

Chemical Speciation of Trace Metals in Airborne Particles at An Industrialized Site

Gi-Ho Jeong, Ji-Young Lee, Ji-Yong Moon and Sung-In Lee

Department of Chemistry, Pusan National University, Busan 609-735, Korea

(Manuscript received 19 January, 2005; accepted 16 May, 2006)

Airborne particles collected from a heavily industrialized site were analyzed by chemical speciation of seven trace metals: Pb, Cd, Cr, Cu, Ni, Zn, and As. The average concentrations were as follows: Zn, 502.0 ± 230.7 ; Pb, 176.5 ± 310.9 ; Cu, 111.9 ± 82.7 ; As, 38.0 ± 31.0 ; Cr, 21.5 ± 24.4 ; Cd, 20.8 ± 17.4 ; and Ni, 11.4 ± 8.4 ng/m³. The median enrichment factor (EF) values of Cd (7,280), As (1,030), Cu (215), Zn (214), and Pb (143), with respect to iron, were much larger than 100. We observed that Cd was found in the soluble and exchangeable form (56.9%), and that Pb and Cr were found in carbonates, oxides and the reducible form (69.8% and 61.1%, respectively). These two forms, which are the most easily absorbed into human body tissue, predominated in most of the trace metals investigated in this study.

Key Words : Metal speciation, Airborne particles, Trace metals, PM10, Enrichment factors

1. Introduction

A recent study on the health effects of airborne particles showed that short-term increases in fine particles led to an acute decrease of lung function in healthy children and to an increase in pulmonary symptoms in a risk group¹⁾. Urban populations can be exposed to various trace metals in airborne particles discharged from anthropogenic processes^{2,3)}.

Particulate matters (PM) are discrete particles that exist in atmosphere in either the solid or the liquid phase. PM₁₀ refers to particulate matter of 10 μ m or less diameter, and it can be absorbed into the alveolar region of the human lung⁴⁾. The amount of metals in airborne particles are commonly described as total metal concentrations. It is, however, well known that metals have different solubility, bioavailability, and geochemical transport according to their chemical speciation⁵⁾. Speciation is also useful in differentiating metals with an anthropogenic origin from those with a lithogenic origin⁶⁾. Thus, chemical speciation of metals is quite necessary in order to de-

termine the nature and extent of the metal activity in the environment. Tessier's scheme⁷⁾, which employed five steps of sequential extraction, is considered to be the most general. In the present study, Obiols' scheme⁸⁾, which simplified Tessier's scheme, was applied to the sequential extraction of metals from airborne particles. Obiols' modification involves determining the carbonates and oxides fractions in a single step (Table 1).

The objectives of this study were to determine the metal contamination levels, and to achieve a knowledge of metal speciation in PM₁₀, at a certain location in Ulsan Metro City nearby a petrochemical complex.

2. Experimental

2.1. Description of sampling site

Ulsan is the seventh largest city in Korea, and is located on the south-eastern coast, as illustrated in Fig. 1. It covers an area of 1,056 km² and had a population of some 1.1 million inhabitants at the end of 2003. Large-scale industrial zones are located in the coastal area of the city. The urban area of Ulsan accounts for 28.5% of the total area, while its population is about 900,000, which accounts for 84% of

Corresponding Author : Gi-Ho Jeong, Department of Chemistry, Pusan National University, Busan 609-735, Korea
Phone: +82-51-510-2246
E-mail: ghjeong@pusan.ac.kr

Table 1. Sequential extraction scheme for the chemical speciation of suspended particles according to Obiols' scheme⁸⁾

Fraction (F1 ~ F4)	Experimental conditions
F1. Soluble and exchangeable metals (Easily interchangeable with water by sorption-desorption process)	12.5 ml of 1% NaOH; Shaker agitation for 60 min. at room temperature
F2. Carbonates, oxides and reducible metals (Susceptible to be released under reducing conditions)	12.5 ml of 0.04M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 25% AcOH; Shaker agitation for 60 min. at 95°C
F3. Bound to organic matter, oxidisable and sulphidic metals (Easily soluble under oxidizing conditions)	12.5 ml of 0.02M HNO_3 + 5 ml 30% H_2O_2 , Shaker agitation for 90 min. at 85°C; +1.5 ml of 30% H_2O_2 , continuous agitation 60 min. at 85°C; +2.5 ml of 3.2M NH_4OAC in 20% HNO_3 , continuous agitation for 30 min. at room temperature
F4. Residual metals (Elementary form, residuals in the crystalline structure. Only extractable under hard acid conditions)	2.5 ml of conc. HNO_3 + 1 ml of conc. HCl ; Shaker agitation for 90 min. at 95°C

the total population. The main industrial activities in this area are automobile manufacturing, shipbuilding, oil refining, petrochemical, chemical, fertilizer and machine industries. This area is characterized by an annual temperature range of -16°C to 38°C with an average value of 14°C, and 1,440 mm of average rainfall, for the last five years. The prevailing wind directions are S/SW during summer and N/NW during other seasons according to data from the Meteorological Service of Ulsan Metropolitan City. The sampling station, Jangsaengpo in Ulsan, is located near a large-scale industrial complex, which consists of oil refining, fertilizer, chemical, and petrochemical plants. Thus, this station can represent a heavily industrialized urban area. The station was considered to be influenced mainly by industrial emissions and sea-salt scattering.

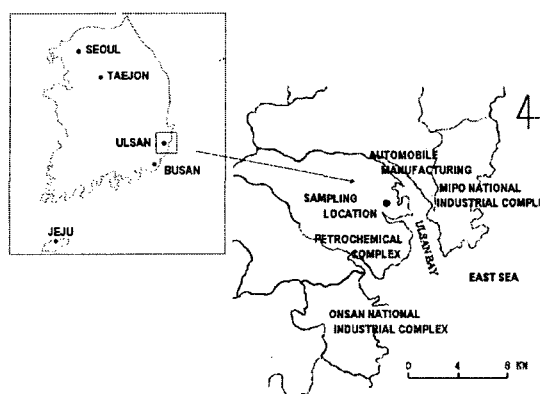


Fig. 1. Location of the sampling station in Ulsan. (129°23' E, 35°30' N)

2.2. Sampling

The samples of airborne particulate matter (PM_{10}) were collected every three weeks from 27th March to 17th October, 2001, using a high-volume air sampler (HVAS, Kimoto Electric Co.). Sampling was performed ten times, and the meteorological data corresponding to the sampling sequence are presented in Table 2. The sampler was placed on the roof of a local building at a height of about 10 m, and was operated continuously for 24 hours. The particle cut-off size was 10 μm , and airborne particles of this size or less were collected on borosilicate glass microfiber filters (Whatman, EPM 2000, 20.3 × 25.4 cm^2) at a flow rate of 1.3 m^3/min . The filters were kept in an auto-desiccator (SK-CO15A, Samgwang Co.), which maintained a temperature of $20 \pm 2^\circ\text{C}$ and a relative humidity of $50 \pm 10\%$, until it reached a constant weight. The masses of collected PM_{10} were measured gravimetrically using an analytical balance (A200S, Sartorius) after getting constant weight by keeping filters in an auto-desiccator. The concentration of PM_{10} was determined by dividing the mass by the air volume.

2.3. Reagents and apparatus

The reagents employed were sulfuric acid (96%, Suprapur, Merck), hydrochloric acid (30%, Suprapur, Merck), acetic acid (100%, Suprapur, Merck), nitric acid (electronic grade, Matsunoen), hydrogen peroxide (30%, Medical Extrapure, Merck), sodium chloride (Suprapur, Merck), and hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$, 97%, Acros). Deionized

Chemical Speciation of Trace Metals in Airborne Particles at An Industrialized Site

Table 2. Meteorological data corresponding to the sampling sequence in Ulsan

Sampling sequence, Date	PM ₁₀ ($\mu\text{g}/\text{m}^3$) [*]	Average Temp. ($^{\circ}\text{C}$)	Relative Humidity (%)	Precipitation (mm)	Prevailing wind direction	Wind speed (m/s)
1st. 27 Mar.	43	7.4	28	0	NE	2.2
2nd. 17 Apr.	200	16.6	47	0	NW	1.6
3rd. 09 May	37	19.4	58	0	N	1.9
4th. 29 May	71	22.6	46	0	WSW	1.3
5th. 21 June	30	19.6	77	0	ENE	1.5
6th. 10 July	43	26.5	57	0	WSW	1.7
7th. 31 July	33	29.6	68	1.3	WSW	2.0
8th. 22 Aug.	37	27.0	69	0	N	1.7
9th. 27 Sep.	39	20.9	66	0	N	1.8
10th. 17 Oct.	18	17.6	56	0	ENE	2.2

* The level of PM₁₀ at a control site was 13 $\mu\text{g}/\text{m}^3$

water was manufactured by further treatment with a Mill-Q system (Millipore).

The four chemical fractions for the seven metals (Pb, Cd, Cr, Cu, Ni, Zn, As) were determined by an inductively coupled plasma mass spectrometer (ICP-MS, Hewlett-Packard 4500). The operational conditions of ICP-MS were as follows: the coolant gas, plasma (auxiliary) gas and carrier (nebulizer) gas was argon, the flow rate of the coolant gas was 15 L/min, of the plasma gas 1.0 L/min, of the carrier gas 1.09 L/min, the sample intake peristaltic pump speed was 0.1 rps, and the integration times were optimized.

2.4. Extraction and analysis

As the first step of sequential extraction, the experimental conditions for the soluble and exchangeable metals (F1) were applied to a part of the collection filter, and then the experimental conditions for the second fraction (F2) were applied to the residue of the filter treated with the first fraction (F1), continuing in this way until the fourth fraction (F4). The sample collection filter was cut to suitable sizes and each portion was weighed. Chemical speciation was performed in polypropylene centrifugal tubes by adding a portion of the collection filter and reagents specified in Table 1. Centrifugation was carried out at 5,000 rpm for 20 min. After the extraction and centrifugation were completed, the tube was left to decant by pouring the liquid into another analysis sampling tube, this liquid was then measured by ICP-MS. The extracted samples were then transferred to a 25-mL polyethylene bottle and diluted to the mark with 5%(v/v) HNO₃, followed by a 1 : 5 dilu-

tion for ICP-MS analysis. A set of unexposed filters was analyzed by applying the same procedure used for the actual samples. The mean unexposed filter value was subtracted from each sample to obtain the best estimate of each element in airborne particle.

The instrument detection limit (IDL) was determined by analyzing five blank samples. The standard deviation (stdv) of the measured value for each element was obtained, and then the detection limit was calculated with the equation⁹⁾

$$\text{IDL} = 3 \text{ stdv.}$$

The IDLs were 0.005 ng/m³ for Pb, 0.006 ng/m³ for Cd, 0.03 ng/m³ for Cr, 0.003 ng/m³ for Cu, 0.004 ng/m³ for Ni, 0.017 ng/m³ for Zn, and 0.025 ng/m³ for As. The values of relative standard deviations for all metals were ranged from 1% to 3%.

The reference solution of each element was spiked to a blank collection filter, and then the recovery rates were obtained from triplicate determinations. The results were as follows: Pb, 91.5 ± 0.7%; Cd, 105 ± 3%; Cr, 79.1 ± 1.2%; Cu, 109 ± 2%; Ni, 84.2 ± 2.1%; Zn, 88.3 ± 3.3, and As, 105 ± 2%. A five-point calibration curve was used to quantify each metal element. The standard for the calibration curves was the AccuTrace™ Reference Standard, which contains 10 g/mL of each metal element in 5%-HNO₃ solution.

3. Results and Discussion

3.1. Total concentrations of trace metals

The experimental results are presented in Table 3. The observed concentrations varied widely according

Table 3. Concentrations (ng/m³) of four metallic fractions corresponding to the 7 metals in airborne particles (- : below detection limit)

	JSP	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	Average	Stdv
Pb	F1	-	12	22	41	12	15	4.7	-	-	7.2	11.4	12.7
	F2	7.0	36	16	23	11	260	860	10	5.9	2.5	123.1	270.4
	F3	6.2	9.3	3.2	12	29	230	49	-	0.9	1.6	34.1	70.5
	F4	1.2	-	5.5	5.4	3.6	51	12	-	-	-	7.9	15.6
	Sum	14.4	57.3	46.7	81.4	55.6	556	925.7	10	6.8	11.3	176.5	310.9
Cd	F1	8.7	28	1.6	7.3	24	9.5	11	28	-	-	11.8	11.0
	F2	0.8	5.7	2.5	4.5	9.3	12	12	13	-	-	6.0	5.2
	F3	-	1.6	-	0.4	1.5	16	4.4	1.7	-	-	2.6	4.9
	F4	-	-	-	-	0.2	4.0	-	-	-	-	0.4	1.3
	Sum	9.5	35.3	4.1	12.2	35.0	41.5	27.4	42.7	-	-	20.8	17.4
Cr	F1	-	2.2	-	4.0	3.0	-	-	-	-	-	0.9	1.5
	F2	-	14	2.3	9.9	11	12	75	7.0	-	0.2	13.1	22.4
	F3	-	-	-	4.0	5.5	4.7	1.9	12	-	-	2.8	3.9
	F4	-	-	3.0	5.5	5.7	17	4.3	9.2	1.6	-	4.6	5.3
	Sum	-	16.2	5.3	23.4	25.2	33.7	81.2	28.2	1.6	0.2	21.5	24.4
Cu	F1	2.8	25	20	54	17	60	23	15	190	7.2	41.4	55.4
	F2	18	32	16	29	17	150	87	32	24	20	42.5	43.1
	F3	17	9.0	8.8	8.2	11	48	49	12	13	9.7	18.6	16.0
	F4	5.7	5.1	36	5.9	9.5	15	4.0	7.2	5.5	0.9	9.5	10.0
	Sum	43.5	71.1	80.8	97.1	54.5	273	163	66.2	232.5	37.8	111.9	82.7
Ni	F1	-	14	5.1	3.9	3.1	6.5	1.3	3.2	-	9.4	4.6	4.4
	F2	-	8.4	4.1	4.5	2.3	1.9	8.7	3.9	-	3.1	3.7	3.0
	F3	-	-	-	-	1.3	0.1	4.5	2.3	-	-	0.8	1.5
	F4	-	-	17	0.2	2.2	0.9	0.8	0.9	-	-	2.2	5.2
	Sum	-	22.4	26.2	8.6	8.9	9.4	15.3	10.3	-	12.5	11.4	8.4
Zn	F1	70	250	49	140	87	81	5.0	110	0.0	39	83.1	73.1
	F2	110	140	41	97	78	280	120	120	39	600	162.5	167.8
	F3	210	110	280	17	43	220	320	150	-	45	139.5	114.2
	F4	57	-	410	17	23	59	390	68	140	4.6	116.9	254.7
	Sum	447	500	780	271	231	640	835	448	179	688.6	502.0	230.7
As	F1	1.0	15	3.8	15	5.0	16	38	5.5	2.6	4.1	10.6	11.2
	F2	1.5	19	5.0	18	6.8	25	25	5.3	2.5	4.8	11.3	9.4
	F3	13	1.3	2.2	7.2	5.0	24	20	12	2.2	3.1	9.0	8.0
	F4	0.9	-	4.0	6.8	5.7	27	10	12	2.3	2.6	7.1	8.0
	Sum	16.4	35.3	15.0	47.0	22.5	92	93	34.8	9.6	14.6	38.0	31.0
Fe	Sum	228	1,402	416	565	594	2,010	2,173	2,120	200	162	987.0	846.1

F1. Soluble and exchangeable metals; F2. carbonates, oxides and reducible metals; F3. bound to organic matter, oxidisable and sulphidic metals; F4. residual metals.

to the collection time of airborne particles. The average concentrations and the median values (in parentheses) were as follows: Zn, 502.0 ± 230.7 (474); Pb, 176.5 ± 310.9 (51.2); Cu, 111.9 ± 82.7 (73.5); As, 38.0 ± 31.0 (28.6); Cr, 21.5 ± 24.4 (19.9); Cd, 20.8 ± 17.4 (19.8); and Ni, 11.4 ± 8.4 (9.2) ng/m³. Only Pb showed an extraordinarily large difference between the average and median values, and

showed very large values of standard deviation. This is because the measured concentrations of Pb at the 6th and 7th sampling times were strikingly higher than usual, and these trends were also observed for the other trace metal elements except Ni. These sampling times were July 2001, and the prevailing wind direction was WSW (Table 2). A large petrochemical complex is located to the WSW of the sampling lo-

Chemical Speciation of Trace Metals in Airborne Particles at An Industrialized Site

cation, as shown in Fig. 1. Thus, it is believed that the influence of substances discharged from the petrochemical complex on the concentrations of trace metals was the main reason for the extraordinarily high concentrations of Pb during this time.

The concentrations of Pb showed the widest distributions from 6.8 to 925.7 ng/m³. Zinc showed the highest average concentration but relatively even distributions, and its total concentration ranged from 231 to 835 ng/m³. Based on the magnitude of the average concentrations, the trace metals can be grouped into two categories: (1) >10² ng/m³: Zn (502 ng/m³), Pb (176), and Cu (111); (2) <10² ng/m³: As (38.0), Cr (21.5), Cd (20.8), and Ni (11.4). The ranking of Category-2 for the highest, average, and median concentrations were fixed as follows (Table 5): As > Cr > or ~ Cd > Ni. These values showed relatively even distributions compared to those of Category-1. For the Category-1, although the highest concentrations of Pb and Zn were substantially higher than those of Cu, the average and median concentrations of Pb and Cu were comparable to each other, and Zn showed extraordinarily higher values than Pb and Cu.

In Table 4, the airborne trace metal concentrations

measured in two other cities in Korea were compared with those in Ulsan. Data from Ulsan were obtained from PM₁₀, those from Taejon were averaged from TSP for 1 year and PM₁₀ for 2 years and those from Seoul were from TSP. Only a general trend of concentrations can be compared among these cities since the source of data was different each other, even though the majority of heavy metals were known to be adsorbed on PM₁₀.¹⁰⁾ The average concentration of Zn was two-fold higher, and As was about six times higher in Ulsan than in Taejon. But the average concentration of Cd was about seven times higher in Ulsan than in Taejon and Seoul. The average concentrations of Pb and Ni were the highest in Taejon, and that of Cu was the highest in Seoul. The city of Ulsan has been generally recognized by the public to be the most polluted city in Korea. These observations, however, revealed that concentrations of some trace metals were significantly lower in Ulsan even though the observation site was located in the vicinity of a large petrochemical complex.

Comparing with La Plata City in Argentina¹¹⁾, even though data from this city were TSP based values, average concentrations of six airborne metals

Table 4. Comparison of the airborne trace metal concentrations measured from other cities in Korea [average±stdv, (median), range (unit: ng/m³)]

Metals	Ulsan/PM ₁₀ (This study)	Taejon/TSP, PM ₁₀ (Ref. No. 17) ^a	Seoul(I) [*] /TSP (Ref. No. 2)	Seoul(G) [*] /TSP (Ref. No. 2)
Pb	176.5±310.9 (51.2) 6.8-925.7	243±135 (227) 41.7-593	87.7±65.1 (73.9) 7.0-246	74.1±53.9 (64.0) <DL [*] -237
Cd	20.8±17.4 (19.8) <DL-42.7	3.24±2.46 (2.34) 0.26-8.55	3.04±3.17 (2.23) <DL-15.7	3.24±2.55 (3.20) <DL-11.1
Cr	21.5±24.4 <DL-81.2	25.1±22.1 (17.3) 2.25-103	16.1±11.1 (14.2) <DL-47.2	13.5±10.1 (12.4) <DL-38.7
Cu	111.9±82.7 (73.5) 37.8-232.5	41.1±22.0 (36.5) 9.01-103	308±388 (151) <DL-1,835	157±124 (136) <DL-731
Ni	11.4±8.4 (9.2) <DL-26.2	37.9±21.6 (33.0) 4.69-97.8	21.5±22.4 (14.9) <DL-121	13.6±15.5 (8.21) <DL-72.5
Zn	502±231 (474) 179-835	240±133 (217) 26.1-551	(No data)	(No data)
As	38.0±31.0 (28.6) 9.6-93	6.06±4.58 (4.88) 0.33-20.5	(No data)	(No data)

* I: Industrial site, Guro; G: Grassland site, Bangi; DL: Detection limit
a: TSP data for 1 year and PM₁₀ data for 2 years

(Pb: 64.5 ± 61.8 ng/m³, Cd: 0.41 ± 0.42 ng/m³, Cr: 4.32 ± 2.39 ng/m³, Cu: 29.5 ± 27.3 ng/m³, Ni: 3.15 ± 3.52 ng/m³, Zn: 273 ± 227 ng/m³) were much higher in Ulsan. Thessaloniki in Greece has been encountered serious air-quality problems³), but concentrations of Pb, Cd, Cr, and As were substantially higher in Ulsan, and those of Zn were comparable but those of Cu and Ni were lower in Ulsan.

3.2. The enrichment factors

Enrichment factors (EFs) of trace metals in airborne particles, relative to the earth's crustal abundances, have been used to evaluate anthropogenic versus natural sources^{3,11-14}). Some elements such as Al, Fe, and Mn are commonly considered as references for crustal material. In this study, Fe was used as a reference to calculate the EFs of the trace metals (M), and the composition of the earth's crust was taken from Taylor and McLennan¹⁵).

$$EF = [M/Fe]_{\text{airborne}}/[M/Fe]_{\text{crust}}$$

The results of the EF values are presented in Table 5. The EF values varied widely for the same metal element according to the sampling time. Pb, Cd, Cu, and Zn are mainly transported through the atmosphere, whereas Cr and Ni are principally transported by streams¹⁶). As expected, the calculated EF values for Cr and Ni were much lower than those for the other trace metals. For this reason it is usually assumed that, to suggest an anthropogenic origin, the EFs should be more than an order of magnitude higher than unity¹¹) due to the natural variations of the crustal composition at different locations.

The basis of enrichment is also assumed to be the EF value of 100¹⁷). Then the relatively lower EF values

of Cr and Ni are compatible with prevailing natural sources. Cd showed the largest EFs, which ranged from 10.7 to 21,000 with a median value of 7,280. The median EF values of Cd (7,280), As (1,030), Cu (215), Zn (214), and Pb (143) were much larger than 100; therefore concentrations of these trace metals were substantially higher than the values expected from the normal crustal weathering process.

Comparing these with the results in Taejeon, Korea¹⁷), the relative magnitudes of concentrations and EF values are consistent; that is, the metals that have higher concentrations showed larger EF values excluding Ni. Compared with the range of EFs in the La Plata City area, Argentina¹¹), based on TSP values, Cd, Cu, and Zn showed larger minimum and maximum values in Ulsan, whereas those of Pb were similar. The EF values calculated from the metal concentrations of airborne PM₁₀ particles in Thessaloniki, Greece³), also showed higher values (average > 100) for Pb, Zn, Cd, Cu, and As. The extraordinarily high EFs of Cd and As characterized the concentrations of airborne trace metals in Ulsan, compared to the concentrations in Taejeon, La Plata City, and Thessaloniki.

3.3. The speciation results

The chemical speciation results of the trace metals in airborne particles for ten consecutive measurements at Jangsaengpo, Ulsan, are presented in Table 3. The speciation results and relative contributions of each fraction are illustrated in Fig. 2 and Fig. 3, respectively. The results of chemical speciation revealed predominant fractions of each trace metal. The first group, which has high percentages in the soluble and exchangeable fraction, consists of Cd (56.9%), Cu (37.0%), and Ni (40.9%). This fraction is known to be most easily absorbed into the human body through breathing¹⁸). Chemical forms which are almost totally insoluble pass through the human body without doing much harm²⁰). We determined that all seven trace metals had high percentages in carbonates, oxides and the reducible fraction, as follows: Pb (69.8%), Cd (28.8%), Cr (61.1%), Cu (38.0%), Ni (32.5%), Zn (32.4%), and As (29.7%). This second group is also absorbed through the lung, and the first two fractions are the most bioavailable. Excluding Zn and As, which showed relatively even distributions in four metallic fractions, the remaining

Table 5. The enrichment factor (EF) values obtained from the airborne trace metal concentrations in Ulsan

	Average	Stdv	Median	Min	Max
Pb	221	227	143	8.25	746
Cd	7,520	6,470	7,280	10.7*	21,000
Cr	18.5	16.0	13.0	0.13*	42.4
Cu	327	466	215	43.7	1,630
Ni	35.5	47.4	19.3	0.03*	135
Zn	548	629	214	104	2,100
As	1,160	569	1,030	383	2,100

*: Detection limit was used when the measured concentration was below detection limit

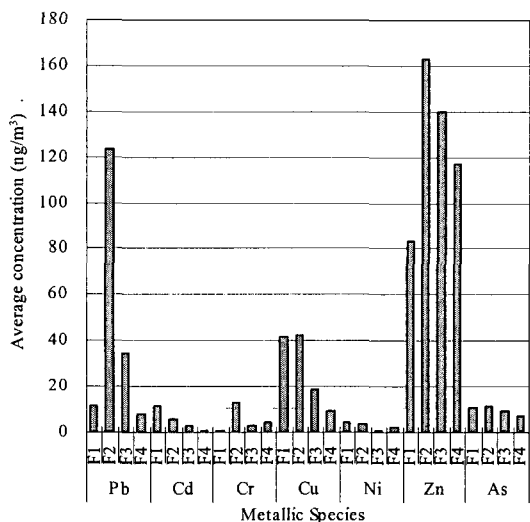


Fig. 2. Speciation of trace metals in the airborne particles (PM₁₀) during ten consecutive measurements. (F1: Soluble and exchangeable metals, F2: carbonates, oxides and reducible metals, F3: bound to organic matter, oxidisable and sulphidic metals, F4: residual metals)

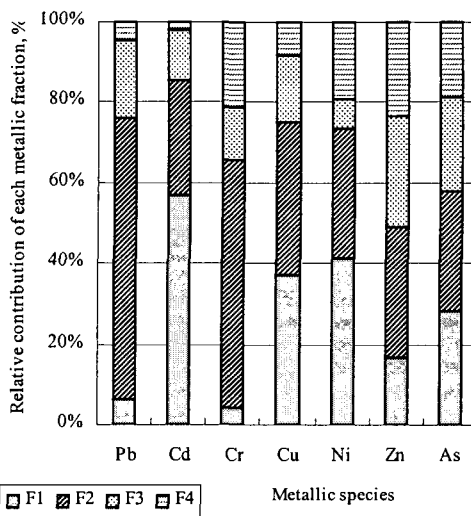


Fig. 3. Relative contribution of metallic fractions in airborne particles (PM₁₀) during ten consecutive measurements. (F1. Soluble and exchangeable metals; F2. carbonates, oxides and reducible metals; F3. bound to organic matter, oxidisable and sulphidic metals; F4. residual metals)

five metals had much higher percentages in the first two fractions. Since it is believed that elements from anthropogenic sources exist mainly as easily water-soluble forms^{18,19}, these fractions could be attributed to the industrial activities of the nearby petrochemical complex.

The third fraction, metals bound to organic matter, the oxidisable and sulphidic fraction, accounted for relatively lower percentages than the first and second fractions. Only Zn (27.8%) and As (23.7%) had significant percentages. In the residual fraction, Cr (21.5%), Ni (19.4%), Zn (23.3%), and As (18.8%) had significant percentages.

Pb, Cd, and As together with mercury are considered to be the greatest environmental hazards due to their extensive use, their toxicity, and their widespread distribution²⁰. Among these three toxic metals investigated in this study, Pb was shown to be the most hazardous due to its high concentrations, followed by Cd and As due to their high percentages in the bioavailable fractions. But the average value of the sum of the four fractions of Pb over ten consecutive measurements was far lower than the World Health Organization²¹ guidelines, 500 ng/m³. Attention, however, should be devoted to the level of Pb because

its concentration exceeded the WHO guidelines twice. The largest variation of Pb concentrations revealed that the Pb emission levels were highly dependent on the various environmental parameters. Even though the numerical value of the Cd concentrations was low, it was four times higher than the WHO guidelines²¹) (5 ng/m³), and the Cd levels reached far beyond the WHO guidelines in seven of the ten measurements.

The statistical correlation coefficients between the chemical species of each metal were calculated, and the results that showed a correlation coefficient above 0.70 are listed in Table 6. It is notable that the third fraction of Pb, Cd, Cu, and As, and the residual fraction of Pb, Cd, Cr, and As were highly inter-correlated with each other. Correlations between the first fractions and between the second fractions of each metal were relatively poorer than those between the third fractions and between the fourth fractions. This implies that the metallic fractions mainly originated from natural sources show much closer correlations than those from anthropogenic sources.

4. Conclusions

The speciation of metals in airborne particles collected

Table 6. Main correlation coefficients among the parameters (>0.70)

Correlated parameters	Coefficients (r^2)
Pb(F2), Cr(F2)	0.96
Pb(F3), Cd(F3)	0.99
Pb(F3), Cu(F3)	0.77
Pb(F4), Cd(F4)	0.97
Pb(F4), Cr(F4)	0.83
Pb(F4), As(F4)	0.91
Cd(F3), Cu(F3)	0.80
Cd(F4), Cr(F4)	0.83
Cd(F4), As(F4)	0.88
Cr(F4), As(F4)	0.97
Cu(F2), As(F2)	0.77
Cu(F3), As(F3)	0.89
Cu(F4), Ni(F4)	0.95

from a highly industrialized site was performed. The concentrations and enrichment factors varied widely according to the collection time over ten consecutive measurements for seven months. The extraordinarily high EFs of Cd and As characterized the concentrations of airborne trace metals in Ulsan. The predominant fractions of each metal were the soluble and exchangeable fraction (F1) or carbonates, oxides and the reducible fraction (F2). Pb and Cd might be very hazardous due to high concentrations and high percentages respectively, in F1. The common characteristics of chemical speciation in this study were high proportions of the first two fractions, which are the most easily available to the human body through the lung.

Acknowledgements

Ulsan Metropolitan City and Ulsan Regional Environmental Technology Development Center supported this project. We gratefully acknowledge financial support from them.

References

- 1) Moshhammer, H. and M. Neuberger, 2003, The active surface of suspended particles as a predictor of lung function and pulmonary symptoms in Austrian school children, *Atmospheric Environment*, 37, 1737-1744.
- 2) Kim, K. H., B. J. Choi, S. T. Yun and S. J. Hwang, 2004, Studies of spatial and temporal distribution characteristics of TSP-bound trace metals in Seoul, Korea, *Environmental Pollution*, 127, 323- 333.
- 3) Manoli, E., D. Voutsas and C. Samara, 2002, Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece, *Atmospheric Environment*, 36, 949-961.
- 4) Hileman, B., 1981, Particulate matter: the inhalable variety, *Environmental Science and Technology*, 15, 983-986.
- 5) Fernandez, A. J., M. Ternero, F. J. Barragn and J.C. Jimnez, 2000, An approach to characterization of sources of urban airborne particles through heavy metal speciation, *Chemosphere-Global Change Science*, 2, 123-136.
- 6) Izquierdo, C., J. Usero and I. Gracia, 1997, Speciation of heavy metals in sediments from salt marshes on the southern Atlantic coast of Spain, *Marine Pollution Bulletin*, 34, 123-128.
- 7) Tessier, A., P. G. C. Campbell and M. Bisson, 1979, Sequential extraction procedure for the speciation of particulate trace metals, *Analytical Chemistry*, 51, 844-851.
- 8) Obiols, J., R. Devesa and A. Sol, 1986, Speciation of heavy metals in suspended particulates in urban air, *Toxicological and Environmental Chemistry*, 13, 121-128.
- 9) Harrison, R. M. and S. J. Mora, 1996, *Introductory chemistry of the environmental sciences*, 2nd ed., Chap. 4, *Analytical Chemistry*, Cambridge University Press, Cambridge, pp.210-214.
- 10) Beceiro, G. E., J. M. A. Garda, E. S. Velasco and L. Mahia, 1997, Metals in airborne particulate matter in La Coruña (NW Spain), *The Science of Total Environment*, 196, 131-139.
- 11) Bilos, C., J. C. Colombo, C. N. Skorupka and M. J. R. Presa, 2001, Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina, *Environmental Pollution*, 111, 149-158.
- 12) Kim, K. H., G. H. Choi, C. H. Kang, J. H. Lee, J. Y. Kim, Y. H. Youn and S. R. Lee, 2003, The chemical composition of fine and coarse particles in relation with the Asian dust events, *Atmospheric Environment*, 37, 753-765.
- 13) Veron, A., T. M. Church, C. C. Patterson, Y. Erel and J. T. Merrill, 1992, Continental origin and industrial sources of trace metals in the

Chemical Speciation of Trace Metals in Airborne Particles at An Industrialized Site

- Northwest Atlantic troposphere, *Journal of Atmospheric Chemistry*, 14, 339-351.
- 14) Zoller, W. H., E. S. Gladney and R. A. Duce, 1974, Atmospheric concentrations and sources of trace metals at the South Pole, *Science*, 183, 198-200.
 - 15) Taylor, S. R. and S. M. McLennan, 1985, *The Continental Crust: Its composition and Evolution*, Blackwell Science, Cambridge, MA, U.S.A., p. 46.
 - 16) Lantzy, R. J. and F. T. Mackenzie, 1979, Atmospheric trace metals: global cycles and assessment of man's impact, *Geochimica et Cosmochimica Acta*, 43(10), 511-525.
 - 17) Kim, K. H., J. H. Lee and M. S. Jang, 2002, Metals in airborne particulate matter from the first and second industrial complex area of Taejon city, Korea, *Environmental Pollution*, 118, 41-51.
 - 18) Fernandez E. A. J., M. T. Rodriguez, F. J. B. Rosa and J. C. J. Snchez, 2002, A chemical speciation of trace metals for fine urban particles, *Atmospheric Environment*, 36, 773-780.
 - 19) Voutsas, D. and C. Samara, 2002, Labile and bio-accessible fractions of heavy metals in the airborne particulate matter from urban and industrial areas, *Atmospheric Environment*, 36, 3583-3590.
 - 20) Baird, C., 1995, *Environmental Chemistry*, W.H. Freeman and Company, New York, pp.347-349.
 - 21) WHO, 2000, *World Health Organization, Guidelines for Air Quality*, 2nd ed., Chapter 3, WHO Regional Office for Europe, Copenhagen, p. 2.