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Inorganic Chemical Characterization of Aerosols in Four Asian Mega-Cities

Tomoaki Okuda[1*], Hideshige Takada[2], Hidetoshi Kumata[3], Fumiyuki Nakajima[4], Shiro Hatakeyama[2], Masao Uchida[5], Shigeru Tanaka[1], Kebin He[6], Yongliang Ma[6]

[1] *Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan*
[2] *Tokyo University of Agriculture and Technology, 3-5-8 Saiwaicho, Fuchu, Tokyo 183-8509, Japan*
[3] *Tokyo University of Pharmacy and Life Sciences, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan*
[4] *The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[5] *National Institute for Environmental Studies, 16-2 Onogawa Tsukuba Ibaraki, 305-8506, Japan*
[6] *School of Environment, Tsinghua University, Beijing 100084, China*

ABSTRACT

This study is a systematic field observation campaign that examines the chemical characteristics of aerosols in four different mega-cities in Asia, namely Beijing (China), Hanoi (Vietnam), Kolkata (India), and Tokyo (Japan). The unity of the analytical method and the synchronicity of the sampling periods are quite important, especially when developing a comparative risk assessment in different places. Sampling was thus carried out in each city continuously for a one-year period between 2008 and 2010, as this enabled consideration of the seasonal variations that are associated with the Asian monsoon system that governs the climate of this region. The study found that the sum of the concentrations of measured elements decreased in the order of BJ > KK > HA > TY, while the sum of the concentrations of measured ions decreased in the order of BJ > HA > KK > TY. The concentration level of chemical species in aerosols in Beijing was one order of magnitude higher than that in Tokyo. The risks associated with carcinogenic metals in the four cities have also been calculated. We conclude that the calculated carcinogenic risks to humans by chromium were higher than the risks caused by nickel in all four cities.

Keywords: Beijing; Hanoi; Kolkata; Tokyo; Hazardous metals; EDXRF.

INTRODUCTION

Many mega-cities around the world are adversely affected by air pollutants such as aerosols and hazardous chemical species. From an air quality perspective, the adverse health effects caused by aerosols are the biggest driver of policies to improve air quality, due to the large amount of epidemiological health effect evidence (Monks *et al.*, 2009). Many Asian cities have undergone rapid development in recent years. It is necessary to investigate the trend towards higher concentrations of aerosols that is associated with the rapid development of these cities (Okuda *et al.*, 2008). Long-term observations are very useful for elucidating how the air quality has changed during the rapid development of the target city (Okuda *et al.*, 2008, 2011). Alternatively, comparative studies using the same method in some different cities are also important for improving our understanding of the chemical characteristics of air quality in different cities. Every mega-city has unique aerosols pollution sources that are determined by their geography and cultural practices (Parrish *et al.*, 2009). The Asian region is one of the most diverse areas in the world; therefore, it is important to understand the pollution characteristics that are associated with each city individually. Comparative studies of cities, such as this one, should be conducted during the same time period, while the cities being assessed are experiencing the same period of rapid development. Most previous studies have considered only a few cities or sites simultaneously.

The unity of the analytical method used and the synchronicity of the sampling periods are especially important when a comparative risk assessment is carried out in different places. Uncertainties that are caused by differences in methodology or sampling period should be avoided as much as possible. This study is a systematic field observation campaign for elucidating the chemical characteristics of aerosols in four different mega-cities in Asian region. Sampling was conducted in each city continuously for one year between 2008 and 2010. This one year time period allowed the study to consider seasonal variations that are

* Corresponding author. Tel./Fax: +81-(0)45-566-1578
E-mail address: okuda@applc.keio.ac.jp

associated with the Asian monsoon system that governs the climate in this region. The risks that are associated with airborne carcinogenic metals in the four cities have been calculated.

MATERIALS AND METHODS

Aerosol Collection in Four Asian Cities

Total suspended particles (TSP) were collected in four different cities in Asian region (Fig. 1). Beijing (BJ): The sampling site was Tsinghua University, located 15 km in a northwesterly direction from the center of Beijing city, China. This site can be considered a good representative of the entire area of Beijing city in terms of the concentrations of particulate matter (Okuda *et al.*, 2004). Sampling has been done for 1 year (n = 47), from October 2, 2008 to October 1, 2009. Hanoi (HA): The sampling site was a private house, located 4 km in a southwesterly direction from the center of Hanoi city, Vietnam. Sampling has been done for 1 year (n = 42), from September 28, 2009 to September 27, 2010. Kolkata (KK): The sampling site was a private house in a center of Kolkata city, India. Sampling has been done for 1 year (n = 48), from January 1 to December 29, 2010. Tokyo (TY): The sampling site was the University of Tokyo, located in a center of Tokyo metropolitan area, Japan. Sampling has been done for 1 year (n = 46), from January 5 to December 27, 2010. The sampling periods for HA, KK, and TY were almost the same, whereas that for BJ was earlier than the other sites. This was due to a mechanical trouble happened at BJ site. According to Beijing Municipal Environmental Protection Bureau (2010), the mean concentration of PM_{10} in 2010 was almost the same as that in 2009. Therefore we considered the sampling periods for our four sites in this study were almost simultaneous. Populations of these cities in 2005 were, BJ: 12.4, HA: 2.8, KK: 15.6, and TY: 36.7 (in million, United Nations, 2010). Quartz fiber filters (QFF, Pallflex 2500QAT-UP) were used for collecting aerosol samples. High volume air samplers (Kimoto Model-120 for BJ; SIBATA HV-1000F for HA, KK, and TY) were operated for 24 h at an air flow rate of 800 L/min. We cut a 47-mm i.d. part of the QFF filter, and then the samples were subjected to the following analytical procedure.

Sample Analysis

Filter samples were analyzed by an energy-dispersive X-ray fluorescence spectrometry (EDXRF) without any pretreatment using the EDXL300 spectrometer manufactured by Rigaku Corp., Japan. For emitting primary radiation, an X-ray tube (I_{max} = 2 mA, V_{max} = 50 kV) with a 50W Pd anode was used. EDXL300 has three-dimensional (Cartesian geometry) polarization optics and secondary targets that allow the researchers to optimize the excitation source for analytes of interest. In this study, we used three secondary

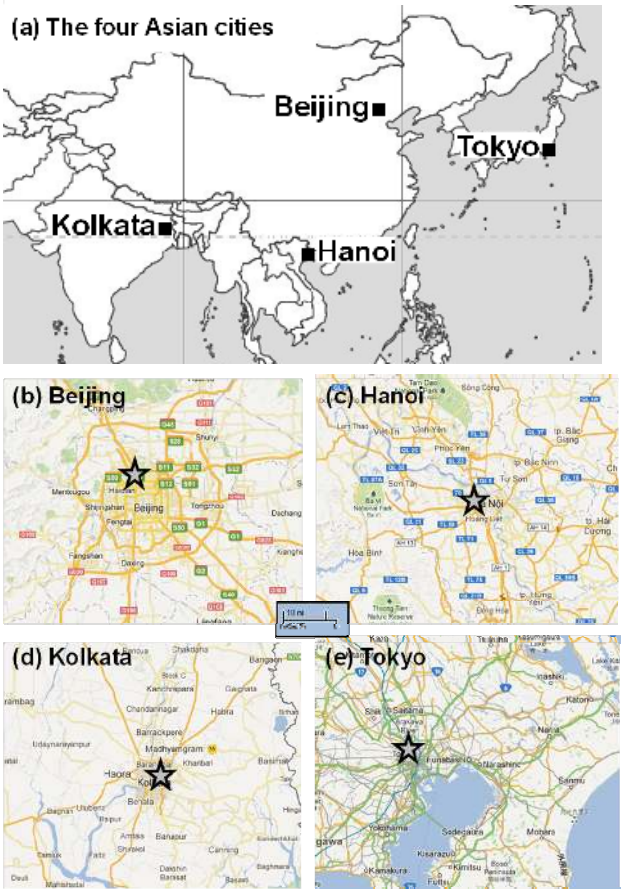

Fig. 1. The maps showing four Asian cities being investigated in this study.

targets. The secondary targets and duration time were, Mo: 400 s, Cu: 400 s, and RX9 (graphite crystal): 100 s. The quantification of each element in aerosol samples was performed using the fundamental parameter (FP) method called Rigaku Profile Fitting - Spectra Quant X (RPF-SQX). Thirteen elements (Al, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, and Pb) were measured in this study. Detection limits for each element were 1.7–28 ng/m^3, and repeatability (precision, as described as relative standard deviation (RSD)) was smaller than 5% in most elements except for V (28%) and Cr (12%). The analytical results obtained by EDXRF agreed well with those obtained by ICP-MS (EDXRF/ICP-MS ratios for each element were 1.1 ± 0.3). Instrument calibration was performed daily using a Herzog glass pellet with known elemental composition. In order to check of the instrument condition, NIST SRM2783 (Air Particulate on Filter Media) was analyzed daily. Detailed procedure for this multi-elemental analysis has been described elsewhere (Okuda *et al.*, submitted).

Water-soluble inorganic ions (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) in aerosol samples were extracted by mechanical shaking (15 min) with deionized water (10 mL, 18.3 MΩ cm), and analyzed by ion chromatography using ion exchange columns (Dionex CS-12A and AS-12A) (Okuda *et al.*, 2008).

Meteorological Data

Meteorological data for each sampling site were obtained from the National Climatic Data Center, National Environmental Satellite, Data, and Information Service, National Oceanic and Atmospheric Administration (NCDC, 2011). Since data for Hanoi was not available on the NCDC system, we used alternative data for Nanning, where the distance from Hanoi was about 300 km. In this study, we defined two periods, winter/dry season (from November 15 to March 15) and summer/rain season (from May 15 to September 15), for considering the seasonal variation of concentrations of measured species due to the following reasons; (1) in Beijing, Coal combustion for residential heating is permitted from November 15 to March 15, (2) the differences in average temperature between the two seasons for Beijing and Tokyo were as large as 25°C and 18°C, respectively, and (3) the total rainfall amounts in the summer/rain season were 12-, 5-, and 23-times higher than those in the winter/dry season for Beijing, Hanoi, and Kolkata, respectively.

RESULTS AND DISCUSSION

One-year Average Concentration of Each Component in Aerosols

Table 1 shows the concentrations of elements and water-soluble ionic species in aerosols in four Asian cities. The sum of the concentrations of measured elements were in the order of BJ > KK > HA > TY. The sum of the concentrations of measured ions were in the order of BJ > HA > KK > TY. The concentration level of chemical species in aerosol in Beijing was about one order of magnitude higher than that in Tokyo. This situation is similar to the pollution level of annual PM_{10} in these cities (BJ: 121 μg/m^3, HA: 89 μg/m^3, KK: 148 μg/m^3, and TY: 23 μg/m^3, Hien *et al.*, 2011; WHO, 2011). Although Tokyo is the most populated mega-city among target cities in this study, Tokyo has the best air quality in terms of the aerosol pollution.

Chemical characteristics of aerosols have been discussed using the enrichment factor, which was the ratio of chemical concentration of an element in aerosol to that in the average crustal rock with Fe as the reference element. Concentration levels of elements obtained in this study were also compared to several previous studies. In Beijing, all elements showed low EF (1.0–2.7) except for S, Cu, Zn, and Pb. This feature is similar to previous studies (Lu *et al.*, 2007, Schleicher *et al.*, 2011). EFs of all elements for Hanoi and Kolkata were less than 10 except for S, Zn, and Pb. Hopke *et al.* (2008) reported the elemental composition of PM_{10} in Hanoi that was similar to this study. As far as we know, this study is the first report that shows comprehensive chemical composition of aerosols in Kolkata. EF for Tokyo showed similar pattern comparing to the other three cities, but several elements showed slightly higher EFs. The EF pattern in Tokyo in this study was similar to a previous study (Furuta *et al.*, 2005). Overall, elemental compositions in aerosols as described using EF for these four cities were basically similar although the concentration level for each city was quite different.

Ionic balances that are defined as the ratio of total cations to anions in aerosols for each city were shown in Fig. 2. The ionic balances were cation-rich for Beijing, Hanoi, and Tokyo whereas it was almost neutral for Kolkata. Ca^{2+}, which was provided as soil particle that contains calcium carbonate, in Kolkata was lower than those in Beijing and Hanoi. In Tokyo, sulfate concentration was low as well as Ca^{2+}. These results suggested that the neutralization potential of aerosols against acidic chemical species in air in Kolkata was lower than the other three cities.

Correlations among the Chemical Species in Aerosols

The time trend of meteorological data and concentrations of selected chemical species were shown in Fig. 3. Correlation matrices for each component were also shown in Table 2. In Beijing, Al, K, Ti, V, Mn, and Fe showed higher correlation ($r > 0.79$) each other. These elements are considered having soil or crustal origin. On the other hand, Pb, NH_4^+, K^+, NO_3^-, and SO_4^{2-} showed higher correlation ($r > 0.75$) each other. Pb was also highly correlated with Zn ($r = 0.84$). These elements are considered having anthropogenic origin.

Hanoi aerosols had a similar feature of the correlation matrix when compared to Beijing. Al, K, Ti, and Fe showed higher correlation ($r > 0.81$) each other in Hanoi. Ca also showed higher correlation with these four elements ($r > 0.72$). Pb was highly correlated with Zn ($r = 0.79$). NH_4^+, K^+, and SO_4^{2-} showed higher correlation ($r > 0.75$) each other. The correlations were high between Ca^{2+} and NO_3^-, ($r = 0.87$), and between NH_4^+ and SO_4^{2-} ($r = 0.81$). This was different from Beijing case where NH_4^+ had high correlation with both NO_3^- and SO_4^{2-} but Ca^{2+} didn't. It seems that very high concentration of ammonia easily neutralized nitric acid in Beijing whereas alkaline particles that have calcium in

Table 1. The concentrations of elements and water-soluble ionic species in aerosols in four Asian cities.

Site	Beijing				Hanoi				Kolkata				Tokyo			
Period	2008/10–2009/10				2009/9–2010/9				2010/1–2010/12				2010/1–2010/12			
Sample#	47				42				48				46			
(in ng/m^3)	Mean	SD	n	EF[a] (vs. Fe)	Mean	SD	n	EF (vs. Fe)	Mean	SD	n	EF (vs. Fe)	Mean	SD	n	EF (vs. Fe)
Al	14426	6244	47	1.0	2332	705	42	0.5	10661	5701	48	1.1				
S	7640	5170	47	168	4746	2812	42	350	4099	2228	48	127	1872	1135	46	370
K	4641	2587	47	1.0	1678	667	42	1.2	2896	2040	48	0.9	211	106	46	0.4
Ca	17214	7004	47	2.7	11482	4367	42	6.1	8086	5126	48	1.8	1173	664	46	1.7
Ti	821	491	47	1.1	260	101	42	1.1	686	469	48	1.3	58	30	46	0.7
V	33	23	47	1.4	15	6	42	2.1	27	21	48	1.6	8.7	8.7	42	3.3
Cr	28	12	47	1.6	8.3	3.8	39	1.6	31	20	48	2.5	9.5	7	36	4.9
Mn	276	118	47	1.7	138	71	42	2.8	210	149	48	1.8	47	16	46	2.6
Fe	8724	5227	47	1.0	2611	991	42	1.0	6191	4468	48	1.0	973	563	46	1.0
Ni	27	11	47	2.0	12	5	38	3.1	18	10	42	1.9	9.5	2.9	15	6.5
Cu	1678	2162	47	175	22	9	40	7.7	55	41	47	8.0	19	10	41	18
Zn	683	428	47	56	683	581	42	187	659	873	48	76	97	54	46	71
Pb	291	174	47	128	134	75	42	197	548	663	48	341	28	7	44	112
Total Elements	56481	20175	47		24118	8133	42		33446	19157	47		4493	2177	46	
Na^+	1701	1396	37		1077	683	15		1097	716	35		918	525	39	
NH_4^+	12905	9755	43		3480	3207	42		3144	4062	48		2821	1839	46	
K^+	3055	2716	44		617	479	42		1064	825	32		410	182	5	
Mg^{2+}	877	533	44		207	80	37		289	173	47		315	129	32	
Ca^{2+}	12436	5723	44		7874	3531	42		3526	2710	47		1442	904	39	
Cl^-	4487	4208	44		1545	879	42		3339	2939	44		1272	687	46	
NO_3^-	26134	24071	44		4762	3746	42		6733	6799	40		4002	2625	42	
SO_4^{2-}	27998	24982	44		11406	8378	42		10419	7655	46		4383	2546	45	
Total Ions	89845	65205	44		31133	18369	42		26368	22879	47		14450	7174	46	

[a] Elemental composition of crust was cited from Mason and Moore, 1982.

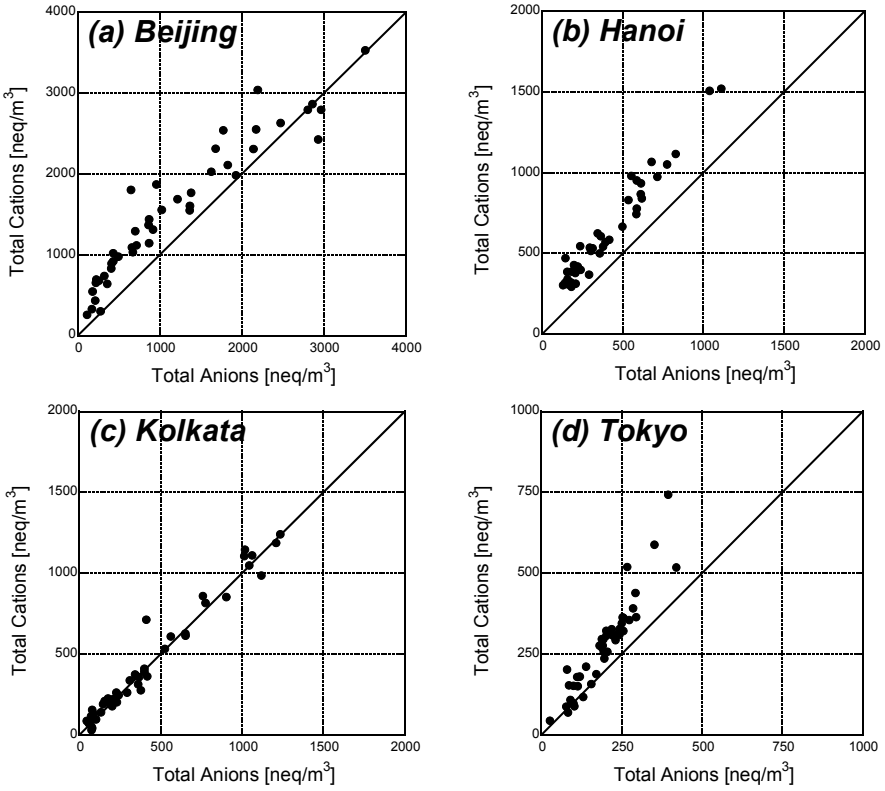

Fig. 2. The concentrations of total cations and anions in aerosols for each Asian city.

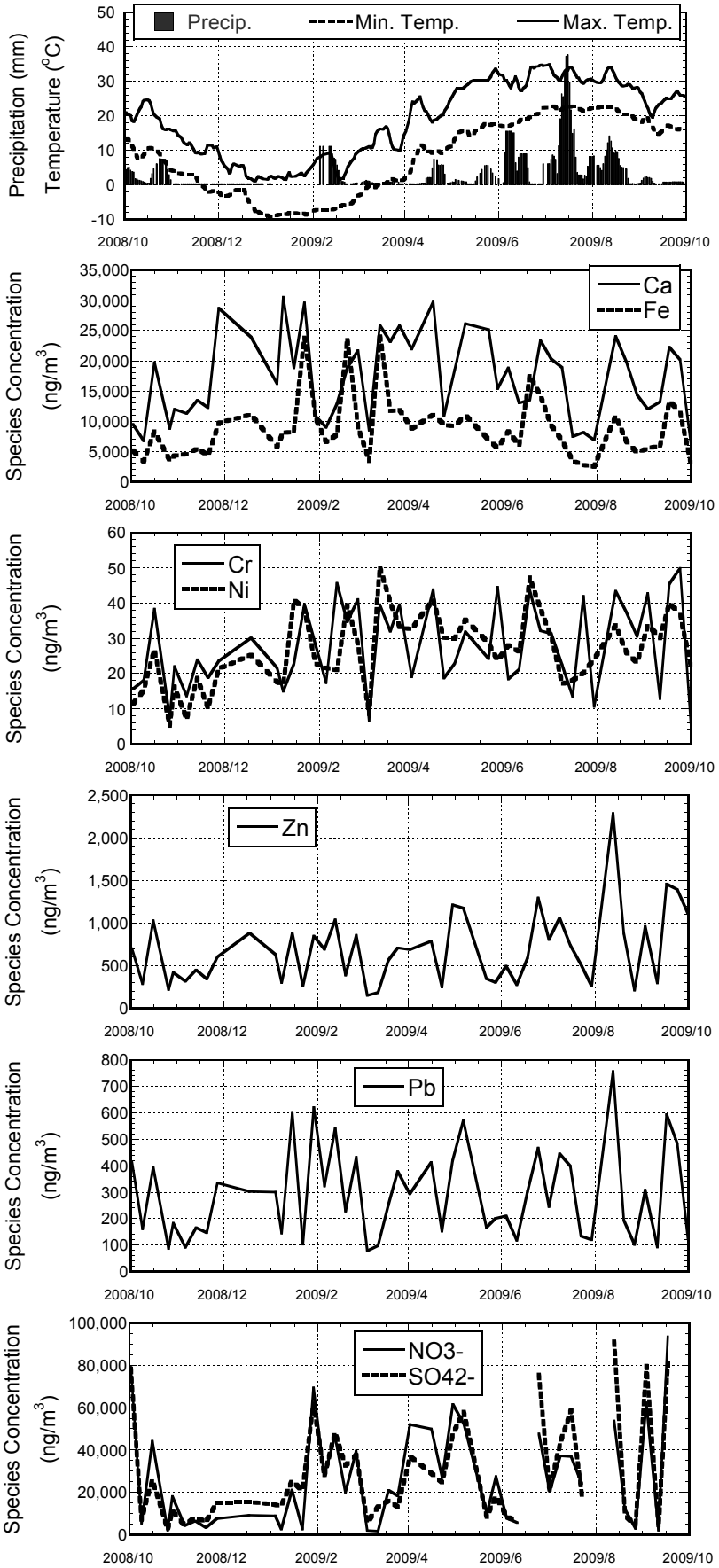

Fig. 3a. Time trend of meteorological data and concentrations of selected chemical species in Beijing.

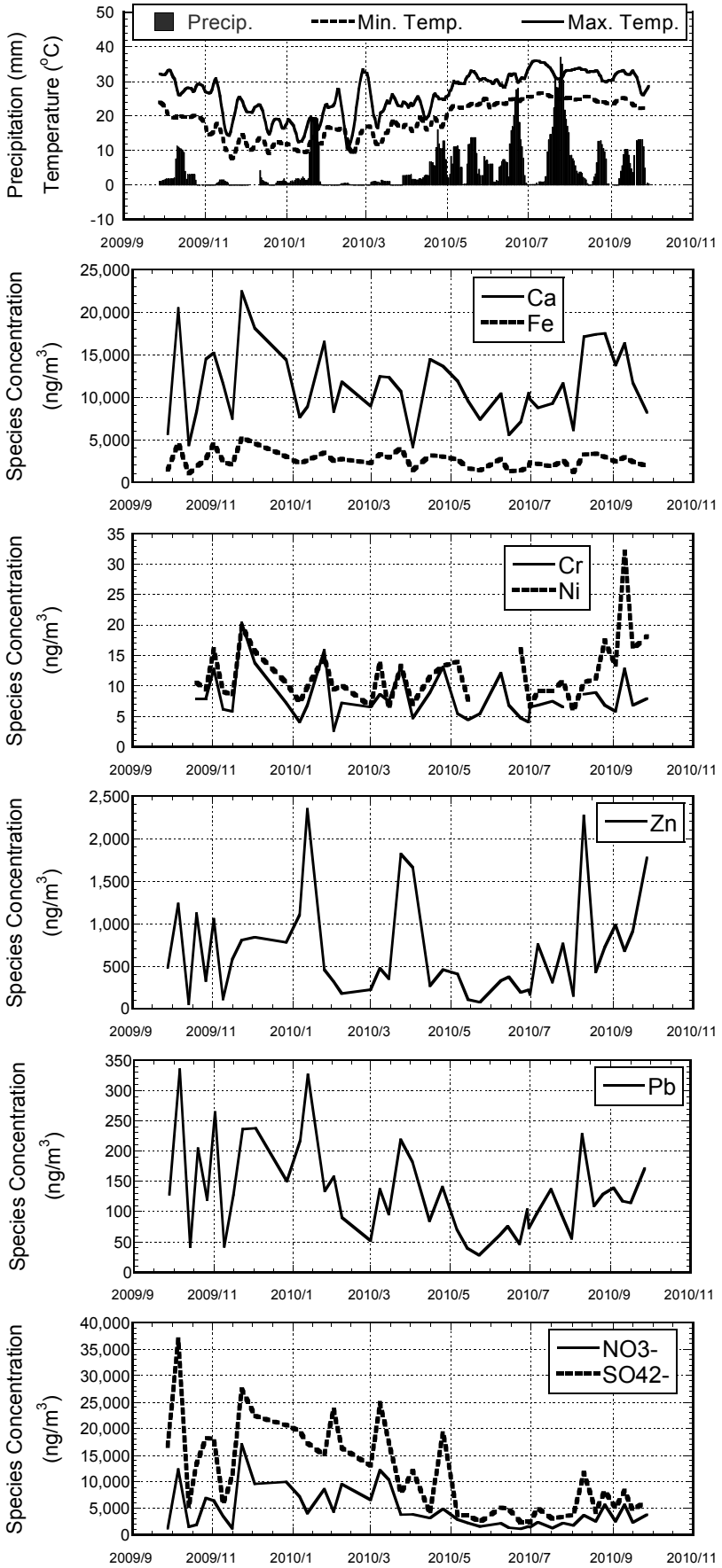

Fig. 3b. Time trend of meteorological data and concentrations of selected chemical species in Hanoi.

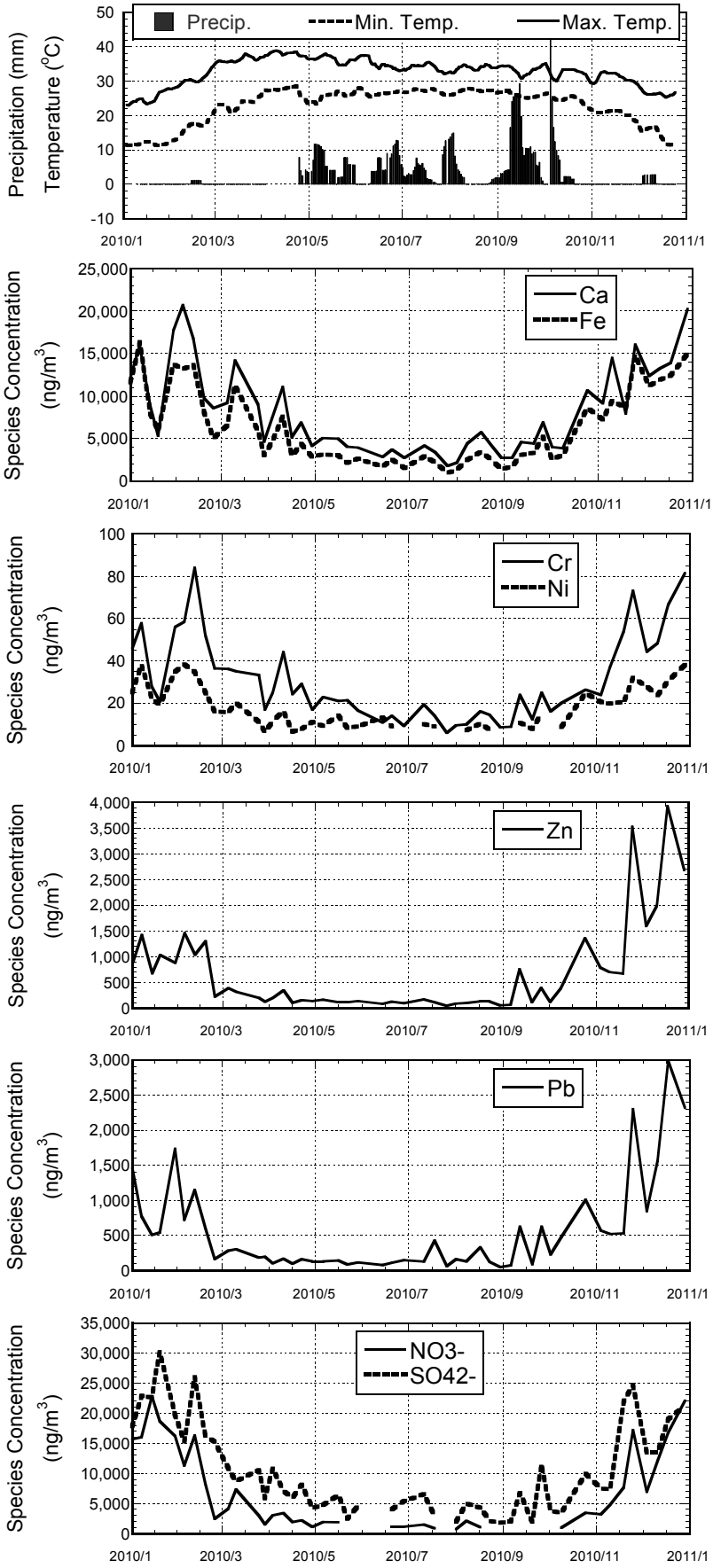

Fig. 3c. Time trend of meteorological data and concentrations of selected chemical species in Kolkata.

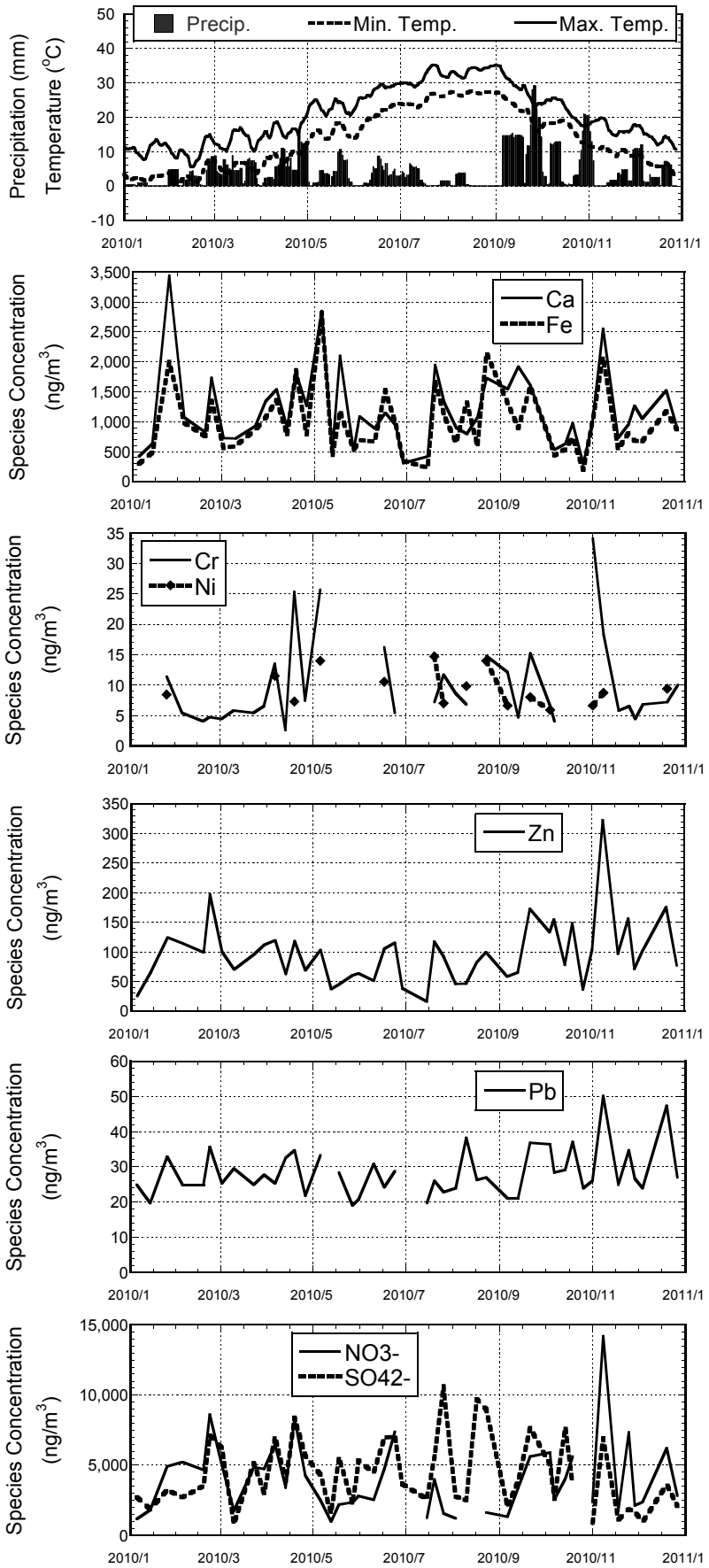

Fig. 3d. Time trend of meteorological data and concentrations of selected chemical species in Tokyo.

it played an important role in neutralizing nitric acid in Hanoi.

The correlation matrix for Kolkata was quite different from the other three cities. Almost all of the measured species showed higher correlation ($r > 0.5$) each other except for Na^+. Chemical species in Kolkata showed a clear seasonal trend (Fig. 3). Obviously, the concentrations were high in the dry season and low in the rain season.

K, Ca, Ti, Mn, and Fe showed higher correlation ($r > 0.74$) each other in Tokyo. The correlations were high among Cu, Zn and Pb ($0.69 < r < 0.78$). The correlation was high ($r = 0.77$) between V and Ni that are often used as tracers for oil combustion (Okuda *et al.*, 2007a, Wang *et al.*, 2006). It should be noted that the correlation was low ($r = 0.422$) between NO_3^- and SO_4^{2-}, and this was quite different from the other three cities. The concentration of NO_3^- was high in winter in Tokyo since it would be dependent on ambient temperature that controlled its gas/particle partitioning. On the contrary, the concentration of was high in summer in Tokyo since it would be dependent on the intensity of solar radiation that would helped converting SO_2 to SO_4^{2-}. In Hanoi and Kolkata, the gas/particle partitioning of NO_3^- would not be so important since the ambient temperature

Table 2a. Correlation matrix for chemical species in Beijing.

BJ	S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Al	–0.05	0.78	0.57	0.95	0.88	0.37	0.91	0.91	0.63	–0.19	–0.09	0.03	0.76	–0.02	0.07	0.22	0.39	0.28	–0.05	0.04
	S	0.37	–0.01	0	0.13	0.29	0.07	0.06	0.17	0.26	0.65	0.8	0.01	0.93	0.86	0.7	0.41	0.39	0.86	0.92
		K	0.44	0.8	0.88	0.54	0.81	0.84	0.66	–0.03	0.26	0.47	0.71	0.41	0.6	0.53	0.43	0.61	0.36	0.39
			Ca	0.62	0.44	0.47	0.7	0.62	0.56	–0.15	0.26	0.29	0.23	–0.04	0.01	0.36	0.72	0.18	0.06	0.1
				Ti	0.91	0.45	0.94	0.95	0.71	–0.1	0.01	0.15	0.77	0.01	0.08	0.28	0.43	0.33	0	0.1
					V	0.42	0.87	0.89	0.6	–0.02	0.05	0.21	0.74	0.13	0.23	0.3	0.3	0.38	0.11	0.2
						Cr	0.51	0.53	0.63	0.08	0.43	0.44	0.39	0.35	0.37	0.61	0.6	0.3	0.4	0.38
							Mn	0.94	0.7	–0.08	0.13	0.24	0.73	0.06	0.15	0.36	0.51	0.36	0.07	0.17
								Fe	0.76	–0.08	0.11	0.19	0.77	0.07	0.13	0.39	0.52	0.26	0.1	0.2
									Ni	–0.04	0.31	0.32	0.49	0.2	0.21	0.51	0.62	0.28	0.27	0.29
										Cu	0.17	0.17	–0.09	0.13	0.09	–0.02	–0.09	–0.09	0.24	0.16
											Zn	0.84	–0.11	0.63	0.55	0.69	0.58	0.21	0.67	0.74
												Pb	0.03	0.81	0.8	0.73	0.55	0.54	0.78	0.8
													Na^+	0.07	0.19	0.26	0.17	0.52	–0.04	0.03
														NH_4^+	0.9	0.77	0.46	0.45	0.93	0.9
															K^+	0.72	0.35	0.66	0.8	0.75
																Mg^{2+}	0.79	0.39	0.78	0.82
																	Ca^{2+}	0.12	0.57	0.59
																		Cl^-	0.29	0.21
																			NO_3^-	0.89

Table 2b. Correlation matrix for chemical species in Hanoi.

HA	S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Al	0.38	0.86	0.72	0.9	0.58	0.7	0.55	0.89	0.41	0.56	0.28	0.55	–0.42	0.42	0.56	0.4	0.6	0.23	0.54	0.51
	S	0.56	0.22	0.38	0.23	0.26	0.62	0.39	0.02	0.46	0.33	0.65	–0.06	0.86	0.71	0.04	0.43	0.22	0.65	0.92
		K	0.77	0.92	0.63	0.69	0.63	0.93	0.38	0.7	0.32	0.7	–0.23	0.66	0.83	0.44	0.7	0.4	0.75	0.74
			Ca	0.85	0.7	0.72	0.36	0.87	0.53	0.7	0.14	0.41	–0.31	0.2	0.48	0.53	0.84	0.39	0.65	0.44
				Ti	0.67	0.81	0.5	0.98	0.46	0.71	0.21	0.53	–0.33	0.45	0.65	0.56	0.79	0.43	0.74	0.59
					V	0.58	0.28	0.66	0.43	0.35	0	0.25	–0.29	0.27	0.53	0.55	0.66	0.39	0.56	0.44
						Cr	0.48	0.82	0.57	0.64	0.18	0.45	–0.37	0.29	0.5	0.43	0.73	0.23	0.6	0.47
							Mn	0.55	0.2	0.46	0.51	0.76	–0.35	0.58	0.66	0.16	0.28	–0.08	0.35	0.65
								Fe	0.45	0.72	0.28	0.6	–0.34	0.45	0.67	0.54	0.77	0.4	0.72	0.6
									Ni	0.34	0.15	0.21	–0.69	–0.05	0.22	0.4	0.43	–0.09	0.27	0.12
										Cu	0.29	0.58	–0.49	0.46	0.55	0.38	0.72	0.31	0.73	0.6
											Zn	0.79	–0.51	0.31	0.25	–0.14	–0.05	–0.12	0.12	0.26
												Pb	–0.4	0.68	0.7	–0.06	0.3	–0.01	0.46	0.68
													Na^+	–0.07	–0.22	–0.11	–0.23	0.59	–0.13	–0.07
														NH_4^+	0.87	0.03	0.38	0.28	0.68	0.92
															K^+	0.24	0.56	0.3	0.74	0.88
																Mg^{2+}	0.58	0.67	0.53	0.18
																	Ca^{2+}	0.58	0.88	0.63
																		Cl^-	0.66	0.34
																			NO_3^-	0.81

Table 2c. Correlation matrix for chemical species in Kolkata.

KK	S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Al	0.66	0.77	0.68	0.77	0.85	0.64	0.69	0.72	0.57	0.65	0.53	0.49	–0.13	0.37	0.23	0.58	0.59	0.2	0.37	0.48
	S	0.72	0.63	0.7	0.66	0.73	0.73	0.7	0.64	0.66	0.57	0.57	0.06	0.74	0.61	0.7	0.64	0.49	0.69	0.88
		K	0.95	0.99	0.89	0.89	0.89	0.98	0.93	0.92	0.74	0.75	–0.25	0.72	0.82	0.86	0.94	0.7	0.82	0.79
			Ca	0.97	0.84	0.91	0.89	0.96	0.92	0.91	0.71	0.72	–0.21	0.59	0.68	0.9	0.97	0.7	0.72	0.69
				Ti	0.9	0.9	0.9	0.99	0.93	0.92	0.72	0.73	–0.26	0.68	0.77	0.86	0.94	0.68	0.78	0.76
					V	0.76	0.79	0.86	0.82	0.84	0.66	0.62	–0.29	0.53	0.57	0.75	0.76	0.49	0.57	0.62
						Cr	0.93	0.92	0.88	0.87	0.78	0.78	–0.16	0.63	0.68	0.83	0.91	0.69	0.74	0.78
							Mn	0.93	0.88	0.91	0.79	0.81	–0.26	0.66	0.71	0.81	0.89	0.66	0.77	0.77
								Fe	0.95	0.95	0.77	0.78	–0.28	0.7	0.79	0.86	0.96	0.71	0.81	0.79
									Ni	0.93	0.76	0.75	–0.4	0.71	0.81	0.79	0.92	0.71	0.81	0.79
										Cu	0.84	0.85	–0.35	0.66	0.75	0.82	0.89	0.7	0.78	0.74
											Zn	0.93	–0.33	0.58	0.63	0.63	0.72	0.62	0.7	0.66
												Pb	–0.35	0.6	0.66	0.63	0.73	0.68	0.74	0.64
													Na^+	–0.3	–0.48	0.09	–0.22	–0.01	–0.39	–0.1
														NH_4^+	0.92	0.58	0.68	0.75	0.92	0.92
															K^+	0.67	0.78	0.8	0.97	0.89
																Mg^{2+}	0.9	0.76	0.7	0.73
																	Ca^{2+}	0.77	0.81	0.76
																		Cl^-	0.81	0.74
																			NO_3^-	0.9

Table 2d. Correlation matrix for chemical species in Tokyo.

TY	S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}
Al																				
	S	0.51	0.42	0.38	0.55	0.28	0.49	0.53	0.3	0.28	0.51	0.31	0.04	0.72	0.35	0.12	0.35	–0.14	0.55	0.9
		K	0.81	0.88	0.26	0.33	0.79	0.74	0.18	0.55	0.66	0.6	0.18	0.6	0.38	0.46	0.41	0.44	0.66	0.44
			Ca	0.9	0.45	0.39	0.86	0.86	0.32	0.42	0.47	0.38	0.08	0.26	0.38	0.23	0.39	0.25	0.37	0.31
				Ti	0.29	0.32	0.83	0.77	0.06	0.66	0.65	0.54	0.01	0.47	0.56	0.35	0.4	0.35	0.59	0.27
					V	0.29	0.48	0.66	0.77	0.2	0.24	0.07	0.01	0.15	–0.03	–0.14	0.27	–0.31	0.14	0.42
						Cr	0.65	0.62	–0.08	0.29	0.19	0.13	–0.25	0.07	–0.18	0.1	0.17	–0.2	0.1	0.2
							Mn	0.94	0.26	0.61	0.63	0.56	–0.07	0.42	0.25	0.23	0.27	0.14	0.5	0.33
								Fe	0.61	0.45	0.5	0.45	–0.02	0.34	0.27	0.18	0.38	0.09	0.4	0.4
									Ni	–0.05	–0.08	–0.11	0.62	–0.21	0.97	–0.27	–0.03	–0.02	–0.15	0.16
										Cu	0.78	0.69	–0.27	0.53	0.3	0	–0.06	0.05	0.61	0.06
											Zn	0.72	0	0.74	0.25	0.18	0.06	0.23	0.85	0.29
												Pb	–0.02	0.56	–0.1	0.26	–0.02	0.29	0.71	0.16
													Na^+	–0.02	0.6	0.57	0.41	0.65	0.01	0.24
														NH_4^+	0.76	0.27	0.21	0.14	0.84	0.67
															K^+	0.85	0.51	0.67	0.25	0.48
																Mg^{2+}	0.43	0.65	0.44	0.26
																	Ca^{2+}	0.18	0.1	0.56
																		Cl^-	0.23	–0.06
																			NO_3^-	0.42

was not so low through a year. In Beijing, enormous amount of SO_2 input derived from coal combustion in winter could lead the high concentrations of SO_4^{2-} in winter. These are possible reasons why the correlation between NO_3^- and SO_4^{2-} in Tokyo was different from the other three cities.

Seasonal Variation of the Chemical Species in Aerosols

Correlations among each component for each season at each site were calculated. In most cases, the correlation matrices for each season were similar to those for all data at each site. According to this result, the major sources governing the concentrations of inorganic chemical species in each Asian city studied would be generally constant through a year.

The concentrations of measured species in the winter/dry season and summer/rain season were shown in Table 3. The winter/summer ratios for each component ranged 0.7–2.0 in Beijing except for Na^+ and Cl^-. This means that the seasonal variation in the concentrations of chemical species in aerosols was not so large. The dry/rain ratios were 0.9–1.9 in Hanoi except for S, NH_4^+, K^+, NO_3^- and SO_4^{2-}. One of the reasons of this seasonal variation in Hanoi would be

Table 3. Rainfall amount and the concentrations of measured species in the winter/dry season and summer/rain season in four Asian cities.

Site	Beijing									Hanoi								
Period	winter/dry (Nov. 15–Mar. 15)				summer/rain (May 15–Sep. 15)					winter/dry (Nov. 15–Mar. 15)				summer/rain (May 15–Sep. 15)				
Rainfall (mm)[a]	61.9				765					192				1032				
Sample#	14				16					11				16				
Species in ng/m^3	Mean	SD	n	EF[b] (vs. Fe)	Mean	SD	n	EF[b] (vs. Fe)	W/S Ratio	Mean	SD	n	EF[b] (vs. Fe)	Mean	SD	n	EF[b] (vs. Fe)	W/S Ratio
Al	18430	8180	14	1.0	12484	4519	16	1.0	1.5	2605	569	11	0.5	2108	533	16	0.6	1.2
S	7583	5376	14	130	8082	5810	16	212	0.9	7726	1980	11	480	2529	1034	16	220	3.1
K	6060	3215	14	1.0	3817	2373	16	1.0	1.6	2037	528	11	1.3	1271	388	16	1.1	1.6
Ca	19135	7773	14	2.4	15899	5841	16	3.0	1.2	12450	4918	11	5.5	11135	4088	16	6.9	1.1
Ti	1150	680	14	1.2	648	331	16	1.0	1.8	311	111	11	1.1	217	64	16	1.1	1.4
V	49	32	14	1.6	25	19	16	1.2	2	16	6	11	1.9	13	5.0	16	2.2	1.2
Cr	27	11	14	1.2	29	12	16	2.0	0.9	9	5.4	11	1.5	7.2	2.5	15	1.6	1.3
Mn	354	143	14	1.7	230	97	16	1.6	1.5	165	52	11	2.8	101	52	16	2.4	1.6
Fe	11200	7254	14	1.0	7342	4065	16	1.0	1.5	3094	1020	11	1.0	2215	727	16	1	1.4
Ni	26	12	14	1.5	28	8	16	2.5	0.9	11	4	11	2.5	12	7.0	14	3.7	0.9
Cu	1162	733	14	94	1556	630	16	193	0.7	29	13	11	8.4	19	6.0	14	7.9	1.5
Zn	575	301	14	37	706	534	16	69	0.8	738	606	11	170	534	541	16	172	1.4
Pb	304	187	14	104	266	178	16	139	1.1	170	78	11	211	96	50	16	166	1.8
Na^-	2778	1756	13		891	410	11		3.1	1056	811	6		810	124	2		1.3
NH_4^+	12262	10415	14		12287	9675	14		1	6358	2046	11		848	563	16		7.5
K^+	3637	3913	14		2478	1849	14		1.5	912	360	11		286	117	16		3.2
Mg^{2+}	855	448	14		896	583	14		1	248	100	10		175	52	14		1.4
Ca^{2+}	11146	4581	14		12977	4950	14		0.9	10037	4691	11		6762	1910	16		1.5
Cl^-	8057	5080	14		1760	616	14		4.6	2063	1157	11		1096	265	16		1.9
NO_3^-	18710	20588	14		25043	19867	14		0.7	8251	4308	11		2488	1407	16		3.3
SO_4^{2-}	24088	16286	14		31958	31523	14		0.8	19265	5144	11		4805	2607	16		4.0

a Data from NCDC/NESDIS/NOAA. b Elemental composition of crust was cited from Mason and Moore, 1982.

Table 3. *(continued).*

Site	Kolkata									Tokyo								
Period	winter/dry (Nov. 15–Mar. 15)				summer/rain (May 15–Sep. 15)					winter/dry (Nov. 15–Mar. 15)				summer/rain (May 15–Sep. 15)				
Rainfall (mm)[a]	28				641					372				396				
Sample#	17				16					15				16				
Species in ng/m^3	Mean	SD	n	EF[b] (vs. Fe)	Mean	SD	n	EF[b] (vs. Fe)	W/S Ratio	Mean	SD	n	EF[b] (vs. Fe)	Mean	SD	n	EF[b] (vs. Fe)	W/S Ratio
Al	14815	3929	17	0.8	5557	1930	16	1.5	2.7									
S	6332	1590	17	110	2121	1052	16	182	3	1380	722	14	316	2218	1250	16	432	0.6
K	5084	1412	17	0.9	1048	331	16	0.9	4.9	219	109	14	0.5	163	66	16	0.3	1.3
Ca	13121	4441	17	1.6	3641	1084	16	2.2	3.6	1141	750	14	1.9	1162	555	16	1.6	1.0
Ti	1182	330	17	1.2	261	88	16	1.3	4.5	65	36	14	0.9	49	22	16	0.6	1.3
V	44	14	17	1.5	9	4.6	16	1.5	4.8	4	2.4	12	1.8	12	12	16	4.6	0.3
Cr	52	18	17	2.3	14	5	16	3.1	3.7	6.3	2.3	12	3.8	9	4.2	11	4.6	0.7
Mn	367	129	17	1.8	85	29	16	2.0	4.3	46	15	14	2.9	45	12	16	2.4	1.0
Fe	11022	3408	17	1.0	2241	727	16	1.0	4.9	840	435	14	1.0	987	517	16	1	0.9
Ni	27	8	17	1.6	10	2	11	3.0	2.7	8.9	0.7	2	7.1	10	3	6	7	0.9
Cu	93	35	17	7.7	21	6	15	8.5	4.5	24	9	13	25	13	5	14	12	1.8
Zn	1413	1072	17	92	146	166	16	47	9.7	105	46	14	90	69	30	16	50	1.5
Pb	1107	827	17	386	175	155	16	301	6.3	29	7	14	132	25	5	15	98	1.1
Na^-	782	344	11		1048	526	13		0.7	699	566	11		943	468	15		0.7
NH_4^+	7607	3873	17		446	463	16		17.1	2944	1805	14		2409	1662	16		1.2
K^+	1654	696	17		233	25	2		7.1	724	1							
Mg^{2-}	445	139	16		150	78	16		3	324	145	8		279	102	13		1.2
Ca^{2+}	6351	2381	17		1252	517	15		5.1	1183	707	12		1521	1079	14		0.8
Cl^-	5572	3549	17		1507	781	14		3.7	1454	665	14		970	616	16		1.5
NO_3^-	13054	6098	17		1318	469	10		9.9	3988	2340	14		2800	1763	13		1.4
SO_4^{2-}	18809	5688	17		4036	1822	14		4.7	2833	1872	14		5246	2760	16		0.5

a Data from NCDC/NESDIS/NOAA. b Elemental composition of crust was cited from Mason and Moore, 1982.

biomass burnings around Hanoi city. The dry/rain ratios were 2.7–17.1 in Kolkata except for Na^+. This is probably due to high concentrations of pollutants in the dry season because almost no wet scavenging of aerosols was expected during the dry season in Kolkata city. Additionally, high dry/rain ratios for Zn and Pb (9.7 and 6.3) suggest that more anthropogenic inputs of particulate pollutants into the air should be considered during the dry season in Kolkata. The winter/summer ratios vary from 0.3 to 1.8 in Tokyo. The minimum winter/summer ratio was shown for V. One of the possible reasons of this is due to increase of the use of oil fuel for power generation around Tokyo metropolitan area in summer season (Okuda *et al.*, 2007b). These data could also serve as the basis for epidemiological studies if appropriate health effects data are also available.

Calculation of the Carcinogenic Risks to Humans Associated with Cr and Ni

Calculation of the carcinogenic risks to humans associated with carcinogenic metals has been done using our dataset presented in this study. We focused on Cr and Ni for this calculation because these two metals are classified into Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC, 2012). The concentrations corresponding to an excess lifetime risk of 10^{-5} have been estimated as 0.25 ng/m^3 for hexavalent Cr and 25 ng/m^3 for Ni (WHO, 2000). We calculated the ratio of the observed value to the concentrations corresponding to an excess lifetime risk of 10^{-5} for Cr and Ni in each city. The results are shown in Table 4. Note that we measured not hexavalent Cr but total Cr. Previous studies have reported that the ratio of hexavalent Cr to total Cr varied from 2.6% to 50% (Świetlik *et al.*, 2011l; Tirez *et al.*, 2011). When we assume the ratio of hexavalent Cr to total Cr was 2%, the ratio of the observed value to the concentrations corresponding to an excess lifetime risk of 10^{-5} for Cr would be 2.2 ± 1.0 for BJ, 0.7 ± 0.3 for HA, 2.5 ± 1.6 for KK, and 0.8 ± 0.6 for TY, respectively. These ratios are still higher than those for Ni. Besides, the higher ratio of hexavalent Cr to total Cr would cause much higher potential of carcinogenic risk. We conclude the following two points: (1) the calculated carcinogenic risks to humans by Cr were higher than those by Ni in wide area of Asian cities, and (2) chemical speciation that allows us to estimate the risks caused by Cr much precisely is needed for further study.

SUMMARY

This study is a systematic field observation campaign for elucidating the chemical characteristics of aerosols in four different mega-cities in Asian region, Beijing, Hanoi, Kolkata, and Tokyo. The concentration level of chemical species in aerosol in Beijing was the highest among four Asian cities. Chemical features of aerosols in the four cities have been characterized in this study. The calculated carcinogenic risks to humans by Cr were higher than those by Ni in wide area of Asian cities. Chemical speciation that allows us to estimate the risks caused by Cr much precisely is needed for further study.

Table 4. The ratio of the observed value to the concentrations corresponding to an excess lifetime risk of 10^{-5} for Cr and Ni[a] in aerosols in four Asian cities.

	Beijing	Hanoi	Kolkata	Tokyo
Cr[b]	111 ± 49	33 ± 15	123 ± 80	38 ± 28
Ni	1.1 ± 0.4	0.5 ± 0.2	0.7 ± 0.4	0.4 ± 0.1

a The concentrations corresponding to an excess lifetime risk of 10^{-5} are estimated as 0.25 ng/m^3 for hexavalent chromium and 25 ng/m^3 for nickel (WHO, 2000).
b Assuming that the observed Cr is in the form of hexavalent chromium.

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