

PA47) Size Distribution and Seasonal Variation of Ionic Species of Atmospheric Aerosols in Ulsan

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1. Introduction

In last decades, atmospheric aerosols have received much attention due to their impact on human health, visibility and global climate change (Dockery and Pope, 1994). Water-soluble inorganic ions are the major components of atmospheric aerosols and can comprise up to large fraction of particulate matter (Yao et al., 2002). Sulfate, nitrate and ammonium are known as secondary inorganic ions and are the most abundant species in atmospheric particles.

The air quality associated with industrial emissions is a keen environmental issue in Ulsan. Major emission sources in Ulsan are industrial and mobile sources. The large amount of precursor gases (SO_2 , NO_x , and NH_3) of sulfate, nitrate and ammonium species are emitted from these sources. Air emissions from industrial activities may transport to some residential areas which are even located in a remote distance from the industrial sectors. This study investigated the levels and seasonal variations of ionic species in the airborne particles at a residential area in Ulsan for a year.

2. Methods

Samples were collected on the roof of the Mugeo-dong office, located in a residential area of Ulsan city. This site also closes to a highway of 6 lanes and a busy rotary within approximately 100-120m. An ambient cascade impactor was utilized, which consists of eight steps for particle size separation (10, 9, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7 and $0.4\mu\text{m}$). Daily samples were collected from April 2008 to January 2009, at a flow rate of $28.3\text{L}/\text{m}^3$ on glass fiber filters with diameter 81mm. The filters were kept in a desiccator in a conditioned room with RH of $45\pm 5\%$ and temperature of $20\pm 2^\circ\text{C}$ for 48 h. PM mass concentrations were determined by a gravimetric analysis using an electronic micro-balance which has 0.01 mg of sensitivity. The ions were extracted from the filter by placing them into 15ml ultra-pure water and ultra sonification for 30 min. Eight major ionic species (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) were measured by Ion chromatography(DIONEX DX-80). A CS12A and AS14 A column ($4\times 250\text{mm}$) were used for determinations of cations and anions, respectively.

3. Results and Discussion

Fig. 1 showed the annual mean concentrations of PM mass and ionic species in $\text{PM}_{1.1}$, $\text{PM}_{1.1-2.1}$ and $\text{PM}_{2.1-10}$. For PM mass, the concentrations of $\text{PM}_{1.1}$, $\text{PM}_{2.1}$ and PM_{10} were 19.9, 30.1 and $54.8\mu\text{g}/\text{m}^3$, respectively. For ionic elements, sulfate was the greatest contributor, followed by nitrate and ammonium. Other ions had low concentrations, except Na.

Since cascade impactor sampler does not have a $2.5\mu\text{m}$ cut point, $2.1\mu\text{m}$ is defined as the boundary between fine and coarse particles in this paper. The ionic concentrations in fine and coarse particles were summarized in Table 1. As shown, ions accounted for 40.4-61.7% in fine particles and 30.9-43.0% in coarse particles. This indicated that ionic species were the major fraction of the atmospheric aerosols in Ulsan. The total ionic concentrations showed a small seasonal variation for fine and coarse particles. For four seasons, SO_4^{2-} was the most abundant species which had the highest level in summer for fine and coarse particles; while NO_3^- and NH_4^+ had the highest level in winter for fine

particles, and in spring for coarse particles. Ulsan is located nearby the East Sea and has large petrochemical plants and many other factories, and the high level of sulfate in summer was due to the effect of prevailing wind direction more passed through industry and sea areas compared to other seasons. Besides, high temperature and long sunlight duration were in favor of the photochemical reactions, resulted in high sulfate concentration. A significant portion of nitrate results from the atmospheric conversion of nitrogen oxides (NO^+ and NO_2) and ammonia (NH_3) (Seinfeld and Pandis, 1998). The high nitrate and ammonium concentrations were observed in winter, probably due to the high emission rates of nitrogen oxides and ammonia in winter as well as the less dissociation of NH_4NO_3 at low temperature in winter. For other ions, Na^+ , Ca^{2+} and Mg^{2+} had slightly higher concentrations in fine particles than in coarse ones.

The mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ has been used as an indicator of the relative importance of stationary vs. mobile sources of sulfur and nitrogen compounds in the atmosphere (Arimoto et al., 1996). In this study, $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios in four seasons were in range of 0.23–0.84 in fine particles and 0.32–0.40 in coarse particles. Generally, $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios were less than 0.5, except fine particles in winter. It means stationary sources from industrial areas were major sources in Ulsan. In fine particles, lower $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio was found in summer and higher its ratio was found in winter. It was reasonable because the high levels of sulfate in summer and nitrate in winter. It also showed that ion levels in fine particles were better indicator than in coarse particles.

The mass ratios of Cl^-/Na^+ in the fine mode were in range of 0.61–0.71 while the ratios were in range of 0.16–0.20 in the fine mode. It is observed that the Cl^-/Na^+ ratios in both the coarse and fine aerosols were much less than the sea water ratio of 1.8 (Parmar et al., 2001), especially in the coarse mode. Chloride deficit is the result of the reaction of sea salt with acidic species, nitrate and sulfate followed by the loss of Cl^- in the form of HCl gas (Hu et al., 2002).

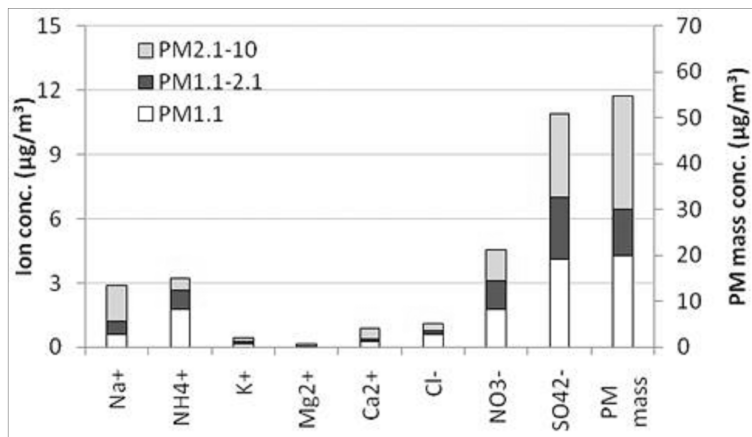


Fig. 1. Comparison of average size distribution of particle mass and ionic components for whole year.

Table 1. Seasonal variation of particulate and ionic concentrations($\mu\text{g}/\text{m}^3$).

	Spring		Summer		Fall		Winter	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Na ⁺	1.37	1.73	1.18	1.68	1.25	1.70	1.14	1.48
NH ₄ ⁺	2.11	1.03	2.79	0.42	2.46	0.32	3.32	0.44
K ⁺	0.39	0.20	0.24	0.15	0.28	0.15	0.29	0.13
Mg ²⁺	0.18	0.20	0.06	0.09	0.03	0.07	0.03	0.06
Ca ²⁺	0.58	0.58	0.33	0.52	0.37	0.45	0.34	0.47
Cl ⁻	0.90	0.27	0.72	0.34	0.79	0.28	0.81	0.27
NO ₃ ⁻	3.10	1.75	2.04	1.73	2.16	1.02	5.26	1.07
SO ₄ ²⁻	7.27	4.40	9.02	4.83	5.51	2.94	6.24	3.37
Σ ions	15.89	10.15	16.39	9.77	12.87	6.93	17.42	7.29
PM mass	32.9	30.4	26.6	22.7	31.8	22.4	29.3	23.1
% ions in PM	48.3	33.4	61.7	43.0	40.4	30.9	59.5	31.6
NO ₃ ⁻ /SO ₄ ²⁻	0.43	0.40	0.23	0.36	0.39	0.34	0.84	0.32
Cl/Na	0.66	0.16	0.61	0.20	0.63	0.17	0.71	0.18

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