Characteristics of chemical species in gaseous and aerosol phase measured at Gosan, Korea during ABC-EAREX 2005

J. S. Han, K. J. Moon*, M. D. Lee, I. R. Jung

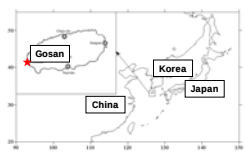
Air Quality Division, National Institute of Environmental Research (NIER), Environmental Research Complex, Kyeongseodong, Seogu, Incheon, 404-170, Republic of Korea, nierhan@me.go.kr, iamiyan@me.go.kr, Tel: +82-32-560-7103, Fax: +82-32-568-2035

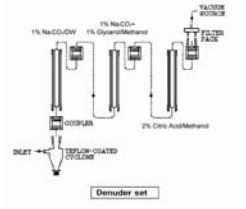
INTRODUCTION

- Northeast Asia is known to emit a large amount of Asian dust particles as well as anthropogenic pollutants due to its high population density and high rate of energy consumption.
- In order to estimate the potential impact of various pollutants in radiative and climate forcing, it is necessary to investigate the chemical characteristics of air pollutants in this region.
- Gas-phase nitric acid (HNO_3) and particulate nitrate are important atmospheric chemical constituents. HNO_3 is an end species in NO_x (NO and NO_2) photochemical reactions that directly affect regional ozone budget and NO_3^- aerosol has become the important light scattering aerosols component.
- This study presents the daily average concentrations of particulate inorganic components and related gases measured by the cyclone/denuder/filter pack sampling system

SAMPLING AND ANALYSIS

- Ambient aerosol collection was continuously made at Gosan super site (33° 17'N, 126° 10'E, 70m ASL) from 8 March to 4 April 2005.
- During the measurement period, two Asian dust outbreaks were observed from 17 to 18 March and 29 March 2005.



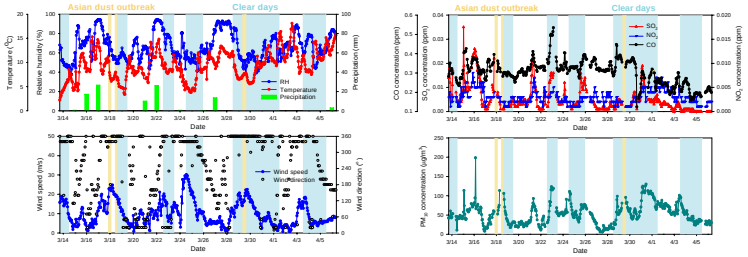


Low volume sampler : URG $PM_{2.5}$ Cyclone (URG-2000-30UB), 16.7 LPM for 24 hours
Teflon membrane filter (Gelman, 47mm Zefluor)
← distilled and deionized water, 20ml
Shaking 120 min
Filtration 1㎛ cellulose filter (Toyo, 5C)

SO_4^{2-}, NO_3^-, Cl^-	Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+
IC (Dionex, DX-2000)	IC (Dionex, DX-1000)
IonPac® AS18 column	IonPac® CS16 column
DS6 Heated Conductivity Cell	DS6 Heated Conductivity Cell
ASRS-ULTRAII, 4mm suppressor	CSRS-ULTRA, 4mm suppressor
12m M KOH Gradient Eluent	40m M $MSA_{Gluconic}$
1ml/min flow rate	1ml/min flow rate
25μl sample injection volume	25μl sample injection volume

- Three sets of low volume air samplers with $PM_{2.5}$/PM_{10} cyclone were operated at a flow rate of 16.7 lpm.
- Filter sampling was conducted regularly for 24 hours, from 9:00AM to 9:00AM.
- ➔ Seven species of ion components; SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Mg^{2+}, and Ca^{2+} were measured by ion chromatography for $PM_{2.5}$/PM_{10} samples.
- One set of cyclone/denuder/filter pack sampling system was used to measure the daily concentrations of several gas phase pollutants such as HNO_3, HNO_2, HCl, NH_3.

ATMOSPHERIC CONDITION

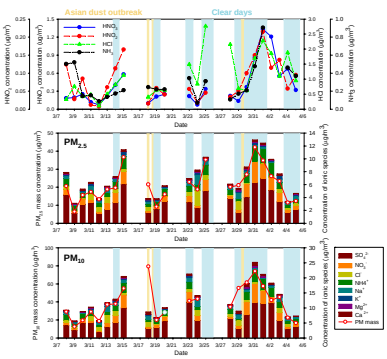


- Two Asian dust outbreaks (3/17~18, 3/29) were observed during ABC-EAREX2005.
- Rainy days were excluded from following analysis.

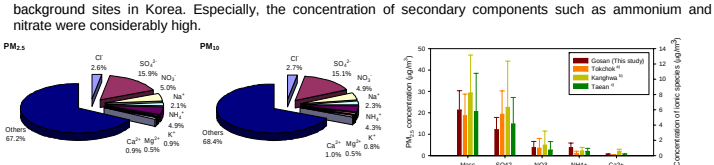
MEAN COMPOSITION

- The mean concentrations of acidic gases, HNO_3, HNO_2, and HCl, were 0.39, 0.08, and 1.07 ug/m³, respectively.
- Average concentrations of sulfate, nitrate, and ammonium in $PM_{2.5}$ were 3.39, 1.06, and 1.04 ug/m³, which occupied about 26% of total $PM_{2.5}$ mass.
- More than 55% of these secondary ion components distributed in fine size range (D_p<2.5um).

Phase	Species	Average	Standard deviation	Maximum	Minimum	No. of samples
Gas	NH_3	0.29	0.2	0.91	0.07	21
	HCl	1.07	0.72	2.76	0.11	23
	HNO_2	0.08	0.05	0.22	0.01	23
	HNO_3	0.39	0.34	1.33	0.07	23
$PM_{2.5}$	Mass	21.3	9.07	42.1	6.4	23
	Cl^-	0.56	0.52	2.4	0.09	23
	SO_4^{2-}	3.39	1.62	7	1.54	23
	NO_3^-	1.06	0.81	3.15	0.22	23
	Na^+	0.46	0.29	1.46	0.16	23
	NH_4^+	1.04	0.61	2.33	0.32	23
	K^+	0.2	0.11	0.53	0.05	23
	Mg^{2+}	0.1	0.05	0.19	0.02	23
	Ca^{2+}	0.19	0.05	0.3	0.12	23
PM_{10}	Mass	39.3	18.2	79.3	12.5	23
	Cl^-	1.06	0.67	2.8	0.16	23
	SO_4^{2-}	5.92	3.24	11.9	1.94	23
	NO_3^-	1.91	1.6	6.44	0.33	23
	Na^+	0.92	0.49	2.29	0.29	23
	NH_4^+	1.69	0.99	4.03	0.42	23
	K^+	0.31	0.19	0.82	0.05	23
	Mg^{2+}	0.21	0.1	0.47	0.09	23
	Ca^{2+}	0.38	0.31	1.17	0.06	23



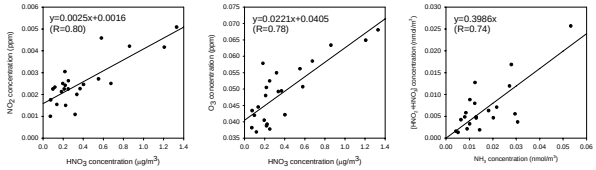
- Average inorganic composition of $PM_{2.5}$ and PM_{10} was similar influenced by Asian dust outbreaks.
- The measured results in this study were similar to Tokchok and Taean but lower than Kanghwa, which are other background sites in Korea. Especially, the concentration of secondary components such as ammonium and nitrate were considerably high.



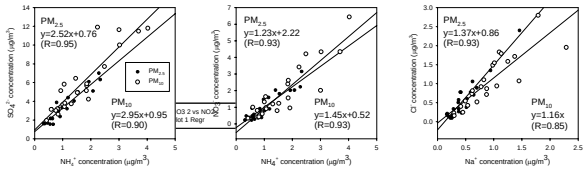
RELATIONSHIPS BETWEEN INORGANIC SPECIES

1. Correlation between gas phase and particulate inorganic species

- Gas phase nitric acid concentrations shown high correlation coefficient with NO_2 (R=0.80), O_3 (R=0.78) in gas phase implying the occurrence of photochemical reactions.
- Correlation between the sum of nitric acid and nitrous acid versus ammonia (in units of nmol/m³) shown that the concentration of ammonia was in large excess compared to the concentrations if individual acidic gases.



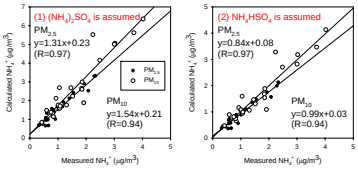
- High correlation coefficients were found between NH_4^+ and SO_4^{2-} (R=0.95 for $PM_{2.5}$ and R=0.90 for PM_{10}), and between NH_4^+ and NO_3^- (R=0.93 for $PM_{2.5}$ and R=0.93 for PM_{10}) during the entire sampling periods.



2. Existing form of secondary inorganic compounds

- Once emitted into atmosphere, NH3 will perferentially react with sulfuric acid o form ammonium bisulfate ($(NH_4)HSO_4$) aerosol or fully neutralized ammonium sulfate ($[NH_4]_2SO_4$). Excess NH3 will then react with HNO_3 to form ammonium nitrate (NH_4NO_3) (Robarge et al., 2002; Koutrakis et al, 1992).
- Particulate phase NH_4^+ can be calculated using the stoichiometric ratios of the different compounds and compared with actual measurements. Ammonium is calculated from nitrate and sulfate, assuming that all nitrate is in the form of NH_4NO_3 and all sulfate is in the form of either $(NH_4)_2SO_4$ (Eq (1)) or NH_4HSO_4 (Eq(2)) (Chow et al., 1996).

(1) Calculated ammonium = 0.38×sulfate+0.29×nitrate
(2) Calculated ammonium = 0.192×sulfate+0.29×nitrate



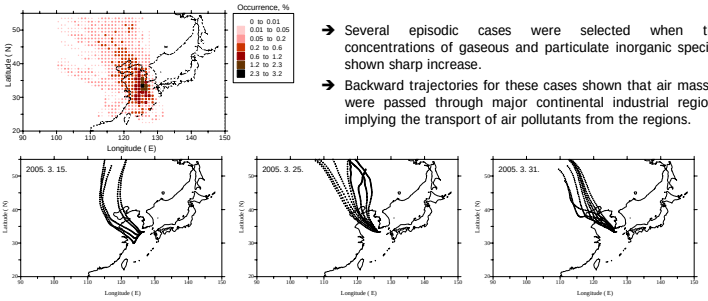
- Comparison of these calculated values and the measured ammonium values shows reasonable agreement of PM_{10} when NH_4HSO_4 is assumed and more neutralization of $PM_{2.5}$ then PM_{10} based on the underestimated values (0.84) when NH_4HSO_4 is assumed.
- Good correlation between Na^+ and Cl^- implies that the measured results were considerably influenced by abundant sea salt particles. The concentration of non-sea salt SO_4^{2-} are calculated as nss-SO_4^{2-}=[SO_4^{2-}]-[Na^+]×0.2516 (Millero and Shon, 1992). Average concentration of nss SO_4^{2-} is 2.6 and 4.5 for $PM_{2.5}$ and PM_{10} respectively, which occupy more than 76% of total sulfate concentration in each size range.
- Equivalent molar ratios between major ion components, NH_4^+/nss SO_4^{2-} (0.83 for $PM_{2.5}$, 0.86 for PM_{10}), also reveals that the existing forms of the secondary aerosols were probably $(NH_4)HSO_4$ and $(NH_4)_2SO_4$.
- Especially, $(NH_4^+ + K^+ + Ca^{2+} + Mg^{2+})/(NO_3^- + \text{nss } SO_4^{2-})$ (0.99 for $PM_{2.5}$, 1.05 for PM_{10}) indicates that some of them existed not only as NH_4NO_3 but also as $CaSO_4$ or KNO_3 combined with the abundant soil components during Asian dust periods.

	$PM_{2.5}$	PM_{10}
NH_4^+/nssSO_4^{2-}	0.83	0.86
NH_4^+/nssSO_4^{2-}+NO_3^-	0.68	0.70
NH_4^+/nssSO_4^{2-}+NO_3^-+Cl^-	0.56	0.54
NH_4^++K^+/nssSO_4^{2-}+NO_3^-	0.75	0.76
NH_4^++K^++Ca^{2+}/nssSO_4^{2-}+NO_3^-	0.88	0.90
NH_4^++K^++Ca^{2+}+Mg^{2+}/nssSO_4^{2-}+NO_3^-	0.99	1.05

➔ These neutralized types of secondary aerosols show that pollutants could be aged and transported from a distance. Moreover, considering Gosan is a relatively clean area free from the industrial pollution sources, the secondary aerosols could be originated from distant sources and transported to the site depending on wind direction.

3. Trajectory analysis for episodic cases

- Backward air trajectory analysis was carried out to find out the possibility of atmospheric transport of secondary inorganic components from distant source.
- 3-day backward trajectories of air masses were calculated at 1000m height (below average mixing height) using FNL achieved meteorology data and HYSPLIT 4 in 1hr time interval.
- During this campaign, about 60% of air masses were transported from North China.



➔ Several episodic cases were selected when the concentrations of gaseous and particulate inorganic species shown sharp increase.

➔ Backward trajectories for these cases shown that air masses were passed through major continental industrial regions implying the transport of air pollutants from the regions.

SUMMARY AND CONCLUSION

- The characteristics of acidic gas pollutants and $PM_{2.5}$/PM_{10} ionic species during ABC-EAREX2005 were evaluated.
- Good correlations between gas phase HNO_3 and NO_2 and between SO_4^{2-} and NO_3^- imply the occurrence of photochemical reaction and secondary aerosol formation in the atmosphere.
- The ratios between sum of nitrate and nitrous acid versus ammonia shown large excess of ammonia, which is the major neutralizing agent in the atmosphere.
- The average mass contribution of particulate secondary ion components was about 26% and 24% of the total $PM_{2.5}$/PM_{10} mass.
- Existing form of secondary aerosol was estimated to NH4HSO4 in PM_{10}, but $PM_{2.5}$ partially shown more neutralized form, $(NH_4)_2SO_4$.
- Trajectory analysis for episodic cases shown these neutralized secondary aerosol can be transported from continental industrial regions.

National Institute of Environmental Research