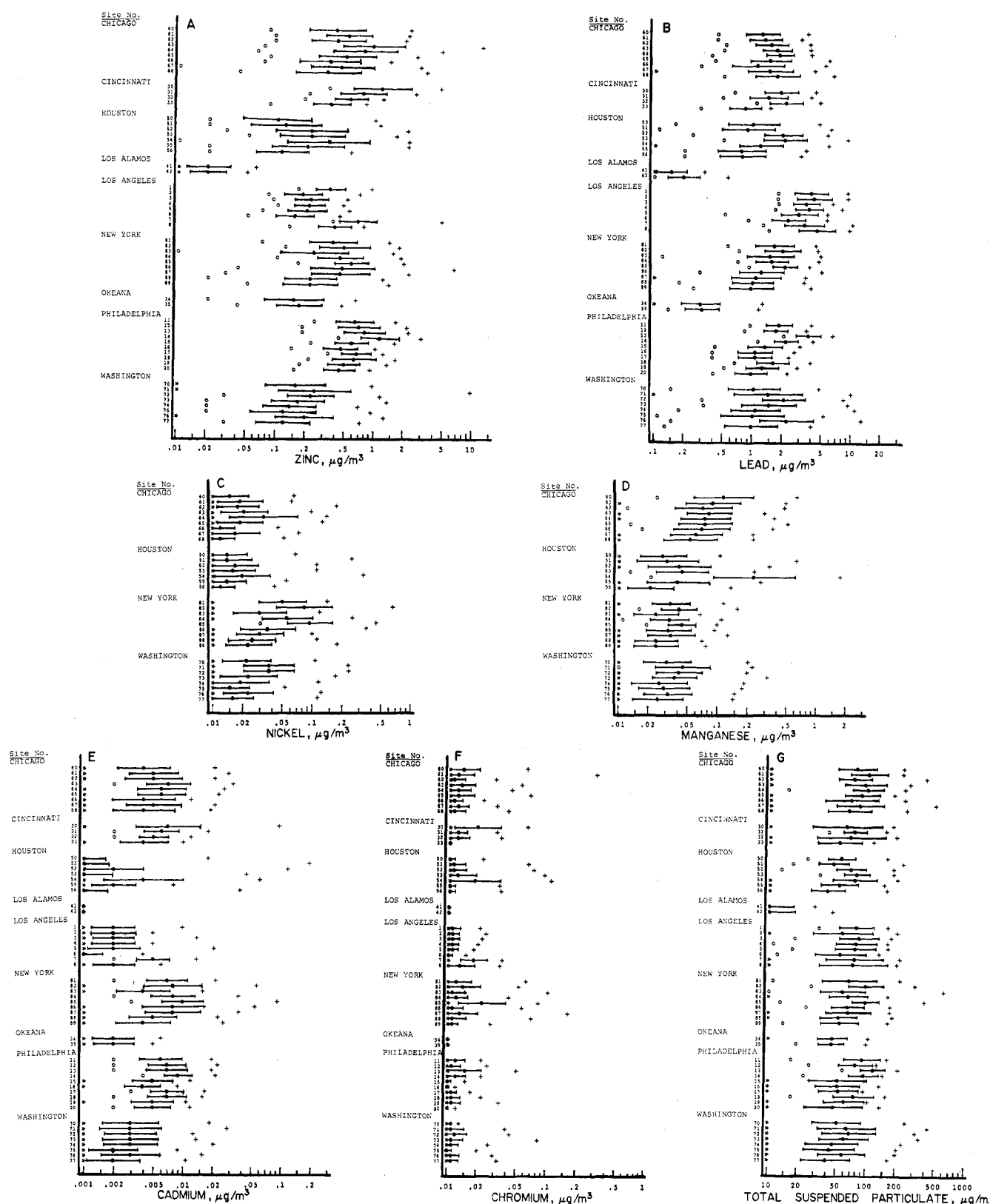
Figure 2. Summary of the 1968–1971 data for the 59 sites: A, Zinc; B, lead; C, nickel; D, manganese; E, cadmium; F, chromium; G, total suspended particulate. (O) Minimum; (*) less than nominal detection limit; (+) maximum; (⊢●⊣) geometric mean ± 1 geometric standard deviation.

only 3%. The geometric mean and geometric standard deviation may be applied for designing sampling programs and for estimating extreme values. Simplified nomographic methods have been presented (6) for these purposes.

The current EPA air quality standards are promulgated for only two particulate pollutants: particulate matter 75 (primary) and 60 $\mu g/m^3$ (secondary) annual geometric mean; lead 1.5 $\mu g/m^3$ (primary and secondary) 3-month arithmetic mean. Criteria documents (7, 8) discuss the sources and significance of these pollutants. About 60% of the sites exceeded the 60 $\mu g/m^3$ secondary EPA standard for total particulate, but only 15 of the 59 sites exceeded the primary standard of 75 $\mu g/m^3$. The annual arithmetic mean concentration of particulate lead exceeded 1.5 $\mu g/m^3$ for 33 sites, including all those in Los Angeles,

Table II. Comparison of Analyses of Samples from the Same Sites[a]

site no.[a]	NADB[b] periods	NADB[b] no. of samples	PM, μg/m³	Cd, ng/m³	Cr, ng/m³	Pb, μg/m³	Mn, ng/m³	Ni, ng/m³	Zn, μg/m³
					geometric mean concentration[c]				
			Chicago (3/70–2/71)[d]						
10H01/60	82/70	57/70	57/95/75			0.249/–/1.21			
7H01/62	79/70	108/140	71/93/71						
5H01/64	79/70	115/134	85/24/97						
6H01/65	75/70	15/130	96/103/84						
4H01/67	82/70	57/132	55/104/80			0.261/–/1.44			
3H01/68	79/70	112/138	60/79/63						
			Cincinnati (12/68–11/69)[d]						
1A01/30	79/68	28/26	75/99/60	4/3/7	–/13/19	0.87/1.28/1.87	–/50/–	24.8/9/–	
14G01/32	82/69	59/18	71/98/66						
			Houston (3/70–2/71)[d]						
7H01/51	79/–	55/–	54/–/144			0.349/–/0.88	5/–/31		
1A01/53	80/68	9/26	69/74/76	1/1/<1	12.8/8/12	0.57/1.49/2.07	27.1/20/44	4.8/8/16	0.10/–/0.22
			Los Angeles (12/68–11/69)[d]						
1A01/1	80/60	16/26	99/129/77	1/2/2	6/12/11	0.57/2.64/3.82	22.8/–/<10	7.4/–/–	
			New York (3/70–2/71)[d]						
6H01/81	79/71	26/153	52/91/66						
14A01/82	79/–	11/–	75/–/97	4/–/8		0.872/–/1.99		24.8/–/85	
			Philadelphia (12/68–11/69)[d]						
3H01/12	82/68	80/365	58/109/78			0.22/–/1.71			
			Washington, DC (10/70–9/71)[d]						
1P01/71	76/68	9/26	50/86/65	–/2/3	–/5/11	–/0.61/1.46	–/10/45	–/16/37	
3I02/72	78/71	42/18	98/102/69						
7I02/73	79/71	33/28	71/62/61			1.34/–/1.48			
mean ratio recent/old[a]			0.75/0.99	0.94/0.89	1.05/0.81	0.43/0.35	1.36/1.78	1.68/0.30	–/0.46
N[a]			15/17	3/4	2/2	3/9	1/3	2/2	–/1

[a] NADB/this study. [b] Recent/old. [c] Recent NADB/old NADB/this study, generally from 150 samples. [d] Sampling period for this study.

6 of the 9 in Chicago, 5 of the 9 in New York, and 5 of the 10 in Philadelphia. With the more recent reduction of the lead content of gasoline, the current lead levels are decreasing (9–11). Standards for industrial workers for metals also are available (12).

Before these values are compared with those of other studies, certain differences in evolving sampling and analytical methodologies must be considered. The only current regulatory requirement, that for lead instituted after the publication of the criteria document (8) in 1977, is for 3-month arithmetic mean values. Since future applications of trace metal data are unclear, the strategy has been to collect as much information as practicable. Advances in technology during the past decade have resulted in the current adoption of the inductively coupled argon plasma atomic emission spectrometer, which provides analyses of multiple elements simultaneously at a reasonable cost. This has partly displaced the atomic absorption spectrometer (which replaced the older spectrophotometric methods). The differences between the results of these methods have never been fully characterized. Examination of recent EPA National Aerometric Data Bank data for metals in samples collected in the same place and time, however, shows substantial differences between results by the atomic emission and atomic absorption methods. Also, the values in the NADB listed for the 1968–1971 period of this study were obtained by an earlier hi-vol emission spectra (low-temperature ash) method. The recent proposal of an inhalable particulate (<10 μm) standard will result in replacement of the high volume sampler with new devices with sharply different sampling efficiencies for different particle sizes. When sampling from air at varying velocities, the inertial, viscous, and gravitational forces affect large and small particles dif-

ferently. High volume sampler inlets do not sample isokinetically and, thus, collect large and small particles with different efficiencies. The nonrepresentativeness of the samples varies with wind velocities and directions and thus cannot be accurately characterized. All of these changes are being adopted to improve the quality and scope of the information collected. Statistical difficulties obviously result when comparisons over a time period are made, since exact effects of changing methodologies are not known, but the advantages overrule the objections. Thus, the available historical data must be compared with newer data with appropriate allowances as far as possible.

This comprehensive study was initiated during the early development of sampling networks, before EPA was formally established in 1970. The high volume sampler utilized in other studies employed an 8 in. × 10 in. flash fired glass-fiber filter as a compromise adapted for both organic an inorganic analyses. For this study a mixed cellulose ester membrane filter with a 3-μm pore diameter was selected in preference because it was better suited for trace metal analysis. Sample extraction before ashing and possible extraction of interfering silica was eliminated, and blanks were very low. It was also the method used in the earlier 1961–1962 lead study which was being followed up. The efficiency of the membrane filters was at least as good as that of glass-fiber filters. The ashing procedure was less likely to suffer from loss of metals in possible insoluble material than the EPA extraction method with dilute nitric acid.

In order to compare the particulate size selective characteristics of the sampler used in this study with those of the widely used high volume sampler, the minimal areas between the gabled roofs of the sampling boxes and the filter housings were determined as 670 and 645 cm², re-

spectively. The related air flow rates of 0.17 and 1.6 m³/min thus produced upward air velocities of 4.3 and 40 cm/s. The unit density aerodynamic particle diameters which settle at those rates in still air were calculated according to Stoke's law. These sizes, 37.5 μm for this study and 116 μm for the standard high volume sampler, approximate their sampling cutoff diameters. Unless one samples near a dust source, particles larger than 37.5 μm would be uncommon because of their rapid fall out. In any event, the 37.5-μm cutoff size is closer to the now recognized 10-μm inhalable particle size, and the data should be more relevant to the new standard.

In comparing maximum values of data sets the numbers of samples must be taken into consideration. If 150 samples per year are collected, one can expect a higher maximum than if only 20 are collected. The numbers of trace metal samples per year in the EPA data file are highly variable but are rarely as large as in this study.

Despite these statistical difficulties, it is useful to compare these data with the corresponding recent ones in the EPA National Aerometric Data Bank file from 1975 to 1983 and with the older ones from 1968 to 1971. There were no data from Okeana in this file. Most of the recent data were for particulate matter. There were no other data from Los Alamos. There were some data for lead, and very little for the other metals from the other seven cities. The current method used for samples from all these cities for five metals was the Jarrell-Ash Emission Spectra ICAP, for which the minimum detectable concentrations (in μg/m³) were listed as follows: Cd, 0.001; Pb, 0.01; Mn, 0.0408; Ni, 0.0056; Zn, 0.0133. Neutron activation was generally the method used for Cr, with a sensitivity of 0.0104 μg/m³. These sensitivities were about the same as those of the present study for Cd, Cr, and Zn, more sensitive for Pb and Ni, and less sensitive for Mn. Five cities also analyzed for lead by atomic absorption, with a detection limit of 0.002 μg/m³. This method was also applied to four other metals in Houston samples, with detection limits (in μg/m³) as follows: Cd, 0.002; Cr, 0.002; Mn, 0.001 μg/m³; Ni, 0.004. Houston also analyzed for the six metals by X-ray fluorescence, which exhibited much poorer sensitivities (μg/m³): Cd, 0.06, Cr, 0.05, Pb, 0.05; Mn, 0.04; Ni, 0.02; Zn, 0.01. The samples for trace metals were usually 24-h samples collected at frequencies varying from bimonthly to semimonthly. Where several analytical methods were applied at the same site, there were often substantial differences between the results for the same metal. In some cases the differences might be related to random variations among the differing numbers of samples collected at the same sites and/or work done by a different agency.

Seventeen sites in the present study appeared to be at the locations identical with those in the EPA data bank file. Table II shows the data comparisons. When the listed geometric mean was below the detection limit of the method, it was not regarded as accurate enough for listing here. Results for this study are the geometric means for about 150 samples at each site. The data bank results were based on far fewer samples, as given in the third column. The comparative data selected were the most complete data during 1968–1971 and most recently on or after 1976. In all cases the lead concentrations declined substantially. The average ratio of the recent/old values was 35%. The particulate matter declined at most sites. Most of the values for Cd, Cr, Mn, and Ni also showed declines.

Comparison of geometric mean values found in this study for each city with recent data collected by others at different sites is difficult. Recent data were collected

generally at more sites in each city for particulate matter and generally at fewer sites for the metals. Similar relationships were found.

A number of other studies have been made of suspended particulates in some of the same or nearby cities such as New York City (11, 13–15), Los Angeles (10), and Pasadena, CA (16). Sources of trace metals have been tracked by calculating the enrichment factors of their concentrations over those encountered in soil (17) and also from their concentrations in fuels and in industrial materials and emissions (18). Lead has been shown to be mainly from automobile emissions and vanadium in Northeastern U.S. from combustion of fuel oil. Cadmium and zinc may come from some incinerators. Chromium, manganese, and nickel do not show any significant urban enrichment.

The large mass of data presented here should serve as a useful historical reference point. Recent studies have not provided data for these cities of comparable completeness for most of these metals.

Supplementary Material Available

Eight tables with one listing the classification and location of sampling sites and with seven summarizing the concentrations of total suspended particulate and six metals (Cd, Cr, Pb, Mn, Ni, and Zn) (28 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24X reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Full bibliographic citation (journal, title of article, author, page number) and prepayment, check or money order for $43.50 for photocopy ($45.50 foreign) or $6.00 for microfiche ($7.00 foreign), are required.

Registry No. Cd, 7440-43-9; Cr, 7440-47-3; Pb, 7439-92-1; Mn, 7439-96-5; Ni, 7440-02-0; Zn, 7440-66-6.

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Continuous Removal of Both Mutagens and Mutagen-Forming Potential by an Experimental Full-Scale Granular Activated Carbon Treatment System

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■ Trends in the removal of mutagens and of total organic carbon (TOC) were measured for granular activated carbon (GAC) in use at the Cincinnati Water Works. Fourteen sets were analyzed, one set for each of the first 3 weeks beginning Nov 29, 1982, and 11 others at 2–4-week intervals during the next 32 weeks. Sample points per set were settled river water, chlorinated sand filtered water, GAC-treated water, water from these two latter points stored 3 days in the presence of a free chlorine residual, and distributed water. Residues were extracted by using XAD-2 resin and bioassayed by using the Ames test strains TA98 and TA100. No mutagens were detected from the settled water, so the great majority of mutagens entering GAC treatment were products of the chlorination step. These mutagens were preferentially removed by GAC treatment, and GAC effluent was greatly reduced in its potential to form mutagens upon rechlorination, even when the GAC was used several months beyond normal use for TOC removal. Analyses of residues extracted from the used GAC also indicated the efficient removal of waterborne mutagens.

Introduction

Drinking water sources, particularly surface waters of major river systems, may be burdened with a broad range of natural and man-made chemicals. Most of these are unknown compounds of low volatility that are present at low concentrations. Nevertheless, known mutagens and carcinogens have been detected among organics extracted from such waters (*1*), and bioassays conducted on subfractions of extracted organics have documented the presence of additional as yet unidentified mutagens (*2–4*). Some of these genotoxic compounds originate from industrial sources while others are known to arise as products

of disinfection during the treatment process (*5–8*). These discoveries have raised concerns of possible adverse health affects, particularly in relation to the long-term exposure possible from drinking water.

Such concerns have stimulated a number of responses in regulation and in research. For known genotoxic compounds, regulations have been developed or proposed that limit their presence in public water supplies (*9, 10*). For the unidentified contaminants, research has been conducted on methods for extraction and concentration to obtain residue organics as complex mixtures (*11*). Additionally, surrogate mixtures of nonvolatile mutagens have been obtained by chlorination of humic substances (*4, 6, 12–15*). Such mixtures have been examined for short-term and long-term toxicological effects and by the use of short-term bioassays in conjunction with chemical fractionation for compound identification (*17–20*). We have developed a general preparative procedure for the isolation (*21*), separation (*17*), and chemical characterization (*22*) of mutagenic components from drinking water. This procedure features the extraction of nonvolatile residues by using XAD resins and the subfractionation of mutagenic mixtures by high-performance liquid chromatography (HPLC) on the basis of activity for *Salmonella* strains TA98 and TA100. The *Salmonella* mutagenesis assay is used both for its convenience as a short-term test and for its utility based on extensive use in detecting potential carcinogens (*23*).

Meanwhile, treatment plant procedures are being examined for the removal of such products. Adsorption by granular activated carbon (GAC) is an effective method for removal of many water contaminants (*24*) and has proven successful in pilot scale experiments for the removal of mutagens (*25, 26*). In recent years an experimental full scale GAC system for water treatment has been developed at the Cincinnati Water Works (*27*). A preliminary test of this system by Monarca et al. (*28*) indicated an efficient removal of drinking water mutagens, on the basis of single

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