Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina

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"Capsule": *Exhaust from vehicles appeared to be the major source of metal aerosols in the La Plata, Argentina region.*

Abstract

Airborne particulate trace metals have been measured bimonthly during day and night hours in four permanent stations located in residential, industrial and commercial sectors of La Plata City region, to characterize the sources and variability of atmospheric inputs. Airborne trace metal regional averages (Pb 64 ± 62, Cu 30 ± 27, Mn 26 ± 20, Zn 273 ± 227, Fe 1183 ± 838, Ca 5343 ± 3614, Mg 1472 ± 967, Cr 4.3 ± 2.4, Ni 3.2 ± 3.5 and Cd 0.41 ± 0.42 ng/m^3) are comparable to the values reported for not grossly polluted cities and below the general trend described for urban particulates. Two- and three-way analysis of variance and variance components tests ($P < 0.05$) were performed to assess the contribution of the diurnal (day vs. night), spatial (inter-station) and temporal (inter-month) components of variability. Trace metal concentrations followed the behavior of total suspended particles with higher concentrations during the day and at the Downtown station and lower at the Residential site. In general, spatial and temporal variations prevailed over diurnal differences. Spatial differences were clearly most significant for Pb, which presented higher values at the Downtown site reflecting the importance of motor exhaust inputs. In contrast, diurnal differences were more important for Mn due to increased dust resuspension during day hours. A seasonal trend with concentrations usually increasing during winter months and decreasing in spring–summer was also detected. Enrichment factors (EF) were calculated to evaluate anthropogenic versus natural element sources. High EF (21–376) were obtained for Pb, Zn, Cd and Cu reflecting the importance of anthropic inputs. The comparison with EF calculated for high-emitting vehicle particle emissions indicated that motor exhausts are the most important source of these elements in La Plata region. In contrast, the EF calculated for Mn, Cr, Ni, Ca and Mg were low (1.3–7.5) suggesting chiefly natural sources, i.e. soil-derived dusts. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Man-induced mobilization of trace metals into the biosphere has become an important process in the global geochemical cycling of these elements (Nriagu and Pacyna, 1988). This effect is most evident in urban areas where several stationary and mobile sources (industrial activities, energy production, construction, urban waste treatment, vehicle exhausts) release large quantities of trace metals into the atmosphere, soils and aquatic ecosystems very often exceeding the natural emission rates. The atmosphere, in particular, is a key compartment in the global geochemical cycling of trace elements (Lantzy and Mackenzie, 1979). The main inputs of trace metals to the atmospheric cycle are strongly related to particle emission processes. For most of the toxic trace metals (e.g. Pb, Cd, Zn, Ni, Cu) anthropogenic inputs are more important than natural sources such as continental dust, volcanic dust and gas, sea spray, and biogenic particles (Bertine and Goldberg, 1971; Nriagu, 1979, 1989).

From a toxicological perspective, the airborne particulate material has important health implications, basically through the inhalation of small particles with diameters of 10 μm or less which can be absorbed in the alveolar region of the lung (Hileman, 1981). It is well established that these inhalable particles have higher concentrations of many trace elements, such as Pb, Cd, Zn, Cr, Ni, Mn and Cu (Natusch et al., 1974; Hlavay et al., 1992), and thus, are considered of major health concern. However, some sources have been reported to have emissions highly enriched in toxic metals without a

significant increase in PM10 levels (Sweet et al., 1993). Thus, from a biogeochemical perspective, characterization of the total suspended fraction is relevant to identify the sources and variability of the airborne material.

In this study we determine the concentration of selected trace elements in airborne particles from La Plata region in order to: (1) assess the heavy metal concentration status of the region; (2) characterize the principal sources of atmospheric particulate trace metals; (3) characterize diurnal versus nocturnal trends; and (4) evaluate spatial and temporal variations.

2. Materials and methods

2.1. Study area and sampling

The study area is centered around La Plata City, capital of the Buenos Aires state situated 15 km away from the Río de la Plata Estuary coast. It includes the nearby cities of Berisso and Ensenada and comprises a total population of about 1,000,000 people and a heavy industrial sector oriented to petrochemical activities.

In order to characterize the contamination status and the most important emission sources of airborne particulate metals, four permanent sampling stations were established in a 25-km-long NE–SW transect passing through the petrochemical zone and La Plata City center (Fig. 1). The stations were located in La Plata Port (Port), in the limit of the petrochemical area between Ensenada and La Plata cities (Petrochemical), in La Plata City center (Downtown), and in a less urbanized area 12 km away from La Plata (Residential). Total suspended particles (TSP) were collected at each station for seven to nine samplings carried out during the year 1993 (January, February, March, April, May, July, August, September, December), using two General Metals Works BM 2200X portable high volume samplers (HVS). For security reasons, the HVS were located ≈5 m above the ground. To establish day–night differences, the HVS were operated for 48 h in two discontinuous periods of 12 h, during the day (from 09:00 to 21:00) and night (from 21:00 to 09:00). During normal operation the HVS pumped 631–3418 m^3 of air. Due to electricity failures and incorrect operation of the sampling equipment, the data set is incomplete for some months and stations (especially for July and the Residential site). TSP were collected on Whatman EPM 2000 borosilicate glass microfiber filters (99.999% retention for 0.6 μm NaCl particles). TSP masses were determined by gravimetry, drying and weighing the filters in glass tubes (40°C to constant weight). Dried filters were cut into two equal halves, re-weighed, and frozen ($-20°C$) until analysis of trace metals and hydrocarbons (Colombo et al., 1999).
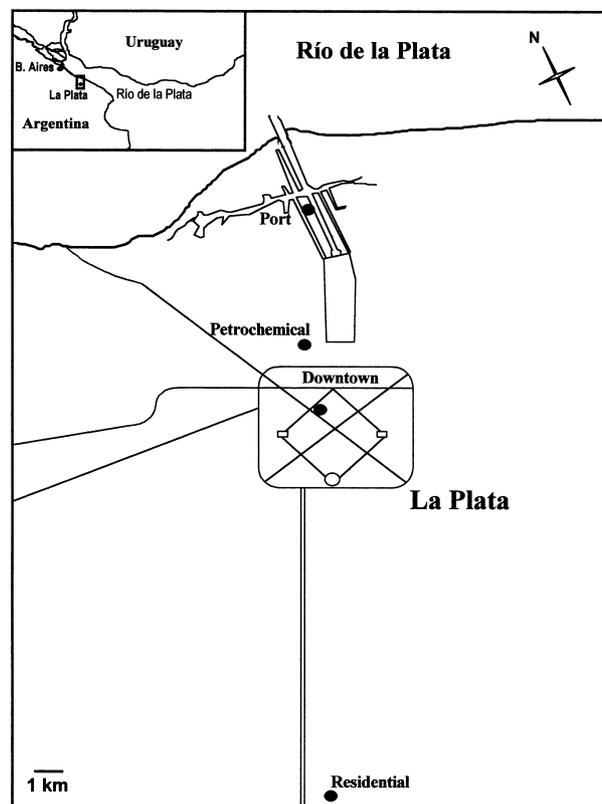

Fig. 1. Study area and station location. Major roads and parks (open circles and rectangles) of La Plata City are indicated. Sampling stations are shown as filled circles.

2.2. Chemical analysis

The filters for trace metals were extracted in glass tubes with 25 ml of concentrated hydrochloric acid–nitric acid–deionized water mixture (5:3:2) in a hot water bath (20 min at 70°C), followed by ultrasonic treatment (20 min at 30–40 kHz working frequency and 300 W ultrasonic power). This extraction scheme was repeated five times plus an additional extraction with deionized water. All the extracts were pooled and concentrated to 10 ml at 60°C in polyethylene flasks. The extracts were centrifuged (20 min at 4000 rpm) and solid potassium chloride was added as a modifier. The extraction efficiency was tested by re-extracting two previously treated filter-samples from each station. The recovery was null for Cd, Ni, Fe and Zn, averaged 1% for Pb and Cu, and 11% of the first extraction for Cr. Extracts were brought to a final volume of 25 ml with deionized water and stored at room temperature in polyethylene bottles until analysis.

Trace metal analysis was performed with a Perkin Elmer 3110 Atomic Absorption Spectrometer and an air–acetylene flame with a Deuterium Lamp background correction to overcome molecular interferences. The instrument operating conditions and general settings for the different elements (flame stoichiometry, slit

height and width, lamp current and wavelength) were defined according to the optimum recommended for the instrument. Determinations were done with Perkin-Elmer (Cu, Fe, Pb, Zn) and ISTC (Cd, Cr, Mn, Ni) hollow cathode lamps; Ca and Mg were determined by flame emission analysis. Working standard solutions were prepared with high-purity Johnson Mathey PLC original standard materials. Multi-element standard solutions were made for Cd, Cu, Mn, Ni, Pb, and Zn; two-element standard solutions for Ca and Mg, and single-element standard solutions for Cr and Fe.

Filter and reagent blanks were processed following the sample treatment. The average metal content of the blanks for Pb, Mn, Cu and Zn represented less than 5% of the samples average metal content. For the other metals the blank contents averaged 9% up to 41% for Cr. The analytical detection limits were 0.012 µg/ml for Cd, 0.020 µg/ml for Zn, 0.022 µg/ml for Cu, 0.041 µg/ml for Mn, 0.055 µg/ml for Cr, 0.065 µg/ml for Ni, 0.068 µg/ml for Fe, and 0.081 µg/ml for Pb.

3. Results and discussion

3.1. Trace metal concentrations in La Plata area

Table 1 shows the concentrations of airborne trace metals at each station and the regional average for La Plata area compared with other world cities. In general, most airborne trace metals in La Plata area are lower than the average values reported for urban particulates (Lantzy and Mackenzie, 1979). La Plata Pb average (65 ± 62 ng/m^3) is 12 times lower than the urban particulates average (790 ng/m^3), similar to the values reported for Birmingham and Bondville, a rural site in Illinois. La Plata average concentration for Pb is well below the national regulation (2 µg/m^3, 30 min average). Other cities in USA or Greece show much higher Pb levels (400 to > 1000 ng/m^3) whereas the background values reported for Antarctica (0.07–5.4 ng/m^3) are several orders of magnitude lower comparable to the atmospheric continental USA baseline (8.0 ng/m^3; Chow et al., 1972).

The concentrations of Cu, Mn, Cr, Ni and Cd in La Plata area are four to 10 times lower than those reported for urban particulates, comparable to the values registered in Birmingham and Sindos; Antarctica background levels are two to four orders of magnitude lower. Fe follows broadly the same pattern; the concentrations in La Plata air (1183 ± 838 ng/m^3) are below the general urban average and similar to the values reported for Chicago, St. Louis and Mallipo but are higher than the levels registered in Birmingham. The sole heavy metal which appears to be enriched in La Plata air is Zn, with levels (273 ± 227 ng/m^3) more comparable to the average urban particulates (359 ng/

m^3). The values are similar to those of Mallipo, Birmingham and many USA cities, whereas Beijing and Grecian cities show higher Zn concentrations. Ca is another major element which appears to be enriched in La Plata area relative to other world cities; the average concentration (5343 ± 3614 ng/m^3) is ≈ 10 times higher than those reported for Chicago, St. Louis and Birmingham (171–1918 ng/m^3). This high Ca abundance is probably related to the composition of the carbonaceous soil-source material (loess and loess-like sediments with CaO contents of 2.8–3.1% of total oxides; Camilión, 1993).

In summary, the concentrations of airborne metals in La Plata area are relatively low, similar to the values reported for not grossly polluted cities and below the general trend described for urban particulates, probably reflecting the major administrative and trade-oriented character of the city. Zn and Ca are the sole elements showing some degree of enrichment relative to other world cities.

3.2. Diurnal, spatial and temporal variability of trace metal concentrations

Table 2 presents trace metal and TSP concentrations during day and night for each station. The general mean concentrations of non-detected elements were calculated using one-half of the detection limit. The data evidence a considerable degree of variability including diurnal (day vs. night), spatial (inter-station) and temporal (inter-month) differences. Fig. 2 shows all these variability components. In general, as has been previously observed for airborne hydrocarbons (Colombo et al., 1999), trace metal concentrations tend to follow the behavior of TSP with concentrations usually higher during the day, particularly at the Downtown site (squares in Fig. 2). Spatial differences are also evident in the graphs, with concentrations usually higher at Downtown station and lower at the Residential site (triangles in Fig. 2). In addition to these diurnal and spatial variations, a seasonal trend can also be observed; the concentrations increase during April–May–August (autumn–winter) and decrease in September–December (spring–summer). In addition to these general trends associated with TSP behavior, some metals such as Cu and Zn display a different pattern, e.g. no day–night differences or decreasing concentrations throughout the year. In order to more precisely assess the contribution of these defined sources of variation, two- and three-way analysis of variance (ANOVA) and variance components tests ($P < 0.05$) were performed for the whole log-transformed data set (excluding July, due to incomplete sampling).

3.2.1. Diurnal versus spatial variability

Fig. 3 shows the percentage of the total variability explained by spatial and diurnal differences considering

Table 1
Particulate element concentrations in air of La Plata compared with other urban and remote areas around the world

		Concentration (ng/m³)										References
		Pb	Cu	Mn	Zn	Fe	Ca	Mg	Cr	Ni	Cd	
La Plata area												
Port	Range	9.2–135	8.4–100	6.8–90	5.1–689	467–2319	2923–17742	381–4954	2.5–8.3	<1.0–7.2	<0.17–1.3	This study
Petrochemical	Range	9.5–152	4.5–76	7.4–73	17–695	369–1669	2014–12306	437–4533	0.8–7.2	0.70–16	<0.11–1.4	This study
Downtown	Range	44–268	8.9–73	8.8–92	20–1049	747–5967	3494–15746	696–3158	3.5–12	<1.0–15	<0.16–2.0	This study
Residential	Range	2.0–101	7.6–163	4.1–31	34–658	178–1495	394–7489	544–2674	0.65–7.9	<1.1–5.2	0.13–1.2	This study
Grand mean ± S.D.		64.5±61.8	29.5±27.3	25.5±19.7	273±227	1183±838	5343±3614	1472±967	4.32±2.39	3.15±3.52	0.41±0.42	This study
Urban areas												
General average[a]	Average	790	110	149	359	3710	–	–	32	30	2	Lantzy and Mackenzie (1979)
Washington D.C. (USA)[b]	Average	1420	–	–	150	–	–	–	–	–	3.5	Greenberg (1990)
New York City (USA)[b]	Average	1220	–	–	320	–	–	–	–	–	7	Greenberg (1990)
Boston (USA)[b]	Average	1400	–	–	340	–	–	–	–	–	2	Greenberg (1990)
Chicago (USA)[b]	Average	1500	–	–	590	–	–	–	–	–	6	Greenberg (1990)
St. Louis (USA)[b]	Average	400	–	–	240	–	–	–	–	–	15	Greenberg (1990)
Northwest Indiana (USA)[b]	Average	1700	–	–	270	–	–	–	–	–	12	Greenberg (1990)
Beijing (China)[c]	Range	–	–	73–680	62–1700	4300–23000	–	–	10–77	–	–	Gao et al. (1992)
Mallipo (South Korea)[c]	Range	–	–	13–120	6.5–350	430–4300	–	–	1.3–14	–	–	Gao et al. (1992)
Illinois (USA)[d]												
Bondville site	Average	22.4	5.4	10.1	28.5	233	442	–	1.9	1.2	<4	Sweet et al. (1993)
East St. Louis	Average	209	138	24.3	231	666	1918	–	5.7	3.9	25	Sweet et al. (1993)
Southeast Chicago	Average	127	15.4	86	148	1185	1088	–	11.2	4.8	<4	Sweet et al. (1993)
Thessalomiki (Greece)[e]												
Ionia	Range	46–420	9.0–210	19–340	250–3200	–	–	–	0.01–9.9	–	0.86–6.6	Voutsa and Samara (1996)
Sindos	Range	70–1020	31–93	177–4200	610–4700	–	–	–	3.2–24	–	0.76–7.8	Voutsa and Samara (1996)
Birmingham (UK)[f]	Range	69–113	12–66	10–23	64–641	254–348	171–245	–	7.1–18	2.2–7.4	–	Harrison et al. (1996)
Remote areas												
Atlantic Ocean[g] (30°N–43°N)	Range	0.10–64	0.12–56	0.05–9.7	0.30–154	3.4–240	–	–	0.07–1.1	8.0–12	0.003–0.62	Duce et al. (1975); Veron et al. (1992); Zoller et al. (1974)
Antarctica[h]	Range	0.071–5.41	0.025–1.17	0.004–0.99	0.018–24.8	0.22–46.8	0.15–1003	0.32–2.0	0.0025–0.10	0.03–0.06	0.005–0.5	Loureiro et al. (1992); Rädlein and Heumann (1992); Khandekar et al. (1992)

[a] General average values obtained from a review of published data from USA and European cities.
[b] General average values from some USA important cities.
[c] Range values for 72 daily samples collected during April and May 1989.
[d] Average values for 12- or 24-h samples of PM-10 particles collected over a 2-year period in a rural site and in two urban/industrial areas (Bondville site, E. St. Louis and SE Chicago, respectively).
[e] Range values for 24-h samples ($n=28$) collected during the period summer 1993–summer 1994 in two residential areas.
[f] Range of mean values for a total 55 daily 24-h samples collected during winter (January 2–February28) and summer (July 27–August 23) 1992.
[g] Range values for aerosol samples collected on-board ship during cruises in the North Atlantic.
[h] Range values for aerosol samples collected during different sampling periods and carried out on-board ship and in Antarctica stations.

Table 2
Concentration of particulate elements and total suspended particles in air sampled during day and night in La Plata region[a]

	Pb (ng/m³)		Cu (ng/m³)		Mn (ng/m³)		Zn (ng/m³)		Fe (ng/m³)		Ca (ng/m³)		Mg (ng/m³)		Cr (ng/m³)		Ni (ng/m³)		Cd (ng/m³)		TSP (µg/m³)	
	D	N	D	N	D	N	D	N	D	N	D	N	D	N	D	N	D	N	D	N	D	N
January																						
Port	10.9	9.21	8.52	8.38	8.25	6.85	232	689	467	737	3544	5129	746	2065	3.00	4.53	1.38	1.18	0.17	0.41	42.1	24.7
Petrochemical	40.5	34.5	9.14	12.0	17.0	9.53	286	585	1596	1014	3010	3963	758	2428	3.95	3.09	<1.11	<1.13	0.49	<0.18	39.8	31.2
Downtown	205	124	26.3	25.4	67.7	33.5	1049	457	5967	1917	9324	6344	2621	1761	5.10	3.92	10.0	4.51	0.23	0.25	150	67.3
Residential	5.03	1.99	7.64	12.1	14.7	10.7	658	335	1155	1107	614	394	1101	566	0.74	1.09	<1.24	<1.08	0.19	0.17	34.6	24.3
February																						
Port	22.2	17.6	10.7	9.30	20.9	21.0	225	502	802	525	3607	4584	381	1469	6.42	5.12	<1.13	<1.22	0.28	0.23	65.9	49.3
Petrochemical	9.47	22.8	4.52	8.97	10.2	7.43	293	443	556	845	2378	2648	835	1132	4.62	2.32	3.19	3.23	0.29	<0.18	36.2	28.2
Downtown	181	119	23.1	18.9	52.9	23.3	372	424	1874	1274	11589	3494	1398	1125	5.27	3.51	2.17	<1.14	0.31	0.24	107	68.2
Residential	2.37	11.7	8.64	14.4	16.7	10.3	159	297	1419	1495	1582	1252	567	961	0.67	0.65	<1.12	<1.09	0.17	0.17	47.6	27.1
March																						
Port	70.6	71.2	28.1	35.0	16.6	15.9	347	402	836	1130	3188	2923	457	1030	4.55	4.45	1.37	1.76	0.53	0.42	79.9	63.8
Petrochemical	49.2	79.2	19.4	28.5	33.1	32.3	695	221	1107	1514	4870	4877	1373	557	5.49	7.15	3.38	5.50	0.37	0.48	46.0	69.9
Downtown	132	74.9	26.4	17.8	31.5	16.6	268	438	2847	1728	6805	3639	1075	1497	6.36	4.11	<1.17	<1.10	0.77	0.37	77.7	46.1
Residential	4.57	8.05	20.9	21.7	16.7	9.81	295	471	465	398	1587	1932	1450	2299	0.71	0.70	<1.19	<1.17	0.18	0.18	39.3	23.7
April																						
Port	26.0	24.9	14.5	15.7	14.7	13.2	284	299	602	610	4026	4104	1186	688	3.24	7.95	6.13	2.24	0.32	0.26	52.8	44.2
Petrochemical	41.6	52.6	11.7	21.7	15.4	10.8	519	668	925	318	3197	3120	1137	1333	4.58	0.80	1.69	2.45	0.36	0.18	53.2	35.5
Downtown	231	79.1	42.5	22.6	53.9	16.3	217	61.4	2844	1301	13202	5558	2549	696	7.27	3.51	7.73	3.49	0.57	0.17	147	53.2
Residential	45.8	101	18.7	35.2	30.6	19.3	122	414	1008	915	4034	3111	544	989	4.28	4.99	1.23	5.22	1.20	<0.18	77.2	67.1
May																						
Port	48.0	90.1	21.5	42.6	25.9	17.9	138	174	1422	1309	4689	3596	852	1074	4.39	5.29	4.20	7.25	0.27	0.99	61.5	74.8
Petrochemical	70.0	63.4	30.2	16.6	17.0	10.7	105	60.8	532	453	3195	2014	682	437	0.75	1.85	2.36	0.91	0.48	0.30	54.5	44.7
Downtown	181	68.3	54.5	9.67	48.3	8.84	391	146	2252	1158	15746	5974	2416	804	11.8	3.73	6.21	<1.03	0.34	<0.16	122	34.3
Residential	44.8	33.6	79.4	163	21.7	4.05	461	642	601	388	6786	2897	1750	1428	7.68	7.90	<3.35	<3.80	0.52	0.59	79.2	39.9
July																						
Port	100	31.8	33.4	33.0	20.1	9.99	78.2	26.8	750	741	9202	4115	3964	1944	4.68	3.44	2.36	3.74	0.54	<0.17	72.0	32.0
Petrochemical	26.5		9.51		11.3		16.6		369		5667		2904		2.15		<1.16		0.27		30.4	
Downtown																						
Residential																						
August																						
Port	135	133	53.2	99.9	90.3	61.5	185	614	2319	1748	17742	8434	4954	2950	8.34	5.23	3.85	6.18	0.96	1.26	162	105
Petrochemical	138	152	75.8	64.9	73.1	37.0	186	132	1669	1225	12306	11499	4093	4533	5.55	4.46	16.3	7.69	1.42	1.32	162	110
Downtown	268	165	72.8	57.5	92.0	39.2	281	131	1426	957	9295	8223	3158	2483	11.6	7.15	12.5	15.1	1.98	1.75	219	105
Residential	24.4	24.1	69.1	38.6	31.3	6.27	52.2	34.3	1033	178	7489	3476	2674	1503	3.60	2.13	1.06	1.24	<0.17	0.13	81.1	23.3

Table 2 (continued)

	Pb (ng/m³)		Cu (ng/m³)		Mn (ng/m³)		Zn (ng/m³)		Fe (ng/m³)		Ca (ng/m³)		Mg (ng/m³)		Cr (ng/m³)		Ni (ng/m³)		Cd (ng/m³)		TSP (µg/m³)	
	D	N	D	N	D	N	D	N	D	N	D	N	D	N	D	N	D	N	D	N	D	N
September																						
Port	19.7	11.8	14.1	11.3	55.3	13.4	29.1	35.9	1529	857	11105	5645	1496	1120	4.46	3.02	2.39	1.36	<0.17	0.16	81.5	29.7
Petrochemical	62.0	25.0	22.5	12.6	28.7	13.4	54.0	19.5	739	1082	3732	3227	584	979	2.36	4.38	5.23	7.94	0.66	0.20	51.3	54.2
Downtown	139	44.0	24.9	8.91	33.7	11.9	78.5	20.0	1260	747	9912	3844	1457	1457	5.60	3.69	3.60	<1.04	0.64	<0.16	94.5	55.0
Residential																						
December																						
Port	14.3	13.1	6.25	16.7	15.5	10.7	6.97	5.11	983	986	5396	3174	985	899	2.96	2.52	<1.09	<1.10	<0.17	0.17	29.2	27.8
Petrochemical	14.8	24.7	6.92	21.5	27.2	12.9	20.8	29.4	913	501	3662	2525	961	919	3.76	2.27	0.70	0.80	0.11	<0.11	85.4	37.4
Downtown	88.9	78.7	23.6	37.6	30.6	29.4	79.9	44.0	1284	1229	7897	5942	2097	1842	5.86	4.77	3.32	3.19	0.27	0.20	98.6	101
Residential	4.35	20.3	20.6	62.4	18.0	17.1	36.3	34.4	651	617	4058	4179	909	974	3.38	3.33	<1.07	<1.13	<0.17	0.22	36.2	37.2

[a] TSP, total suspended particles; D, day; N, night.

the whole data set. In general, spatial differences are more important than diurnal variations. Overall, spatial differences explain 24–67% (Cd–Pb) of the total variance, whereas diurnal differences account for 0.5–35% (Ni–Mn) of the total variability.

Spatial differences are clearly most significant for Pb. This trend is almost exclusively determined by the higher values of the Downtown site. This station presents significantly (S–N–K method, $P < 0.05$) higher Pb concentrations (mean $= 136 \pm 64$ ng/m³) compared to the rest of the stations (53.3 ± 40, 47.2 ± 42 and 23.7 ± 27 ng/m³, for Petrochemical, Port and Residential, respectively). This difference, that follows the trend of TSP levels, reflects the well-established relation between atmospheric Pb concentrations and motor exhaust inputs due to the use of leaded gasoline (Chow et al., 1972; Eisenreich et al., 1986; Veron et al., 1992).

Diurnal differences are more important for Mn reflecting the predominant natural soil source of this element and the increased dust resuspension during the most active day hours (see next section).

3.2.2. Diurnal versus temporal variability

The evaluation of the diurnal and temporal variabilities by station evidence different patterns (Fig. 4). Overall, at Residential, Petrochemical and Port sites the temporal variation is more important, whereas at Downtown, diurnal differences prevail.

At the Residential site, the total variance explained by temporal differences ranges from 69 to 96% (Pb–Cr; $P = 0.005$); for Mn, Fe, Mg and Cd the statistical results are not significant. Diurnal variations are significant only for Mn (54%, of the total variance explained; $P < 0.05$). At Petrochemical station, temporal variations explain 58–89% (Cd–Ca; $P < 0.05$); Pb, Fe and Cr temporal differences are not significant ($P < 0.05$). Diurnal differences at this station are only significant for Cd and Mn (22–25%, of total variation, respectively; $P = 0.005$). At Port site, temporal differences explain from 79 to 97% of the total variation for Ca and Pb, respectively ($P < 0.02$). Mg and Cr temporal differences are not significant ($P < 0.05$). At this site, all the elements showed non-significant ($P < 0.05$) diurnal variations.

In contrast with the temporal-dominated pattern previously described, at Downtown site, diurnal variations are more important, accounting for 21–72% of the total variation (Ni–Ca; $P < 0.005$). For Cu, Zn and Mg, the differences are not significant ($P < 0.05$). Temporal differences prevail for Cd, Ni and especially for Zn (45–68%; $P < 0.005$).

The higher incidence of the diurnal variability at the Downtown site was also observed for airborne hydrocarbons (Colombo et al., 1999) reflecting the dominant role of mobile sources, and the generally higher activity during the day (construction, material handling, etc.), which in association with higher temperatures and lower
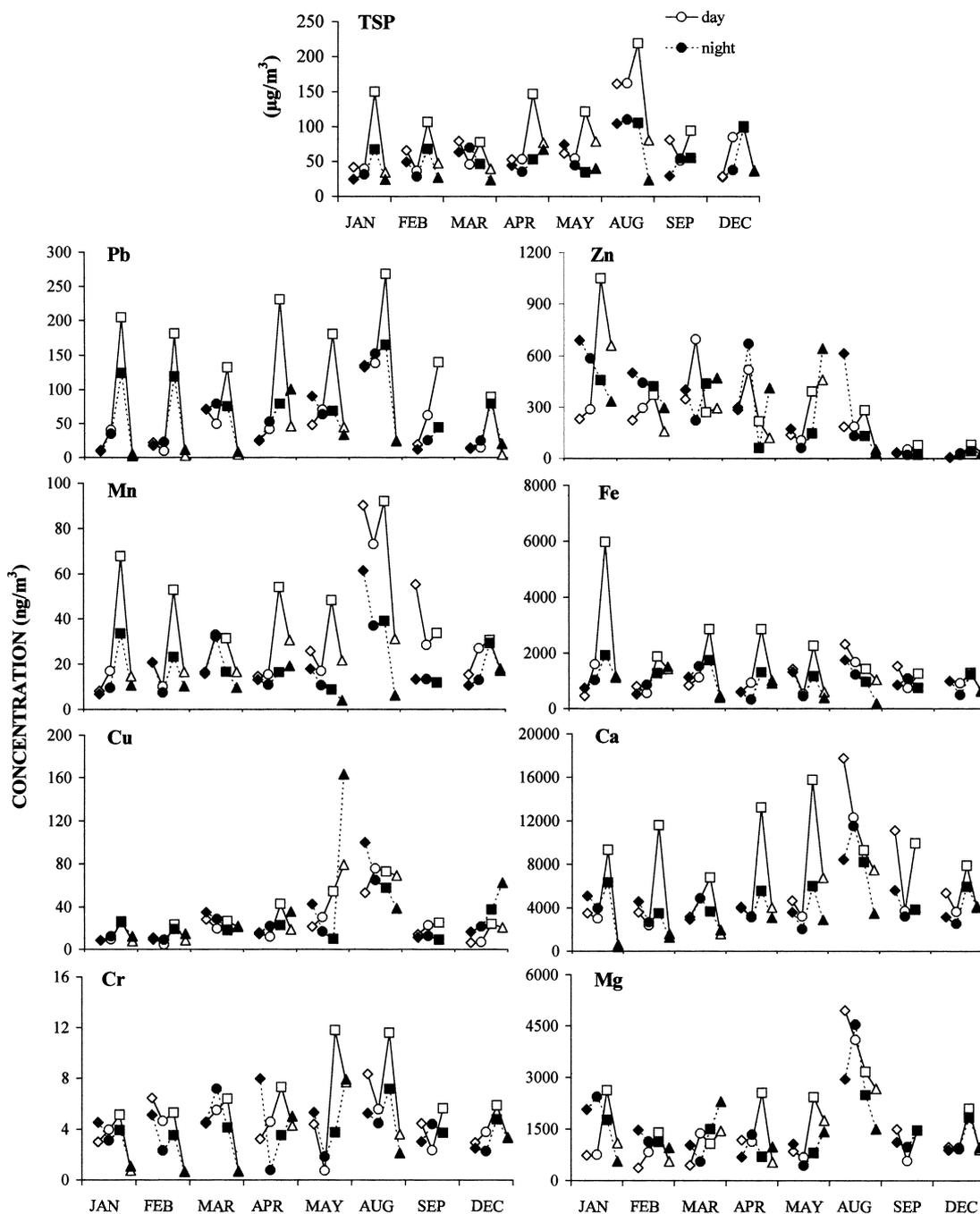
Fig. 2. Concentrations of airborne trace metals and total suspended particles in the day and night air samples at the four stations and eight sampling months. Stations are identified by diamonds (Port), circles (Petrochemical), squares (Downtown) and triangles (Residential).

ambient humidity favors dust resuspension. At this site, TSP concentrations during the day are significantly higher ($P = 0.005$) than night values (Fig. 2). The annual average increment of day versus night TSP, expressed as percentage of night values, is 92%. This clear TSP trend is also followed by Pb and Mn, which present significantly higher values during the day, e.g. 90 and 129% annual average day increment, respectively.

Simultaneously to this TSP-related volumetric trend (concentrations in ng/m^3), an opposite mass proportion

pattern (concentrations in µg/g TSP mass) is also suggested. Although this trend has no statistical significance ($P < 0.05$) for the whole data set, a trend of higher mass concentrations during the night is suggested for most of the metals. This is clearly evidenced by the annual average night increments expressed as percentage of day values, e.g. Pb 4–150%, Cu 23–175%, Zn 39–160%, Cd 9–70%, Ni 7–115%, Cr 15–61%, Fe 8–33%, Ca 1–21%, Mg 36–77%. The only exception is Mn, which shows an opposite pattern, i.e. day mass

concentrations are higher than night values (7–32% annual average increment). Hydrocarbons showed a similar trend of night enrichment to most of the metals (Colombo et al., 1999). These different patterns of the trace element mass concentrations (night vs. day enrichment) reflect the existence of two particle pools: a smaller size pool enriched in anthropogenic metals, chiefly derived from gasoline combustion, which due to longer atmospheric residence time prevails during the night, and a larger-size, dust-derived rapidly sedimenting particle pool more abundant during the day. Mn enrichment in the coarser day particles supports a predominant soil-origin associated with mechanic resuspension of street-dust (Sweet et al., 1993).

3.2.3. Overall diurnal, spatial and temporal variability

Fig. 5 shows the results of a three-way ANOVA test performed to simultaneously evaluate all three sources of variation. Analyzing the percentage of the total variability explained by each source, four different patterns can be identified. TSP, Mn and Ca present a similar pattern, with temporal, spatial and diurnal differences of the same order of magnitude, explaining each 16–23% ($P < 0.001$), for TSP, 13–31% ($P < 0.001$), for Mn, and 8–34% ($P < 0.001$), for Ca.

Pb pattern is comparable to the previous group, but lacks significant diurnal differences. Temporal and spatial differences dominate, explaining 16 and 52% ($P < 0.001$), respectively, of the total variation.

A third group is formed by Cu–Mg–Zn–Ni–Cd with a clear predominance of the temporal variability (26–69%

Fig. 3. Diurnal versus spatial variance components test results for the whole data set.
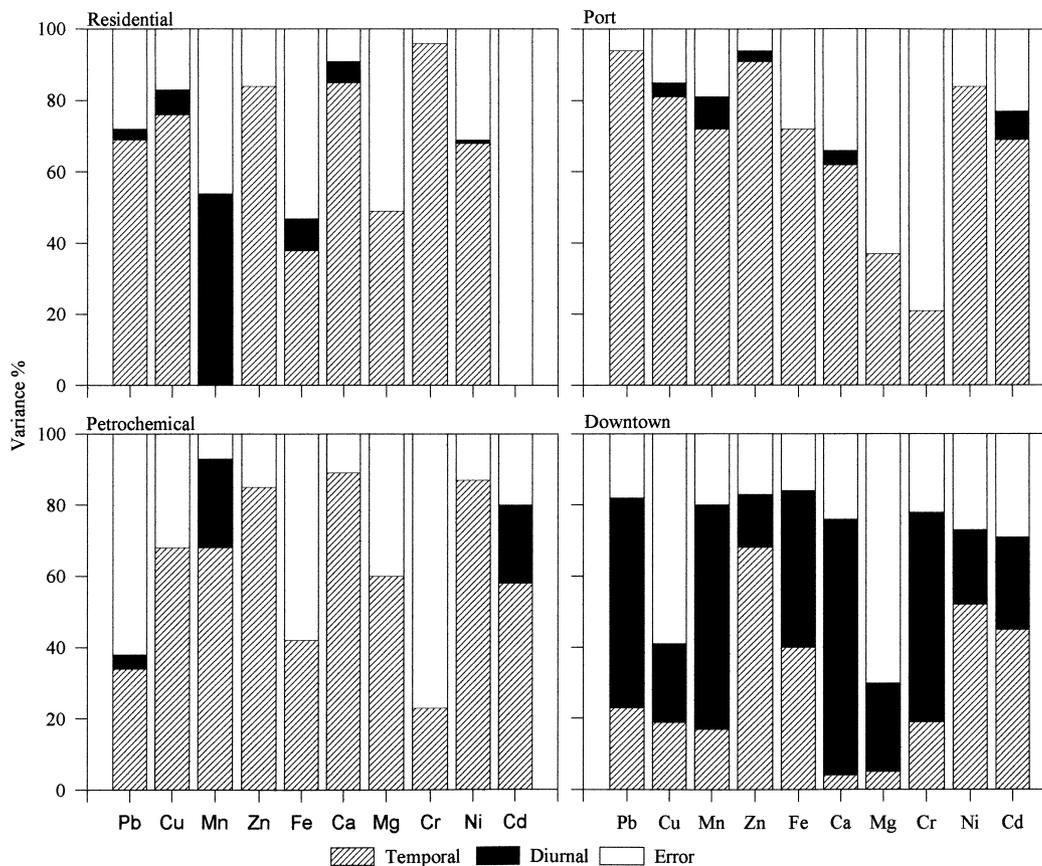

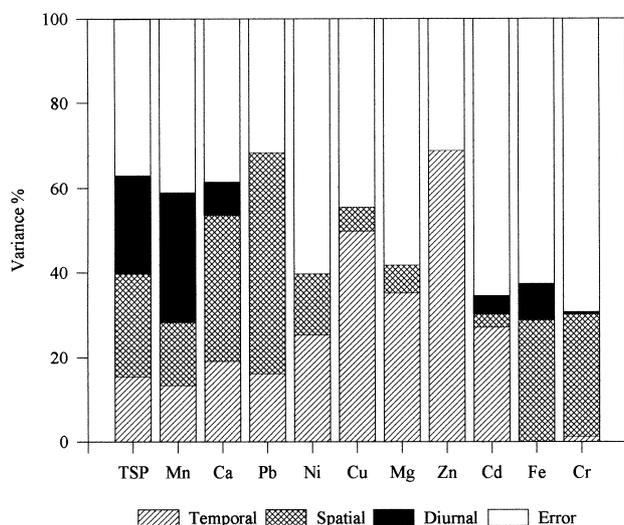Fig. 4. Diurnal versus temporal variance components test results for the whole data set.

Fig. 5. Overall diurnal, spatial and temporal variance components test results for the whole data set.

of the total variation explained, $P < 0.001$). The spatial variability is significant only for Cu and Ni (5.8–14%, $P < 0.05$, respectively), whereas day–night differences are not significant for all the metals ($P < 0.05$).

Fe and Cr are the last group, characterized by the prevalence of spatial differences, which explained 29% ($P < 0.001$) of the total variability for both metals. Day–night variations are low, significant only for Fe (8.5% of variation explained, $P < 0.05$), and temporal variations are not statistically significant ($P < 0.05$).

This descriptive classification of the elements' behavior is difficult to interpret on a source-base perspective, probably because of the large variability of the whole data set. In order to complement the interpretation based on variability components, in the next section enrichment factors (EFs) are calculated to more clearly identify the principal element sources.

3.3. Trace element EFs

The calculation of trace metal EFs in airborne particles, relative to soil or crustal abundances, has been used to evaluate anthropic versus natural sources (Zoller et al., 1974; Duce et al., 1975; Rädlein and Heumann, 1992; Veron et al., 1992). In this study, within the elements which are commonly considered as reference for crustal material (e.g. Al, Sc, Ba, Fe), Fe was used to calculate the EF_{Fe}s of the trace metals (Me), according to:

$$EF = \frac{[Me/Fe]_{TSP}}{[Me/Fe]_{crust}},$$

where $[Me/Fe]_{TSP}$ and $[Me/Fe]_{crust}$ refer, respectively, to the TSP and mean crustal concentration ratios of the metal and Fe. The EFs were calculated on the basis of Earth's Crust mean abundances of the elements given

by Taylor (1964). Trace element EFs include some degree of uncertainty related to the natural variations of the earth crustal composition. For this reason it is usually assumed that the EFs should be more than an order of magnitude higher than unity to suggest an anthropic origin.

On the basis of the EFs calculated at the four stations, TSP collected at La Plata region appear as enriched in Pb, Zn, Cd and Cu, whereas Mn, Cr, Ni, Ca and Mg EFs are lower, compatible with prevailing natural sources.

Pb shows the highest EFs, ranging from 8 to 860 with the highest values at Downtown (average = 376) and lowest at Port and Residential stations (average = 180). For Zn, the EFs oscillate between 4 and 1700, with highest values at Petrochemical and Residential sites (300–366, respectively) and lowest at Downtown station (113). In the case of Cd, the EFs range from 10 to 456 with rather homogeneous station averages (90–116). Cu EFs are 5–429 with highest values at the Residential site (84), perhaps reflecting the use of Cu as biocide in the numerous swimming pools of the area, and lower homogeneous values in the other sites (22–28).

The high EFs calculated for Pb, Zn, Cd and Cu indicate that they are present in the airborne particles in concentrations too high to be explained in terms of normal crustal weathering processes. On a global basis, anthropogenic inputs of these elements predominate over natural sources accounting for 96, 66, 85 and 56% of the total emissions, respectively (Nriagu, 1989). Among these anthropogenic inputs, vehicle particle emissions are a relevant source. EFs calculated for particles from high-emitting vehicles (Cadle et al., 1997) are 560, 550, 480 and 24, for Pb, Zn, Cd and Cu, respectively. These values are similar to those calculated for our TSP samples supporting the interpretation of vehicle emissions as the most important source of these elements in La Plata region. The existence of two particle populations, a larger–low concentration diurnal one and a smaller–high mass concentration pool prevailing during the night, is also supported by the EFs which are higher in the night samplings (e.g. annual average night EFs increments expressed as percentage of day values = Pb 8–137%, Cu 8–178%, Zn 15–75%, Cd 15–38%).

Pb, Zn, Cd and Cu are considered relatively volatile metals (Zoller et al., 1974; Duce et al., 1975) and, because they are mainly transported through the atmosphere, they have been termed atmophile elements (Lantzy and Mackenzie, 1979). In contrast, Mn, Cr and Ni have been termed litophile elements because their masses are principally transported by streams (Lantzy and Mackenzie, 1979). As expected, the calculated EFs for these elements are not significantly different from unity (station mean range = 1.3–3.1), indicating that their main source in airborne particles are soil-derived dusts. For these metals, natural emissions are very important and normally exceed anthropogenic

sources, especially in the case of Mn and Cr where they account for 89 and 59%, respectively (Nriagu, 1989). Related to these elements are Ca and Mg, which present comparable EFs (station mean range = 2.8–7.5) also suggesting a prevailing natural origin.

4. Conclusions

Airborne particulate trace metals have been determined bimonthly during day and night hours in four permanent stations located in residential, industrial and commercial sectors of La Plata City region. Concentrations of airborne metals in La Plata area were relatively low, similar to the values reported for not heavily polluted cities, probably reflecting the major administrative and trade-oriented character of the city.

The data set show an important degree of variability including diurnal (day vs. night), spatial (inter-station) and temporal (inter-month) components which were evaluated by two- and three-way ANOVA and variance components tests ($P < 0.05$). In general, trace metal concentrations follow the behavior of TSP with higher concentrations during the day, particularly at Downtown site. Spatial differences were also evident with higher levels at Downtown station and lower at the Residential site. Overall, spatial differences were more important than diurnal variations; these differences were clearly most significant for Pb, which presents higher values at the Downtown site reflecting the importance of motor exhaust inputs. In contrast, diurnal differences are more important for Mn indicating increased dust resuspension during day hours. A seasonal trend of increasing concentrations during April–May–August and decreasing values in September–December was also detected.

EFs relative to earth crust abundances were calculated to evaluate anthropic versus natural sources. EFs were highest for Pb, Zn, Cd and Cu, indicating that anthropic inputs prevail over normal crustal weathering processes. These TSP EFs were similar to those calculated for vehicle particle emissions suggesting that motor exhausts are the most important source of these elements in La Plata region. EFs calculated for Mn, Cr, Ni, Ca and Mg are 20–60 times lower indicating that their main source in airborne particles are soil-derived dusts.

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