

HISTORICAL TRENDS OF AIRBORNE TRACE METALS IN DETROIT FROM 1971 TO 1992

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Abstract. Ambient concentrations of particulate Fe, Zn, Pb, Ni, Cr, Cd and Hg were measured at nine sites located in the metropolitan area of Detroit from 1971 to 1992. The ambient concentrations of all the trace metals were found to be generally higher at industrial and commercial sites. The concentrations show significant variations between residential and commercial areas and between residential and industrial areas; however, no significant variation was found between the industrial and commercial settings. The spatial variation of trace metal levels within the urban area was influenced by the frequency distribution of the wind direction as well as type and location of emission sources. The ambient concentrations of the trace metals during the decade of 1971–1981 declined by 37–88%. In the 1980s many of the trace metals reversed this trend with the exception of Fe and Pb which continued to decline at annual rates of 2% and 9.8%, respectively. The sharp decrease in Pb concentrations during the 1980s, reflected the significant reduction of Pb content in gasoline from 0.28 g/liter in the 1982 to 0.026 g/liter in the 1989. The ambient concentrations of Zn, Ni, Cr, Cd and Hg showed an upward trend during the 1980s with an annual rate in the range of 0.6% to 10.6%. The long-term trends of selected U.S. market parameters, analyzed as potential long-term indicators of emission sources activities, were consistent with the changes of ambient concentrations, the correlation coefficient being in the range of 0.58 to 0.84 for most of the trace metals.

Key words: urban pollution, trace metal, long-term trend, emission source, Detroit, market parameter, land use

1. Introduction

The health impact of toxic substances emitted into the atmosphere of the industrialized countries has gained a greater attention from governments and scientific community in the last two decades (Salmon *et al.*, 1978; UN, 19898; WHO, 1992). Changes in fuel composition and consumption (Saltzman *et al.*, 1985), in primary and secondary metallurgical processes, and in waste disposal and land fill operations (Pacyna *et al.*, 1984; Pacyna, 1987; Wilber *et al.*, 1992; EPA, 1993a,b) have altered the levels and types of air pollution in urban areas (EPA, 1992; Keeler *et al.*, 1994) and even in pristine remote areas as well (Schroeder *et al.*, 1987; Nriagu, 1990; Lindqvist *et al.*, 1991; Slemr and Langer, 1992; Swain *et al.*, 1992; Harrison *et al.*, 1993; Keeler *et al.*, 1994). However, few studies have been found in the literature dealing with long-term trends in the ambient air concentrations of trace metals in urban and rural areas (Salmon *et al.*, 1978; Schroeder *et al.*, 1987; Cawse, 1987).

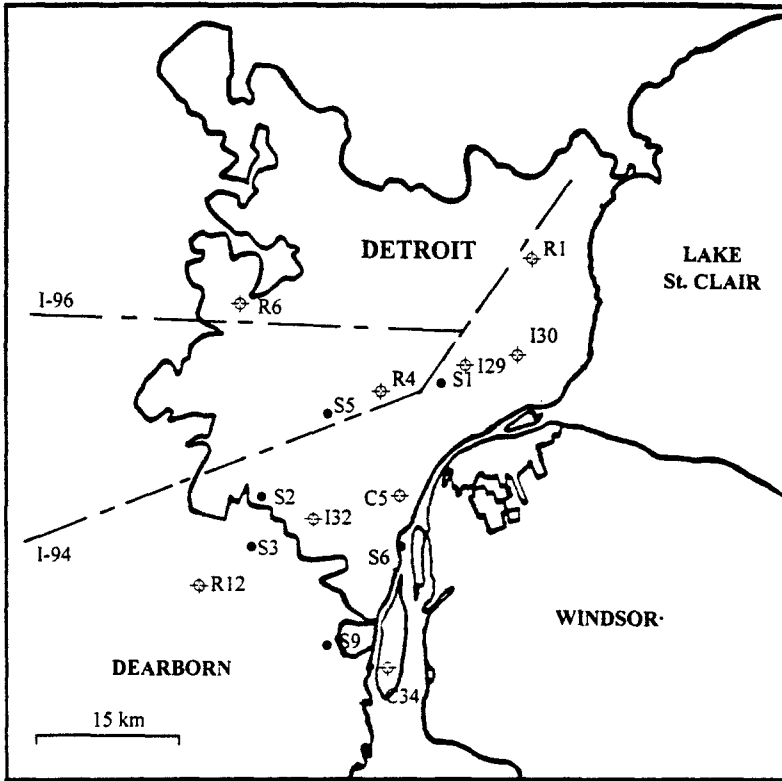


Fig. 1. Sampling sites (⊕) and major emission sources (●) in the urban area of Detroit, MI. Major emission sources include: S1, GDRRA Incinerator; S2, Central Wayne County Sanitation Authority Incinerator; S3, Automotive assembly plants; S5, Incinerator at Henry's Ford Hospital; S6, Zug Island which include coke ovens, iron-steel plants, and coal power plants; S9, Iron-steel plant; I-94, Highway; and I-96, Highway.

This paper presents two-decade time series and a review of atmospheric trace metal concentrations in the urban area of Detroit, Michigan. Historical patterns effecting the trace metals concentration within the urban area were analyzed including type, size and location of emission sources, land use type, meteorological conditions, and selected market parameters used as long-term indicators of the emission sources activity.

2. Methods

2.1. SAMPLING SITES

Ambient air concentrations of trace metals associated with particulate matter were measured in Detroit on monthly basis from 1971 to 1992 by the Wayne County

TABLE I

Coordinates, land use categories and sampling period for each monitoring site in Detroit from 1971 to 1992

Site	Latitude	Longitude	Land use category	Sampling period
R1	42:25:51	83:00:03	Residential	1971–1992
R4	42:21:27	83:05:49	Residential	1971–1992
R6	42:23:42	83:14:06	Residential	1971–1992
R12	42:18:76	83:24:54	Residential	1971–1986
C5	42:18:15	83:06:26	Commercial	1971–1992
C34	42:09:00	83:09:55	Commercial	1971–1989
I29	42:18:00	83:01:11	Industrial	1987–1991
I30	42:23:06	83:01:16	Industrial	1987–1991
I32	42:18:21	83:08:59	Industrial	1971–1989

Department of Public Health. The sampling was done at nine sites located in residential, commercial and industrial areas. Figure 1 shows the location of sampling sites and major emission sources location in Detroit, and Table I gives the coordinates, land use type and sampling period for each site. Measurements were made in four residential areas: two sites located in north-east (R1) and north-west (R6) Detroit, one site (R4) in central Detroit and one (R12) in Dearborn, a suburban area in the south-west side of Detroit. Two sampling sites were sited in areas of commercial land use: one site (C3 4) was in Grosse Isle 5 km downwind of a large iron-steel plant (S9), and one (C5) was in the downtown Detroit located 5 km downwind of Zug Island (S6) which is one of the most industrialized areas of Wayne County. Three sampling sites were sited in industrial areas: two (I29 and I30) were characterized by heavy industries including coke ovens, iron and steel plants, incinerators, power generation facilities and lime and cement operations; a third site (I32) was operated in south-east of Dearborn, also a large industrial area characterized mainly by automotive assembly and steel plants.

2.2. DATA ANALYSIS

The main objectives of this study are (a) to analyze the spatial variability of the ambient air concentration of trace metals within the Detroit urban area and to show how the sampling sites are effected by the location and type of the emission sources. Long-term trends of the ambient concentration of trace metals are compared among sampling sites as well as among land use categories. The Student's t-test is used to test the null hypothesis that the univariate sample population means are equal. The results are supported by an analysis of the type and location of emission sources with respect to the sampling sites, long-term meteorological conditions in Detroit, and

size of the emission source (e.g. for primary and secondary metallurgical processes the overall plant capacity is considered); (b) to analyze the temporal variation of ambient concentrations among cold and warm seasons as well as among the decades 1971–1981 and 1982–1992. Long-term trends of the ambient concentration of trace metals for the decades 1971–1981 and 1982–1992, obtained by least square analysis of the sample-data, are discussed; (c) to identify long-term indicators of the emission sources activity directly or indirectly related with the major U.S. market parameters such as production of metals from primary and secondary metallurgical processes, consumption of metal-based products, import, export and industrial demand of metal-based products as well as the price at London metal exchange; and (d) to compare the long-term trend of the ratio between maximum (C_{max}) and average (Coverage) ambient air concentration of trace metals with those of U.S. market parameters assumed as indicators of the emission source activity for a given trace metal. The ratio of $C_{max}/\text{Coverage}$ is used as indicator of risk-related outdoor exposure to atmospheric contaminants.

2.3. ANALYTICAL METHODS

A high-volume sampler equipped with a glass fiber filter was used to collect total suspended particulate matter (TSP) at a nominal flow rate of $0.075 \text{ m}^3/\text{s}$. Glass fiber strips representing 625 cm^2 of filter were loaded into Whatman cellulose extraction thimbles (33 x 80 mm) and placed into the Soxhlet extraction system (Smoley, 1992). A few boiling chips were added to each receiving flask containing 150 ml of 1:1 nitric acid, and refluxing allowed to continue for eight hours or more. A 99.9% extraction of the inorganics was typically achieved. After extraction, the system was cooled to room temperature. The glass fiber pulp and the extractant in the receiving flask were filtered through Whatman 42 filter paper. Metals, especially transition metals such as Cd, Cr and Ni in small amounts, may suffer considerable losses without repeated rinsing using triple distilled water. A total rinse volume of 350–400 ml was often appropriate. Hot distilled water was best suited for the rinsing in order to optimize recovery. Filtrates were collected in 1000 ml beakers and allowed to evaporate to incipient dryness. The residue was dissolved in 5 ml concentrated nitric acid or 5 ml concentrated hydrochloric acid as appropriate. Since a considerable amount of some metals may be lost by volatilization during dissolution of residues in hydrochloric acid, it was important to avoid prolonged exposure or excessive heat in achieving dissolution. The dissolved residues were transferred into 100 ml volumetric flasks and were diluted to volume. Concurrently with the extraction of samples, 625 cm^2 of clean glass fiber filter was extracted, filtered and evaporated as above. The residue was dissolved with 5 ml hydrochloric acid and diluted to 100 ml volume served as a reagent and filter blank which was used to correct all quantitative sample data. Composite batch filter blanks were prepared using 30 cm width cut strips of glass fiber filters from a given batch. A Perkin-Elmer Atomic Absorption Spectrophotometer P-E 3030 was used to

determine the Fe, Zn, Pb, Ni, Cr and Cd concentrations in the filtrates (Smoley, 1992).

Flameless cold vapor atomic absorption technique was used to determine the mercury (Kermoshchuk and Warner, 1981). In the case of particulate Hg, about 94 cm² of exposed glass fiber filter was decomposed in 5 ml concentrated hydrofluoric acid in the presence of 10–15 drops of 5% potassium permanganate. The decomposed sample was subjected to nitric and sulfuric acid oxidation followed by hydroxylamine hydrochloride and stannous chloride reduction of mercury I and II to metallic form (Kermoshchuk and Warner, 1981). An atomic absorption standard addition technique was used to generate a standard curve over the range used to measure metallic mercury.

3. Results and Discussion

3.1. AMBIENT CONCENTRATIONS

Long-term descriptive statistics are shown in Tables II and III for the decades 1971–1981 and 1982–1992, respectively. Ambient concentrations of Fe and Hg during the 1970s were found to be highest most of the time at industrial site I32. Ambient concentrations of Cr were found to be highest at I32 and C5. Pb concentrations were found frequently higher at C5, and Zn, Ni and Cd were found to be more abundant at C5 and C34. The ambient concentration of trace metals measured in Detroit from 1971 to 1992 were generally consistent with those observed in other conurbations in North America and Europe during the 1970s and 1980s (Table IV) with the exception of Pb and Cd concentrations that were lower than those summarized in Table IV during the 1970s. The Zn concentrations in the 1980s and Ni concentrations in the 1970s tend to be higher than those found in other urban areas.

3.2. NORMALIZED MAXIMUM CONCENTRATIONS VS. EMISSION SOURCE INDICATORS

Long-term trends of the C_{max}/Coverage ratio of trace metals in Detroit during the decades 1971–1981 and 1982–1992 are compared with those of U.S. market parameters which are related to a wide range of metal-based products. The latter have been used as trend indicators for urban areas with a large industrial activity as Detroit. Figure 2 provides, for each trace metal, a comparison between the long-term trends of the C_{max}/Coverage ratio and those of U.S. market parameters such as production and consumption, import and price at London metal exchange of metal-based products.

As shown in Figure 2a, the C_{max}/Coverage ratio and the U.S. production of Fe-based products including pig iron, steel and iron ore have similar trends with maximum values occurring in the 1973, 1976 and 1981 during the first decade

TABLE II
 Long-term descriptive statistics of the ambient air concentration (ng/m³)
 of trace metals measured in Detroit from 1971 to 1981

	R1	R4	R6	R12	C5	C34	I32
Fe							
mean	1406	1942	1182	1802	3431	2944	5250
median	1098	1985	1120	1616	3123	3197	4898
s.d.	990	763	716	1001	1281	1058	2614
min	402	995	222	923	630	1085	819
max	3054	3054	3054	3054	5255	4615	9778
Zn							
mean	244	345	748	263	1135	930	1189
median	228	308	308	318	675	529	620
s.d.	88	115	1001	100	1335	1221	1173
min	160	253	130	148	233	205	355
max	360	513	3383	323	4903	4275	4070
Pb							
mean	621	745	1853	457	758	311	552
median	625	795	648	466	743	255	505
s.d.	192	235	4223	165	295	137	299
min	233	290	183	238	245	168	125
max	978	1115	14563	828	1420	563	1280
Ni							
mean	26.0	46.0	21.5	26.1	51.5	30.7	44.5
median	16.5	37.5	17.7	17.8	34.0	32.1	42.3
s.d.	20.2	39.6	14.4	21.3	39.8	15.4	34.1
min	8.3	10.8	5.5	6.0	8.8	8.0	12.0
max	75.5	148.5	51.8	69.3	116.0	54.5	130.3
Cr							
mean	8.3	9.5	5.4	n.a.	10.6	n.a.	10.8
median	8.3	9.5	5.4	n.a.	10.6	n.a.	10.8
s.d.	2.4	1.4	2.3	n.a.	5.8	n.a.	6.4
min	6.7	8.5	3.8	n.a.	6.5	n.a.	6.3
max	10.0	10.5	7.0	n.a.	14.8	n.a.	15.3
Cd							
mean	5.9	3.8	3.0	3.2	7.2	4.0	6.6
median	3.3	4.1	2.7	3.1	6.3	3.8	5.5
s.d.	8.3	1.1	1.4	1.6	2.7	1.4	3.6
min	1.5	2.3	1.3	1.0	3.7	2.0	2.9
max	30.6	5.3	6.3	6.8	12.0	6.9	15.2

TABLE II
Continued.

	R1	R4	R6	R12	C5	C34	I32
Hg							
mean	0.36	0.57	0.34	0.32	0.62	0.48	0.78
median	0.33	0.53	0.35	0.30	0.62	0.49	0.45
s.d.	0.21	0.28	0.11	0.10	0.29	0.18	0.70
min	0.19	0.27	0.17	0.20	0.33	0.20	0.23
max	0.90	1.08	0.57	0.47	1.13	0.73	2.38

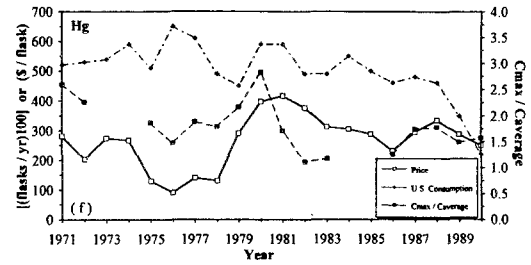
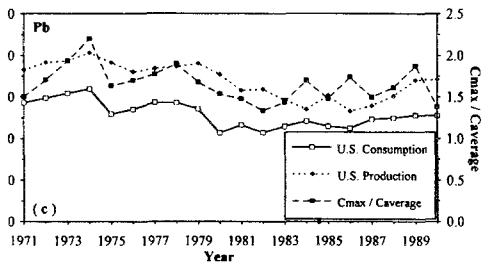
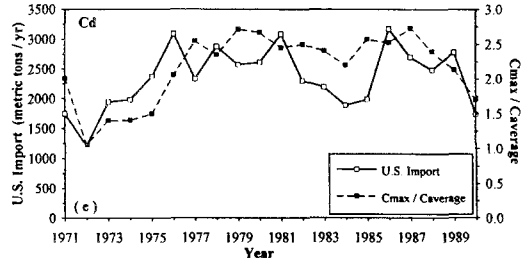
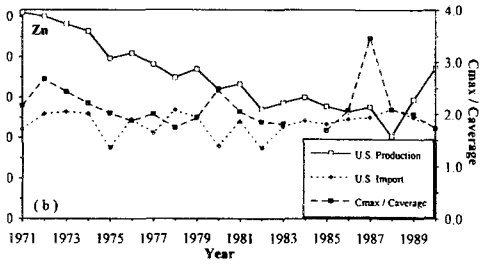
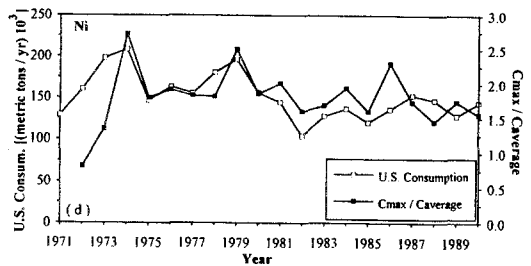
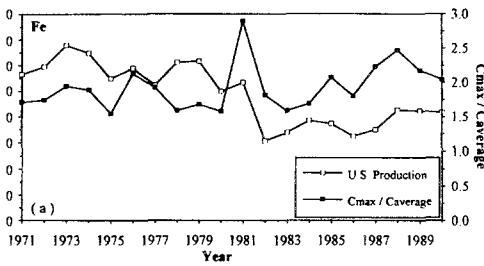


Fig. 2. Comparison between long-term trends of the Cmax/Coverage ratio in Detroit, MI with those of major market parameters observed in the United States from 1971 to 1992.

TABLE III

Long-term descriptive statistics of the ambient air concentration (ng/m³) of trace metals measured in Detroit from 1982 to 1992

	R1	R4	R6	C5	I29	I30	I32
Fe							
mean	522	717	440	1423	804	1538	1974
median	543	673	435	1398	558	1438	1180
s.d.	99	180	109	404	504	994	1788
min	320	420	243	773	253	213	243
max	615	1013	625	2090	1808	3475	5645
Zn							
mean	198	203	127	331	362	302	458
median	129	181	91	269	358	256	517
s.d.	214	83	81	156	283	213	211
min	87	123	68	180	55	57	158
max	793	425	308	695	885	791	825
Pb							
mean	99	119	95	156	86	134	86
median	68	77	57	116	69	111	75
s.d.	84	97	86	105	47	102	32
min	27	35	20	39	49	36	52
max	260	313	265	325	188	360	143
Ni							
mean	9.9	10.3	8.3	14.4	7.5	13.8	11.1
median	8.3	9.8	6.3	12.3	5.6	11.9	12.0
s.d.	3.7	2.9	3.7	4.0	3.6	8.9	5.3
min	5.0	6.8	4.0	9.8	4.5	6.0	4.8
max	15.8	17.8	13.5	19.8	14.5	32.5	20.3
Cr							
mean	6.9	7.6	6.2	10.9	7.2	9.4	11.2
median	6.0	6.2	4.8	9.7	5.3	7.1	11.8
s.d.	2.8	3.1	3.9	4.3	4.0	4.8	6.5
min	3.4	4.7	1.5	6.0	4.2	5.8	2.6
max	12.3	14.8	16.0	19.8	17.0	19.8	24.8
Cd							
mean	2.1	3.1	1.9	6.8	2.6	3.8	3.3
median	2.1	2.8	1.6	6.4	2.3	4.1	3.2
s.d.	0.6	1.8	0.6	2.3	1.4	1.4	1.5
min	1.1	1.0	1.1	4.3	0.9	1.5	1.5
max	3.1	12.0	3.0	11.9	5.5	5.7	5.5

TABLE III
Continued.

	R1	R4	R6	C5	I29	I30	I32
Hg							
mean	0.25	0.20	0.26	0.30	0.25	0.29	0.27
median	0.20	0.22	0.21	0.27	0.19	0.23	0.30
s.d.	0.13	0.09	0.11	0.10	0.12	0.12	0.08
min	0.12	0.06	0.14	0.18	0.12	0.18	0.14
max	0.55	0.38	0.48	0.53	0.48	0.55	0.35

and in the 1985 and 1988 during the second decade. Between the 1971 and 1981 a similar trend was also followed by the export of the major iron-steel products. This is consistent with the maximum of U.S. consumption and minimum of U.S. import established during the same years for the iron-steel products. During the 1980s the U.S. production and Cmax/Caverage ratio showed notable peaks in 1985 and 1988. These peaks can be related to (a) the U.S. consumption of iron ore that reached a maximum in the 1988 with 84 million metric tons; (b) maximum export of the major Fe-based products; and (c) efficiency trend of the U.S. steel production which was highest in the 1988 with a coefficient of raw steel utilization of 89.2% (U.S. Bureau of Mines, 1990; Pirrone *et al.*, 1995).

The long-term trends of the Cmax/Caverage ratio and U.S. primary production of the Zn-based products were downward for both the 1970s and 1980s as shown in Figure 2b. The significant increase of the Cmax/Caverage ratio which occurred for Zn in 1972 and again in 1980 was associated with one of the highest U.S. consumption and lowest price of the Zn-based products observed during the 1970s. However, the highest Cmax/Caverage ratio which occurred in the 1987 was not associated with a comparable variation in the U.S. production and import of Zn-based products, and may be related to local events. It corresponds with the year when the Double Eagle Steel Co. (S6) located in Detroit began the operation of two new electrolytic galvanizers with a combined capacity of 700 metric tons and equipped with six new ceilcote crossflow scrubbers (Pirrone *et al.*, 1995). It may also be noted that the U.S. consumption of the slab zinc, the zinc content of ores and concentrates, and secondary materials also showed a maximum in the 1987 (Pirrone *et al.*, 1995).

The production and consumption of lead in the U.S. were highest in 1971–1974. During the same period, the Cmax/Caverage ratio reached a value of 2.2 which represented the maximum observed during the 1971–1990 period. A downward trend was observed for both market parameters and the Cmax/Caverage ratio during the 1974–1983 period, however from 1984 to 1990 the trends were upwards for all the parameters considered here (see Figure 2c).

TABLE IV

Arithmetic mean concentrations (ng/m^3) of trace metals measured in urban areas in North America and Europe. The range given in Schroeder *et al.* (1987) for North America and Europe includes measurements made in urban areas from the 1960s to 1980s

Urban Area	Sampling Period	Fe	Zn	Pb	Ni	Cr	Cd	Hg	Reference
North America									
U.S.A., reviewed data		130-13800	15-8328	30-96270	1-328	2.2-124	0.2-7000	0.58-458	Schroeder, <i>et al.</i> (1987)
New York - Bronx, NY	1972-1973	1690	593	1790	261	6.2	3.8		Kleinman <i>et al.</i> (1980)
New York - Medical Center, NY	1972-1975	1373	331	1270	39.1	10	5.8		Kleinman <i>et al.</i> (1980)
New York - Queens, NY	1974-1975	552	190	773	10.3	3.8	2.3		Kleinman <i>et al.</i> (1980)
Atlanta, GA	Jan.-July 1981	586	188	278					Marshall <i>et al.</i> (1986)
Reading, PA	July-Oct. 1982	222	48	175	2.9	9.4			Lioy <i>et al.</i> (1989)
Chicago, IL	July-Nov. 1988	489	27	11.2			0.114		Noll <i>et al.</i> (1990)
Claremont - LA Basin, CA	1987	797	16	26	3.7		0.2		Noll <i>et al.</i> (1990)
Canada, reviewed data		700-5400	55-1390	353-3416	4-371	4-26	2-103	< 5	Schroeder <i>et al.</i> (1987)
Europe									
Europe, reviewed data		294-13000	160-8340	10-9000	0.3-1400	3.7-227	0.4-260	0.1-5	Schroeder <i>et al.</i> (1987)
Minster House, London, U.K.	1978-1979	1300	230	720	20		3.1		McInnes (1979)
Brent, London, U.K.	1978-1979	700	120	940	13		2.7		McInnes (1979)
Bolton, London, U.K.	1978-1979	590	170	390	15		2.9		McInnes (1979)
Minister House, London, U.K.	1988-1989	1300	160	730	14				McInnes (1992)
Brent, London, U.K.	1988-1989	700	91	970					McInnes (1992)
Salamanca, Spain	May 1978-May 1982	410	70	140	10				Fidalgo <i>et al.</i> (1988)
Valladolid, Spain	Dec. 1982-Jan. 1984	92.5	47.3	67.5	5.8	2.2	0.31		Gomez and Martin (1987)

In 1974 both the $C_{max}/C_{average}$ ratio and U.S. consumption of Ni-based products reached their highest value of the 1971–1990 period (see Figure 2d). In the 1979 there occurred the second highest variation of the $C_{max}/C_{average}$ ratio, which was associated with the second highest U.S. consumption established during the 1970s. It is interesting that during the same year, the price at London metal exchange ended a long-upward trend which began in 1966; the significance of the similarity in trends is not clear. During the 1980s the largest variation of the $C_{max}/C_{average}$ ratio was found not to be associated with a comparable variation in any of the parameters discussed here; the parameters usually analyzed as indicators of the emission source activity such as U.S. production, U.S. import and export show one of the lowest values observed during the 1980s.

The long-term average (from 1970 to 1990) of the U.S. consumption pattern for Cd is as follow: batteries, 40%; coating and plating, 25%; pigments, 13%; plastic and synthetic products, 12%; and alloys and other, 10% (U.S. Bureau of Mines, 1980, 1990). Based on this consumption pattern, it is clear that the disposal of Cd-based products such as colored paper, plastic and synthetic products through incineration as well as the weathering of painted-building surfaces and corrosion of plated-metal products may represent an important source Cd emitted into the urban atmosphere. The U.S. import of Cd-based products seems to be a good long-term indicator of the emission source activity, since it supplies about the 65% of the total U.S. industrial demand for the element, including waste and scrap as well as cadmium concentrates. From 1976 to 1986 the $C_{max}/C_{average}$ ratio and the U.S. import of Cd-based products were highest on a long-term average basis (see Figure 2e). During the same period the U.S. consumption of Cd-based products followed a similar trend; however, the higher U.S. industrial demand for Cd is consistent with the downward trend of the price at London metal exchange.

In the 1970s and 1980s the long-term average of the U.S. consumption of Hg was 1900 metric tons and 1590 metric tons, respectively. The typical U.S. consumption pattern for Hg in the last twenty years was approximately as follows: batteries, 50%; paints, 13.6%; chlorine and caustic soda preparation, 12.4%; measuring devices, 6%; wiring devices, 4%; dental equipment, 2%; electrical lighting, 1.7%; and miscellaneous, 10.3% (U.S. Bureau of Mines, 1980, 1985, 1990). The significant increase of the $C_{max}/C_{average}$ ratio of Hg occurring in Detroit in the 1980 corresponded with one of the highest increases in the U.S. industrial demand for the metal and the price at London metal exchange, as showed in Figure 2f.

The slope of long-term trends of the $C_{max}/C_{average}$ ratio and those obtained for the major U.S. market parameters are given in Table V for the 1970s and 1980s. The trends of U.S. market parameters are consistent with those of the $C_{max}/C_{average}$ ratio for most of the trace metals (correlation coefficient r in the range of 0.54 to 0.82). For Hg ($r < 0.4$), however, the U.S. consumption follows a downward trend much slower than that observed in the $C_{max}/C_{average}$ ratio. The disparity may be due to the effect of three parallel developments: (a) In 1990 the EPA banned the use of Hg in many industrial processes resulting in a continuous decline in

TABLE V
 Coefficients of annual variations (%/yr) of the U.S. consumption and U.S. production, U.S. import, price at London exchange and ratio between maximum (Cmax) and average (Caverage) ambient concentration of trace metals in Detroit during the decade 1971-1981 and 1982-1990

	From 1971 to 1981					From 1982 to 1990				
	Consumption	Production	Import	Price	Cmax/Caverage	Consumption	Production	Import	Price	Cmax/Caverage
Fe		-1.1			-0.65		3.4			2.6
Zn		-3.9	0.2		-2.6		-1.6	0.4		-0.9
Pb	-2.5	-1.2			-1.7	1.8	2			1.1
Ni	0.1				0.3	3.1				2.3
Cd			9.8		12			-1.1		-1.8
Hg	0.4			1.7	4	-5			1.2	7

the industrial demand of Hg after 1988, and producing a decrease in the U.S. consumption of Hg by 50% in 1990 compared to 1988; (b) the average life time for most of the Hg-based products is in the range of 8 to 16 years (U.S. Bureau of Mines, 1990), implying that a large fraction of the 1970s products concluded their serviceable lives from middle to later 1980s, and were disposed of by waste incineration processes and landfill operations; and (c) the volatilization of Hg from large bodies of water and emissions from natural sources (Nriagu, 1989; Lindqvist *et al.*, 1991) represent an important fraction of Hg lost into the atmosphere which should not be related to any temporal trends in Hg-market parameters observed in the United States during the 1980s.

3.3. SPATIAL AND TEMPORAL VARIABILITY

Table VI shows the t-test results ($\alpha = 0.05$) between pairs of sites operating in the same land use category and between pairs of land use categories. Significant differences ($t > 3$ and $P < 0.003$) were found between populations of Fe, Pb, Ni and Cr at residential sites and between populations of Fe, Zn, Pb, Cr and Cd at commercial sites. At industrial sites all the elements did not show significant differences, with exception of Fe and Cd among the sites I29 and I32, and Pb and Hg among the sites I29 and I30.

The significant differences ($t \geq 3.5$ and $P < 0.003$) in population means of Fe at residential sites suggest the influence of both crustal and anthropogenic sources. Wind-blown soil particles and dust resuspension represent an important source of particulate Fe entering into the urban atmosphere, and this may become even more significant in residential areas where the fraction of exposed soil is larger ($> 60\%$ of the total area). The wind wafting of soil and dust becomes higher during warm seasons compared to the cold seasons (Nicholson, 1988), as shown by the difference in the ratio of the winter and summer ambient air concentrations at residential and commercial sites (Table VII). The higher variance and mean concentrations of Fe and Zn at R4 and C5 suggest the contribution of local sources. The site C5 is in a commercial area with a large number of storing sites for galvanized pipes and steel stubs, which may release Fe and Zn dusts into the atmosphere as a result of both cutting operations and the corrosion of Fe- and Zn-based products stored outdoor. Furthermore, the sites C5 and R4 are down wind of iron-steel and coal power plants (S6), and until the 1978 two Zn-Cu brass and bronze plants were located in an upwind position with respect to C5 and C34.

The strong difference ($t = 10$, $P < 0.000001$) between population means of the Pb concentrations at the commercial sites (which is characterized by high vehicular traffic flows) merely confirms the fact that exhaust emissions from vehicular traffic was the major source of Pb in urban areas during the 1970s and 1980s. Furthermore, the site C5 is downwind to S6, which may represent important sources of Pb, Hg and Cd (Pirrone *et al.*, 1995). The downwind position of R4 to the expressway I94 (see Figure 1) may explain the significant difference between population means

TABLE VI
 Student's t-test results ($\alpha = 0.05$) to evaluate the spatial variability of the ambient concentration of trace metals between sites and between land use categories

	Between sites						Between land use categories			
	R1/R4	R4/R6	R1/R6	C5/C34	I29/I30	I30/I32	I29/I32	Res./Com.	Com./Ind.	Res./Ind.
Fe	-4.7	4.9	4.1	-3.5	-	-	3.4	-7.1	-3.3	5.1
Zn	-	5.6	-	-3.2	-	-	-	3.2	-	-3.1
Pb	-3.5	3.8	-	-10	-3.5	-	-	-	-	-
Ni	-2.3	3.7	-	-	-	-	-	3.7	-	3.0
Cr	2.5	3.5	-	-4.8	-	-	-	5.1	-	3.0
Cd	-	-5.5	-	-4.5	-	-	-4.6	5.2	-	-3.3
Hg	-	-	-	-	3.2	-	-	3.0	-	3.5

Res. = Residential land use; Com. = Commercial land use; Ind. = Industrial land use.

(-) $|t| < |t_{critical-two\ tail}|$.

TABLE VII

Ratio between the winter and summer ambient air concentration of trace metals at sampling sites during the 1971-1992 period

Site	Fe	Zn	Pb	Ni	Cr	Cd	Hg
R1	0.88	2.15	0.73	1.14	0.91	2.27	1.08
R4	0.77	1.13	0.85	3.49	0.92	0.92	2.91
R6	0.86	1.19	4.56	2.08	1.13	0.86	1.67
R12	1.58	1.82	0.72	6.72	1.00	1.25	2.74
C5	1.15	1.33	0.97	2.65	1.06	1.06	2.03
C34	1.90	1.34	1.02	1.67	0.83	1.08	1.55
I29	0.94	1.45	0.97	1.16	0.95	0.80	1.49
I30	0.99	1.12	1.09	1.00	0.70	1.08	1.39
I32	1.02	1.31	0.99	2.06	1.46	1.49	1.39

of Pb at R1 and R4 with the higher variance at R4. Significant differences were obtained between population means of Pb and Hg concentrations at industrial sites I29 and I30, which are frequently downwind to the incinerator GDRRA (S1). The higher mean concentration of Pb and Hg observed at I30 can be attributed to the downwash of the plume emitted from the incinerator.

The significant difference between population means of Ni concentrations at R1 and R4 with highest variance, of 0.4 ng/m^3 , and mean concentration, 23 ng/m^3 , at R4, could be due to the nearby incineration of wastes containing Ni-based products (i.e. hypodermic needles, surgery knives) at Henry Ford Hospital (S5) that is very close to R4. Cadmium concentrations show significant differences between R4 and R6, C5 and C34, and I29 and I32, suggesting important contributions from local sources. A significant amount of colored papers or small plated metal objects, disposed of by incineration at the Henry Ford Hospital may explain the higher variance and mean concentration of Cd at R4. In addition, I32 is also located in an industrial area downwind of automotive assembly plants (i.e. the Motor Ford Co. installations) including car-painting lines (S3).

Population means of Cr concentrations show significant differences between C5 and C34, and between R1, R4 and R6 with higher variance and mean concentrations at C5 and R4. Contributions from the Great Lakes Steel plant upwind to sites R4 and C5 are suggested. Possible contributions from S1 which is most often upwind of the site R4 probably should be noted. No significant differences between population means of particulate Hg were found between sites in residential and commercial areas. However, in industrial areas the Hg concentrations show significant differences between the sites I29 and I30 both downwind of S1.

To evaluate the spatial variation of trace metals concentrations among land use categories, sites located in adjacent urban settings were compared pairwise using Student's *t*-test (population differences are given in Table VI). All the elements show significant differences between residential and commercial, and between residential and industrial population means (Table IV), with the exception of Pb which shows no significant variation among land use categories. The population means of ambient concentrations in commercial and industrial land use categories do not show any significant difference; Fe is the only exception suggesting that wind-blown soil particles and dust resuspension in residential areas may locally affect the spatial distribution of Fe in the urban atmosphere.

The difference in ambient air concentrations between winter and summer seasons are highlighted in Table VII. The concentrations of Zn, Ni and Hg are higher during the winter season, suggesting that the effect of the seasonal activity of sources as well as the decrease of the vertical mixing height available for dispersion which frequently occurs during colder seasons, may result in an increase of the ambient concentration. Moreover, elements emitted into the atmosphere primarily as vapors such as Hg may be influenced by a significant increase of vapor-particle conversion during the winter season, since a decrease of the ambient temperature yields an increase of Hg associated with the particle phase. Fe and Cd show higher concentrations during the summer season in residential areas, confirming the assumption that the wind-blown soil particles and dust resuspension is an important source of Fe in residential areas; the reason for the increase of the Cd concentration is not known. In commercial and industrial land uses the ambient concentrations of Fe and Cd do not show significant seasonal variations. Pb and Cr concentrations are similar or slightly higher during the summer season with the exception of R6 for Pb with a ratio between the winter and summer ambient concentration of 4.5. The unique feature of this station may be related to the fact that the site R6 is frequently downwind of the highway I96 (see Figure 1) which has higher traffic flows during the winter season (DNR, 1989).

3.4. LONG-TERM TREND ANALYSIS

Figure 3 shows the long-term trend of the annual arithmetic mean concentration of trace metals for each land use category, and Table VIII gives the percentage change of the ambient concentrations in each land use category during the decades of 1971–1981 and 1982–1992. Pb, Ni and Cd ambient concentrations were higher most of the time in commercial settings while Fe, Zn and Hg were frequently higher in both commercial and industrial settings. The percentage reductions in long-term mean concentrations between the two decades were higher in industrial areas with the exception of Pb for which higher reductions were observed in residential areas. In the 1980s Cd concentrations showed a substantial increase in the commercial areas compared to the 1970s. However, during the 1970s and 1980s the ambient

TABLE VIII
 Mean percentage reductions of the ambient air concentration (ng/m^3) of trace metals in residential, commercial and industrial areas in Detroit from the first (1971-1981) to the second (1982-1992) decade

	Residential areas			Commercial areas			Industrial areas		
	Mean (1971-1981)	Mean (1982-1992)	Percentage Change	Mean (1971-1981)	Mean (1982-1992)	Percentage Change	Mean (1971-1981)	Mean (1982-1992)	Percentage Change
Fe	1583	560	-64	3188	1424	-55	5250	1438	-73
Zn	400	176	-56	1033	331	-68	1189	374	-69
Pb	919	104	-89	535	156	-71	552	102	-82
Ni	29.9	9.5	-68	41	14.4	-65	45	11.1	-75
Cd	3.9	2.4	-38	5.6	6.8	18	6.6	3.3	-50
Hg	0.4	0.23	-43	0.55	0.3	-45	0.78	0.27	-65

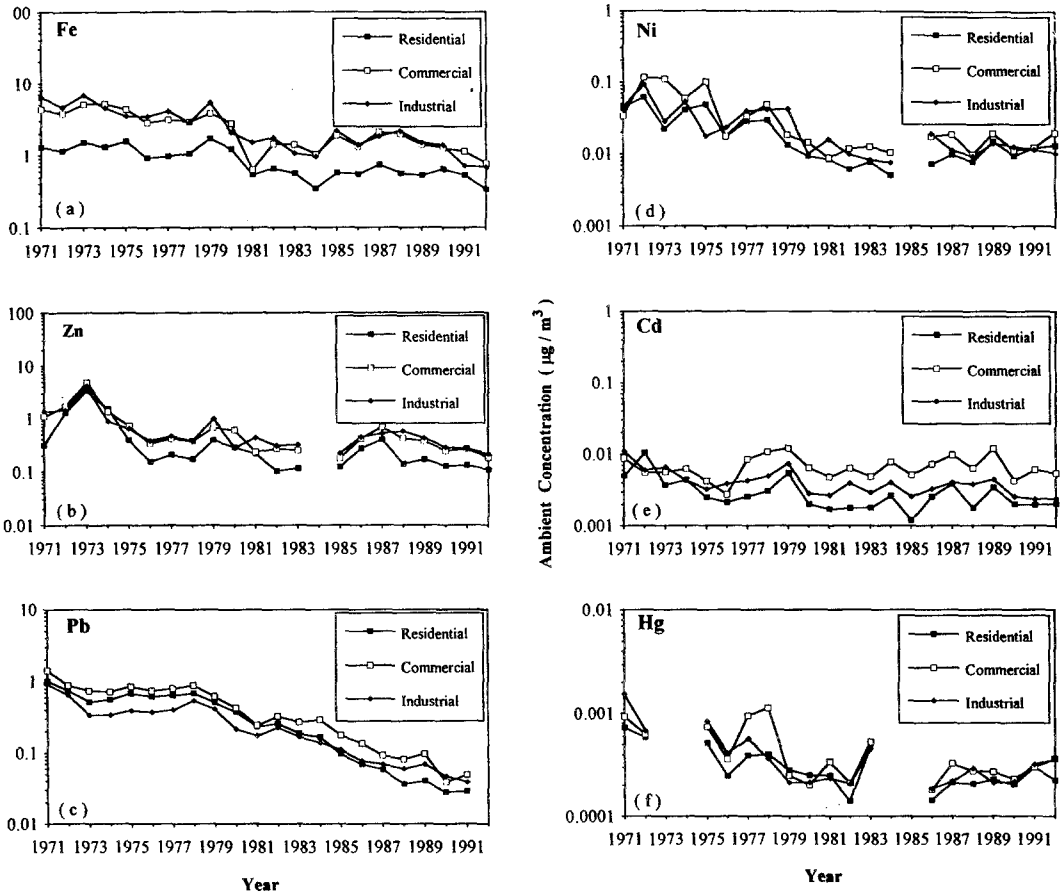


Fig. 3. Long-term trends of the ambient air concentration of trace metals observed in each land use category.

concentrations of most trace metals show significant decrease (in the range of 38 to 89%) for the entire urban scale.

Table IX gives the slope (m) and intercept (b) of long-term trends, and annual variations of ambient concentrations which occurred in Detroit during the last two decades. Ambient concentrations of all the trace metals followed a downward trend during the 1970s, achieving reductions in the range of 38% to 89% in the 10 year-period. From the 1982 to 1992 ambient concentrations of most trace metals reversed the trend with the exception of Fe and Pb which continued the downward trend over the 1980s with an annual rate of 2% and 9.8%, respectively. Trace metals such as Zn, Ni, Cr, Cd and Hg were characterized by upward trends with an annual increase rate in the range of 0.6% to 10.6%.

The significant change in the trend of the Zn concentration seems to be associated with the start up of the two new electrolytic galvanizers (S6) at the beginning of

TABLE IX

Rate of change (slope) $m = dC/dt$ ($\text{ng}/\text{m}^3\text{-yr}$), and intercept b (ng/m^3) of the temporal trend of trace metals in Detroit from 1971 to 1992. ΔC ($\%/yr$) is the annual variation of ambient concentrations

	From 1971 to 1981			From 1982 to 1992		
	m^a	b	ΔC^b	m^a	b	ΔC^c
Fe	-240	4407	-5.4	-33	1692	-2
Zn	-183	2079	-8.8	5.8	163	3.6
Pb	-43	961	-4.5	-25	256	-9.8
Ni	-5.5	72	-7.6	0.47	8.7	5.7
Cr	n.a.	n.a.	n.a.	0.08	8.4	1
Cd	-0.25	6.8	-3.7	0.028	4.7	0.6
Hg	-0.07	0.95	-7.4	0.015	0.14	10.6

^a A negative value implies that the trend is downward.

^b $\Delta C = 100$ (m/b) is obtained selecting the 1971 as reference year.

^c $\Delta C = 100$ (m/b) is obtained selecting the 1982 as reference year.

the 1987. Furthermore, the large number of the incinerator facilities operating in Detroit and surrounding areas (about 1,678 units) and the start up of two major incinerators (i.e. S1 with 83,160 kg/h capacity, and S2 with 19,000 kg/h capacity) during the 1980s in Detroit (Dann, 1992), may have collectively yielded an increase of the Cd, Ni and Hg emissions into the local atmosphere.

However, the average annual variation in the ambient concentration of trace metals given in Table IX is certainly effected by uncertainty. In fact, the exclusion of certain years from the regression would change the slope by up to a factor of 2.

4. Conclusions

A review of the airborne trace metals concentration in the urban area of Detroit from 1971 to 1992 was presented including the influence of local emission sources on the long-term trend of the ambient concentration observed in each land use category.

Most of the trace metals were found to be more abundant in commercial and industrial areas. The observed ambient concentrations were consistent with that reported in literature for other urban areas of the world.

The trend of the ratio $C_{\text{max}}/C_{\text{average}}$ was found to be similar to that observed for selected U.S. market parameters chose as long-term indicators of the emission

sources activity, suggesting that a more detailed analysis of these parameters may be useful to understand the contrast between global versus local scale trends. The effects of type, size and location of emission sources, and prevailing meteorological conditions were found to effect the trends of the ambient concentration of trace metals in each land use category.

Long-term trends were found to be in the 1970s downward for all the trace metals with annual reduction in the range of 3.7 to 8.8%. From 1982 to 1992 ambient concentrations of Zn, Ni, Cr, Cd and Hg reversed the trend with the exception of Fe and Pb which continued the downward trend during the 1980s with an annual rate of 2% and 9.8%, respectively. However, uncertainties up to a factor of 2 were found to effect the annual rates estimate.

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