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ORIGINAL ARTICLE

A Chemical Analysis of Airborne Particulates at the near Coast Site, Ul-jin Geun Gyungbook.

Dong Sub Lee, Jin Sik Park*

School of Healthcare & Biotechnology, Kyungwoon university, Gumi 730-739, Korea

Abstract

East Asia is characterized by anthropogenic emissions resulting from the large population and fast economic growth of this region. Since the prevailing wind is westerly and northwesterly, emissions from Ul-jin can be expected to contribute to acidic deposition increase in downwind direction.

Aerosols collected at the near coast site, Uljin geun, gyungbook and were analyzed for NH_4^+, Mg^{2+}, Na^+, Ca^{2+}, Cl^-, SO_4^{2-}, and NO_3^- from Aug. 2012 to Feb. 2013.

The seasonal averaged aerosol concentration showed the highest potassium and calcium ion in winter and the highest ammonium ion due to a meadow and high solar intensity in summer. Sodium and chloride ion showed the same ratio all seasons and sulfate and nitrate species showed the maximum value in winter

Chemical components of aerosols collected at the near coast site, Uljin geun, gyungbook were lower by 16 to 73% than those collected at other similar environment site such as kanghwa, yangyang. Comparing air quality data at the near coast site, Uljin geun, gyungbook,

There was found that Uljin coast site is less influenced by the sea salts(potassium, magnesium, calcium) and nss-SO_4^{2-} percentage is 3~13% higher than similar condition site.

Key words : Near coast site, Ul-jin geun, Gyungbook, Non-sea salt, Nss-SO_4^{2-}

1. Introduction

The region of East Asia is characterized by anth-ropogenic emissions resulting from the large population and fast economic growth of this region. Especially, China exhausted many SO_X and NO_X emissions in this region. Since the prevailing wind is westerly and northwesterly, emissions from Ul-jin can be expected to contribute to acidic deposition increase in down-wind direction.

The importance of an atmospheric chemistry in East Asia has recently been recognized, and several ground-based observational programs have been studied in the region. For example, background ground-based station has been established at yangyang(kangwon), taean, kanghwa(kyeonggi), and kosan(cheju island) korea.

In this paper, air quality of the near coast site Ul-jin gyungbook were compared with those from ground based stations.

The objective of the paper is to compare the air quality at the near coast uljin geun gyungbook site and to see if there are any differences of other sites on air quality. For this purpose, the meteorological air mass data was used and aerosol data was analyzed.

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***Corresponding author** : Jin Sik Park., School of healthcare and biotechnology, Kyungwoon university, Gumi 730-739, korea
Phone: +82-54-479-1235
E-mail: jspark@ikw.ac.kr

2. Data and Method

2.1. Collection Site

The sampling site in which this study was carried out in the near coast site Uljin geun gyungbook, Korea. Near coast site Uljin is, an ideal location to monitor the atmospheric chemistry of East Asia without large industrial sources. But there is a nuclear power generation. The sampling(Uljin) site is located in the east China sea, about 100km south of the Korean peninsular, about 250km west of Kyushu, Japan, and about 500km east-north of Shanghai, China. The sampling site is located at 37。54'N, 129。24'E, at 200m below mean sea level,

The climate is essentially a temperate climate with high degrees of instability. Wind blows mainly from the northwest and is very strong, especially in winter. The monthly average temperature in sampling site (Uljin) during summer and winter, respectively, range 22℃ to 27℃ and 1℃ to 3℃. During the sampling period, rainfall average recorded was 1,102 mm. Relative humidity was the highest during the summer (range 70～80%) and the lowest in winter (range 6 0～70%).

2.2. Sampling and Analysis

Aerosol samples were collected during three periods representing summer (15 Aug. to 4 Sep. 2012), fall (15 Oct. to 5 Nov. 2012) and winter (15 Jan. to 2 Feb. 2013). Aerosols were collected by air filtration with a high volume pumping system (Kimoto high volume tape sampler, model 195A). Air is continuously sampled through polytetrafluoroethylene(PTFE) filters at the flow rate of 160 to 180 l/min from a (heated) sampling probe mounted on top of the measurement container. The normal operation is 24 hour sampling. The collected samples were removed from their support and trans -ferred to a petridish and sealed in a plastic bag. In the laboratory, these filters were extracted with 50 ml of distilled, deionized water (DDW) in an ultrasonic shaker for 30min. Collected filter was refluxed in 98℃, and agitated on a mechanical shaker for 1 hr. The liquid extract solution was then filtered through 0.45㎛ pore-sized cellulose acetate membrane filter before analysis.

The filters were analyzed for Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+}, K^{+}, Cl^{-}, NO_3^{-}, and SO_4^{2-}. Samples were divided into three parts for filter analysis with different techniques. Major anions such as SO_4^{2-}, NO_3^{-}, and Cl^{-} were analyzed by ion chromatography(I.C.) using a Dionex model DX-100 ion chromatography. NH_4^{+} by catalyzed indophenol blue spectrophotometry was determined using Model UVIKON860 UV-Visible spectrophotometry.

K^{+}, Ca^{2+}, Mg^{2+}, and Na^{+} ions were measured with atomic absorption techniques using Pye Unicam sp-8 Model atomic absorption spectrophotometry.

3. Results and Discussion

3.1. Meteorological Comparison

During the sampling periods, the seasonality of meteorological conditions at Uljin site show that the air mass trajectories reaching at Uljin site distinctly differ with season(Figure 1).

3.2. Aerosol Composition and Seasonal Variation

The seasonally averaged aerosol compositions at Uljin site are summarized in Figure 2, 3 and compared. The figures show that the seasonally averaged aerosol concentrations at Uljin site are lower than those measured at similar condition site. Potassium and calcium ions were the highest in winter at two sites. Ammonium ion is the highest in summer at Uljin site and the highest in fall at similar condition site. The high ammonium values are due to a meadow near the sampling site and high solar intensity. Sodium and chloride showed the same ratio during all seasons at two sites. The highest concentrations of marine borne species such as Na^{+}, Cl^{-} were observed in winter and

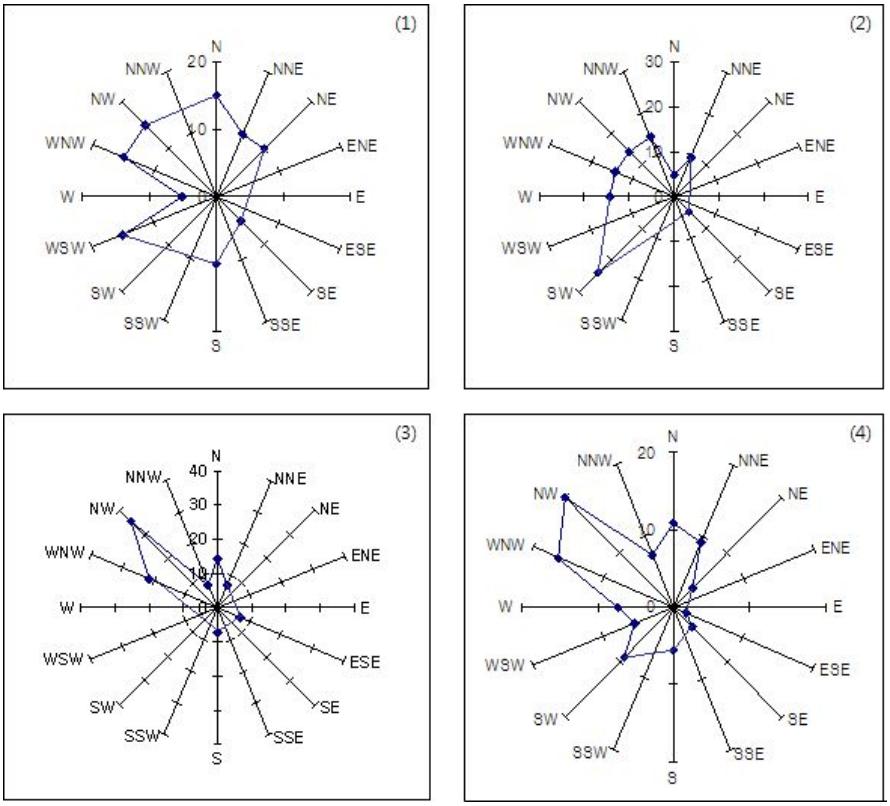

Fig. 1. Comparison of wind direction at Uljin site. (1) summer (2) fall (3) winter (4) Total

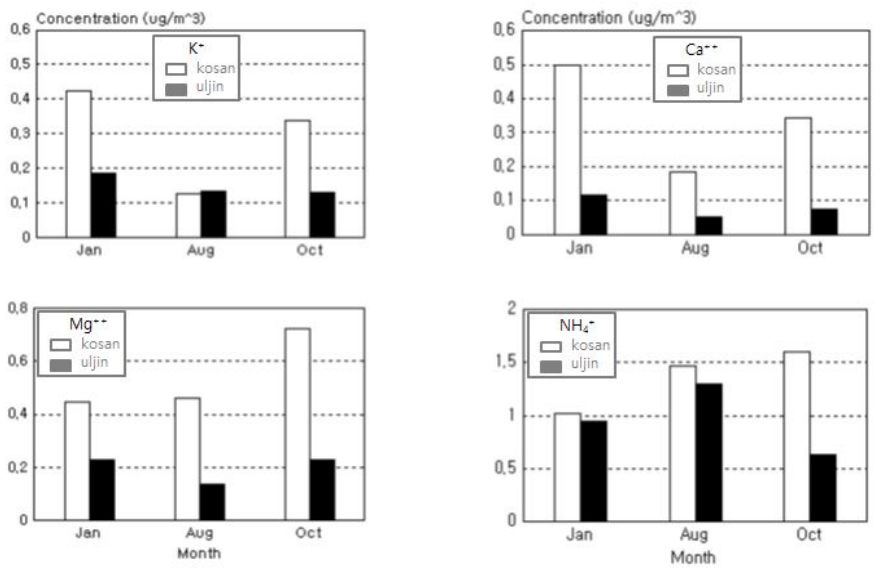

Fig. 2. Seasonally averaged aerosol concentrations. (K^+, Ca^{2+}, Mg^{2+}, NH_4^+)

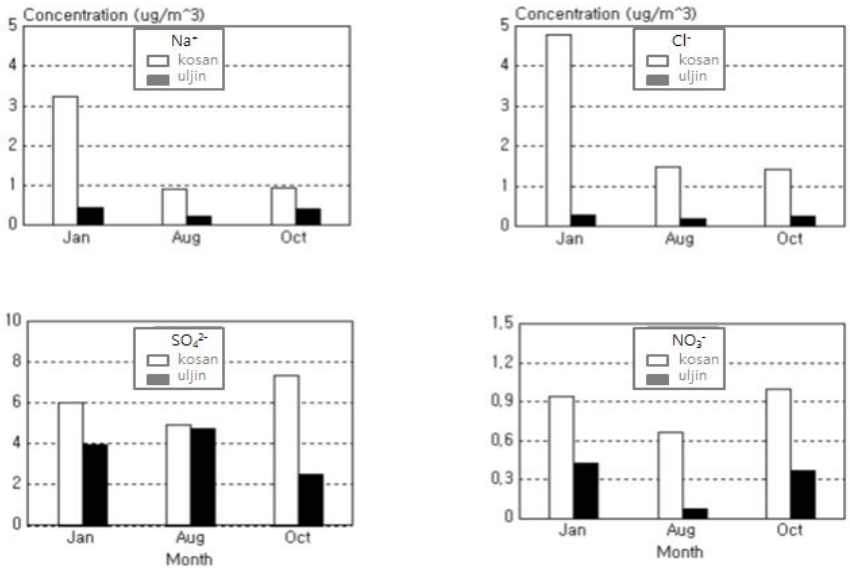

Fig. 3. Seasonally averaged aerosol concentrations(Na^+, Cl^-, SO_4^{2-}, NO_3^-).

generally associated with the cyclonic activity and the higher wind speeds. Sulfate and nitrate species showed the maximum value at Uljin site in winter.

Figure 4 shows the difference of species concentration before the rainfall and after the rainfall at Uljin site. After the precipitation, 20~45% of averaged concentration of species are removed from the atmosphere.

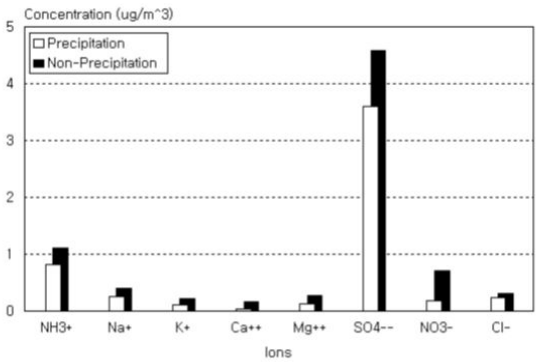

Fig. 4. Scavenging concentration of aerosol at Uljin site.

3.3. Aerosol Enrichment Factors

In order to investigate possible geochemical and anthropogenic sources for dissolved compounds in the aerosol sample, the following analysis was carried out. Enrichment factors(EF) were calculated for each ion relative to sea salt [$EF_{Na}(x)$] and relative to the earth's crust [$EF_{Ca}(x)$].

The enrichment factor for an element x is defined as follows:

$$EF_{Na}(x)=\frac{(x/Na^+)_{aerosol}}{(x/Na^+)_{seawater}} \quad (1)$$

$$EF_{Ca}(x)=\frac{(x/ca^{2+})_{aerosol}}{(x/ca^{2+})_{seawater}} \quad (2)$$

Na^+ was used as an indicator element for sea water and Ca^{2+} for the earth's crust. Typically, enrichment factors to crustal materials are based on ratio with aluminum. However, the tape filters were not analyzed for aluminum. Thus, in this study, enrichment factors were calculated based on calcium ratio.

K^+, Ca^{2+}, and Na^+, respectively are the dissolved concentrations in aerosol, the subscript "aerosol" denotes atmospheric concentration ratio, and the subscripts

Table 1. Aerosol Enrichment Factors at Uljin Site

Species	Seawater Composition	Uljin Site (Ave.)	similar condition (Ave.)
NO_3^-/Na^+	〈0.00001	82767	77380.9
SO_4^{2-}/Na^+	0.25	65.792	16.40
K^+/Na^+	0.04	14.721	5.87
Ca^{2+}/Na^+	0.04	6.720	7.68
Mg^{2+}/Na^+	0.12	4.795	1.34
Cl^-/Na^+	1.80	0.517	0.61

Species	Crust Composition	Uljin Site (Ave.)	similar condition (Ave.)
SO_4^{2-}/Ca^{2+}	0.004	17746	3965.27
NH_4^+/Ca^{2+}	0.004	5282.98	736.65
Cl^-/Ca^{2+}	0.004	1395.39	1064.69
NO_3^-/Ca^{2+}	0.004	1111.03	673.35
Mg^{2+}/Ca^{2+}	0.33	9.14	1.67
Na^+/Ca^{2+}	0.76	8.22	4.54
K^+/Ca^{2+}	0.66	3.49	1.23

"seawater" and "crust" identify the appropriate reference material ratios. The enrichment factors relative to seawater (ratios with Na^+) and crust (ratios with Ca^{2+}) presented in Table 1 shows that the enrichment factor relative to seawater for chloride is lower than 1, indicating the loss of chloride. This means that more active chlorine-releasing gas-solid reactions occured during the sampling period. Possibility includes sea salt reactions with nitrogen oxides and/or ion exchange reactions with strong acids. An enrichment factor(EF) close to 1 means a marine or crustal source and a larger EF imply that other sources might be responsible, that is, anthropogenic sources. The enrichment factors relative to seawater show that the aerosol measured at Uljin site is enriched in sulfate, nitrate, and potassium, indicating that these species are not originating from the marine. The same results have been shown at similar condition site.

Enrichment factors relative to the composition of earth's crust are also presented in Table 1. High enrichment factors relative to crust were found at the Uljin site and Kosan site, except magnesium, sodium, and potassium. This means that sulfate, ammonium, chloride, and nitrate not originate from the soil, but originate from the anthropogenic sources.

Table 2 shows the values of the cross correlation coefficients for collected samples at Uljin site. It is shown that non-sea salt sulfate is much more correlated with potassium and ammonium ion than with other species. Nitrate is much more correlated with chloride, sodium, and magnesium.

In addition, the relationship of species with same origin is stronger than that of species with different origin. It is possible that the higher correlation coeffi -cients mean same combination. Examination of Table 2 suggests that $(NH_4)_2SO_4$, $MgSO_4$, $NaNO_3$, $CaSO_4$, and NaCl are predominant species combinations. They may be formed in the atmospheric water droplets by the scavenging of aerosols and reaction of gaseous species. Generally, sulfate and nitrate are common

Table 2. Cross Correlation at Uljin Site

	nss-SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	NH_4^+	Mg^{2+}
nss-SO_4^{2-}	1							
NO_3^-	0.20	1						
Cl^-	0.17	0.74	1					
Na^+	0.05	0.68	0.54	1				
K+	0.78	0.11	0.02	0.22	1			
Ca^{2+}	0.43	0.54	0.37	0.42	0.72	1		
NH_4^+	0.78	0.23	0.15	0.20	0.54	0.24	1	
Mg^{2+}	0.29	0.65	0.45	0.85	0.72	0.72	0.01	1

components of aerosols.

Table 3 shows that the data collected at Uljin site are compared with those taken at other sites. For example, aerosols were measured at kosan site from Aug. 1992 to Oct. 1994 and at kangwha, gyunggi from June 1992 to May 1993 and at yangyang, gangwon from June 1992 to May 1993. In addition, aerosol compositions were measured at oki island, Japan from June 1992 to May 1993. The aerosol compositions at oki island are very similar to those observed at Uljin site. The magnitudes of the individual species are all very close. Monitoring sites of the marine area at the yangyang, kosan, and kangwha show higher concentrations for many species than those at Uljin site. They are about 16 percent to 73 percent higher than concentration measured at Uljin site.

Especially, concentrations of marine origin species (Na^+, Cl^-) at Uljin site are observed lower than those at kosan site. They are nearly 11 percent to 24 percent of those measured at kosan site. This means that Uljin site is less influenced by marine borne species than kosan site.

In addition, this paper compared non-sea salt ratio for the species at two site (Figure 5,6). Non-sea salt ratios for magnesium and potassium at Uljin site are about 13 percent higher than those at kosan site. And, non-sea salt values for the calcium and sulfate at Uljin site are about 3 percent higher than those at kosan site.

4. Conclusions

The seasonal variation of aerosol composition collected at Uljin site in gyungbook, Korea was presented and compared with those collected at other sites. The seasonally averaged non-sea salts (NSS) for potassium, magnesium, calcium and sulfate ratios

Table 3. Average Compositions of the Aerosol

(Unit : μg/m^3)

	nss-SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	Ca^{2+}	NH_4^+
Uljin site	3.61	0.27	0.25	0.35	0.15	0.08	0.19	0.96
kosan	5.71	0.82	2.26	1.47	0.27	0.32	0.52	1.38
kangwha	6.51	3.99	2.04	1.40	1.50	1.08	0.34	2.03
yangyang	4.90	2.73	2.28	1.27	1.20	0.83	0.29	1.27
oki Island	1.30	0.53	0.62	0.74	0.12	0.17	0.08	0.30

* : total sulfate
nss : non sea salt

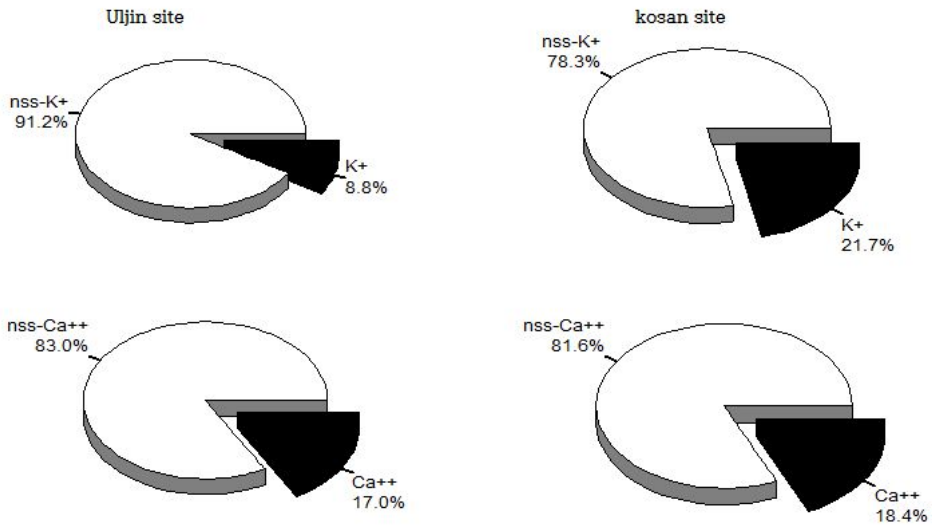

Fig. 5. Comparison of non-sea salt K^+, Ca^{2+} ratio.

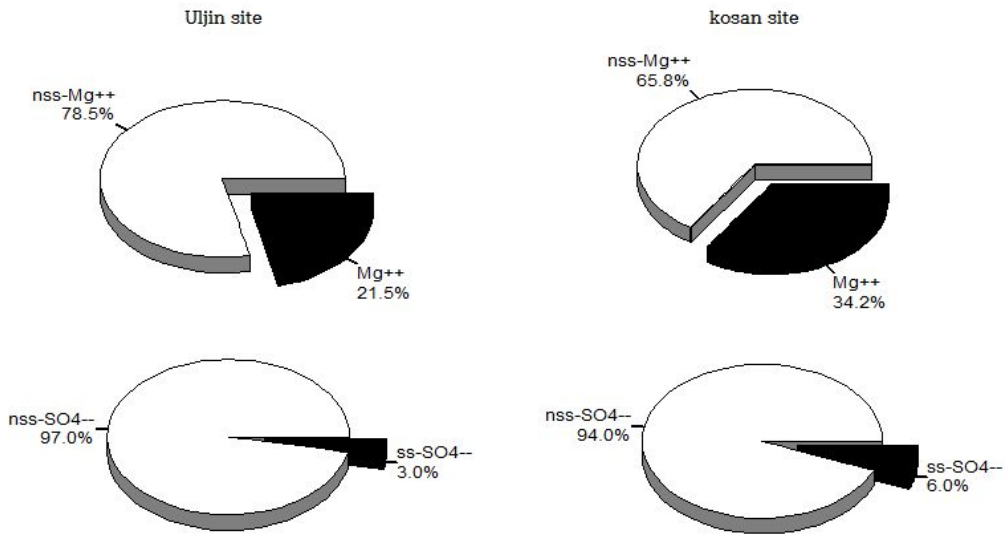

Fig. 6. Comparison of non-sea salt Mg^{2+}, SO_4^{2-} ratio.

were found 91.2%, 78.5%, 83.01%, and 97.0%, respectively. These values are about 3 percent to 13 percent higher than those at similar condition site. All species at Uljin site showed 16 percent to 73 percent lower values than those at other marine site (yangyang, kanghwa, kosan site). Especially, concentrations of marine borne species (Na^+, Cl^-) are lower than those at kosan site (11~24%).

But, the aerosol compositions at oki island are very similar to those observed at Uljin site. The magnitudes of the individual species are all very close.

Wind flows from the west-north west(WNW) to north-north east(NNE) at Uljin site were influenced by Korean peninsular and China under the influence of the anthropogenic activities.

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