

TREND OF VISIBILITY IMPAIRMENT CAUSED BY SMOG PHENOMENON IN SEOUL

Nam-Jun Baik[†], Jong-Hoon Lee, Yong Pyo Kim, Kil-Choo Moon and Yung-II Joe*

Environment Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

*Department of Chemical Engineering, Yonsei University, 134, Shinchon-dong, Seodaemun-gu, Seoul 120-749, Korea

(Received 26 September 1994 • accepted 17 March 1995)

Abstract—The characteristics of visual air quality in Seoul have been investigated from March to November 1993. Optical properties, meteorological parameters, and particle characteristics were measured and analyzed. On the average, light scattering by particles is the dominant process in light extinction. Fine particle mass concentration, and the fraction of sulfate, nitrate and ammonium ions in the particles were found to play a major role in influencing the occurrence of a smog episode in Seoul. The role of ambient relative humidity on Seoul visibility is discussed.

Key words: Visibility, Light Scattering, Fine Particles, Relative Humidity, Seoul

INTRODUCTION

Visibility impairment is a complex phenomenon, mainly caused by fine particles (0.1 μm -1.0 μm in diameter) or aerosols. The characteristics of particles, their size distribution and chemical composition during a smog episode are different from those during a clear period. In addition to causing visibility impairment, fine particles also have adverse effects on human health, especially on the respiratory system. The health effects of airborne acidic particulate compound species such as sulfuric acid and ammonium (bi)sulfate have been appreciated recently. Two different human responses to acidic aerosols appear to be reflex bronchoconstriction and altered mucociliary clearance (which might lead to chronic bronchitis). A Harvard study reported that in four out of six cities where acidic particles were measured, there was a better correlation of the prevalence of chronic bronchitis (as diagnosed by a physician) with hydrogen ion concentration in the particles than with total respirable-particle concentration [Committee on advances in assessing human exposure to airborne pollutants et al., 1991].

In this regard, we have studied the optical and chemical characteristics of airborne aerosol to understand the smog phenomenon in Seoul. The city of Seoul is a mega-city with an area of 605 km^2 (0.6% of the total area of South Korea) but has about 25% (11 million) of the total population, 32% of the total vehicles, and more than 40% of the total national production. As a result, severe environmental problems have risen in Seoul including frequent visibility impairment episodes, commonly known as smog.

Several field measurements and modeling studies have been carried out abroad to understand the relationship between visibility and air pollution and to develop control strategies to improve visual air quality since the early 1970s [Sloane and White, 1986]. However few extensive studies have been undertaken in Korea. Lee et al. [1986] measured the composition of PM-2.5 and TSP and applied multivariate statistical analysis results by Groblicki et al. [1981] to their measurements. It is difficult, however, to apply a statistical result of one area to other areas.

Visual range (VR) is commonly related to the total light extinction coefficient, b_{ext} , as shown in Eq. (1).

$$\text{VR}(\text{km}) = \frac{3.912}{b_{\text{ext}} (\times 10^{-3} \text{m}^{-1})} \quad (1)$$

b_{ext} consists of four terms: scattering coefficient by particles, b_{sp} ; absorption coefficient by particles, b_{ap} ; scattering coefficient by gases, b_{sg} ; and absorption coefficient by gases, b_{ag} .

$$b_{\text{ext}} = b_{\text{sp}} + b_{\text{ap}} + b_{\text{sg}} + b_{\text{ag}} \quad (2)$$

The b_{sg} is known as the Rayleigh coefficient with a value of $0.012 \times 10^{-3} \text{m}^{-1}$. The b_{ag} can be calculated by a Hodkinson relation [Hodkinson, 1966] from the NO_2 concentration. Thus, b_{ap} can be estimated from Eq. (2) if both b_{ext} and b_{sp} are measured simultaneously along with NO_2 concentration.

Generally the contribution by gas molecules is minor compared to that by particles. The fine fraction of particles, especially, between 0.1 μm and 1.0 μm in diameter, are known to be mainly responsible for particle light scattering [Sloane and White, 1986; Baik et al., 1994]. The ionic composition of fine particles is also important since the light scattering and/or absorption capacity of a particle is highly dependent on particle composition. Thus, to understand the characteristics of and to develop control strategies against the smog phenomenon in Seoul, both optical properties and particle characteristics, especially those of fine particles, were simultaneously studied.

From March to November 1993, characteristics of the Seoul smog phenomenon have been studied. Optical properties, the total light extinction coefficient, b_{ext} , and the light scattering by particles, b_{sp} , and particle properties, the particle size distribution and PM-3 particles mass loading and ionic composition are measured with meteorological parameters: (1) to quantify the degree of visual air quality and (2) to identify the major variables that contribute to visibility impairment.

MEASUREMENT

The measurement site for this study is located inside the Korea

[†]To whom all correspondences should be addressed.

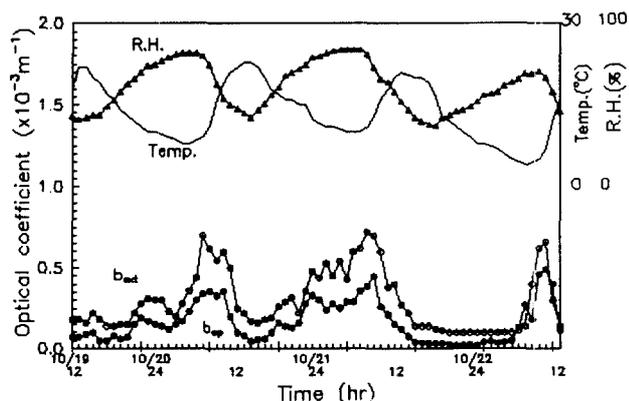


Fig. 1. Variation of optical and meteorological properties during October 1993.

Institute of Science and Technology (KIST) compound in Seoul. The site is located about 1 km from the main streets and 3 km from the business and industry areas and no large stationary pollution sources.

Measurements were conducted between March and November 1993 except during the Yellow sand period to discriminate it from smog phenomenon. Each measurement lasted between three to seven days. In particular, to discriminate the characteristics of smog phenomenon from that of clear period, a transmissometer (Optec model LPV) and a nephelometer (MRI model 1598) were continuously operated to measure b_{ext} and b_{sp} , respectively, along with ambient temperature and relative humidity (RH). A filter sampler with a 3 μm inlet was used to collect fine particles except for the Spring, 1993 measurement for which a cascade impactor has been used. 47 mm teflon membrane filter (Whatman) was used. The nominal aerodynamic $D_{p,50}$ of the sampler inlet is 3 μm and the optical $D_{p,50}$ measured by an optical particle counter is about 2.1 μm . Detailed apparatus and measurement procedures were described by Baik et al. [1994].

RESULTS AND DISCUSSION

Fig. 1 shows a typical diagram of the variations of optical and meteorological parameters. Since the variations of these parameters for other periods show similar trend, only the October results are shown. Optical coefficient values show a typical diurnal variation along with ambient temperature and RH, maximum coefficient values during the morning and minimum values during the afternoon. This trend indicates that the effect of the variation of mixing height is a dominant one that determines the overall visual air quality of Seoul. However, the values of optical properties are clearly distinguished for each measurement period as shown in Table 1 in which average values of optical properties and RH are summarized. During April 1993, the nephelometer was not operated for calibration and no data are available.

During 1993, the average prevailing visibility measured by Korea Administration of Meteorology was about 10.2 km or the b_{ext} value of $0.384 \times 10^{-3} \text{ m}^{-1}$ to which our closest measured value was $0.407 \times 10^{-3} \text{ m}^{-1}$ during August 1993. Thus, the average status of visual air quality at Seoul during 1993 was mild smoggy state. There seems to be no apparent relationship between RH value and optical properties, although, a severe smog episode during November 1993 occurred when RH was high. This point is

Table 1. Seasonal variation of average optical and meteorological properties

Period	Avg. b_{ext} ($\times 10^{-3} \text{ m}^{-1}$)	Avg. b_{sp} ($\times 10^{-3} \text{ m}^{-1}$)	Avg. RH	b_{sp}/b_{ext}	Comment
Mar. 3-5, 1993	0.546	0.367	41	0.67	Smog
Apr. 21-24, 1993	0.497	-	63	-	Smog
Aug. 23-27, 1993	0.407	0.214	78	0.53	Mild smog
Oct. 19-21, 1993	0.297	0.164	62	0.55	Clear
Nov. 3-5, 1993	0.790	0.630	78	0.79	Severe smog

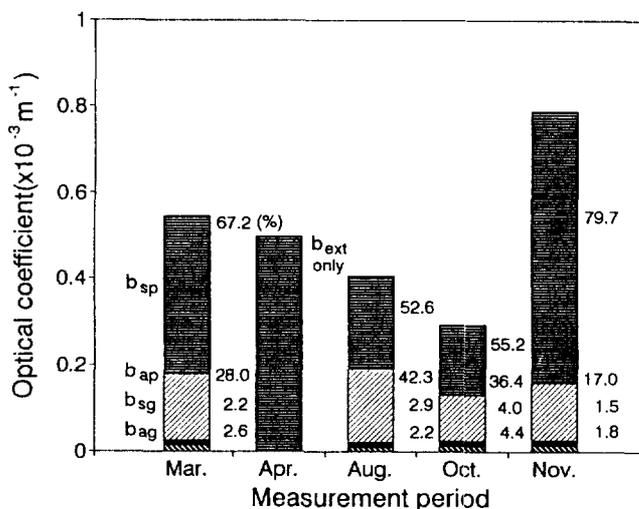


Fig. 2. Seasonal variation of light extinction budget (LEB).

discussed in detail below.

The relative contributions of b_{sp} to total light extinction vary widely as shown in Table 1 and Fig. 2, but fall in two categories, between 50% and 55% for clear and moderately smoggy periods and between 67% and 79% for smoggy periods. The relative contributions of gas molecules are less than 10% for all periods, with similar values for all periods. The contribution by particulate light absorption, b_{ap} , calculated from Eq. (2), is also shown in Fig. 2. The absolute values of b_{ap} do not vary noticeably for all periods, but the relative contributions of b_{ap} to b_{ext} vary between 36% and 43% for clear and moderately smoggy periods and between 17% and 28% for smoggy periods. Therefore, it is concluded that the absolute values of the b_{ap} , b_{sg} , and b_{ag} terms are relatively constant throughout the year while the values of b_{sp} vary widely and thus determine the degree of visibility impairment in Seoul.

The size distribution data shown in Fig. 3 clearly imply that the fine fraction of particles are mainly responsible for light scattering. All the size distribution data were measured by a cascade impactor. The measured histogram was converted to the continuous size distribution by the Twomey algorithm [Twomey, 1975]. The measured size distributions are typical bimodal type with the two mean peak sizes around 0.5 μm and 5 μm . The absolute values of the fine fraction peak during the clear and mild smoggy periods, Aug. and Oct., 1993 (20-40 $\mu\text{g}/\text{m}^3$) are smaller by a factor of two to eight than those during the smoggy periods, Mar., Apr., and Nov., 1993, (100-170 $\mu\text{g}/\text{m}^3$). Furthermore, the peaks at the coarse particle fraction during the clear and mild smoggy periods are generally higher than those at the fine particle fraction for the measurements during Aug. and Oct., 1993.

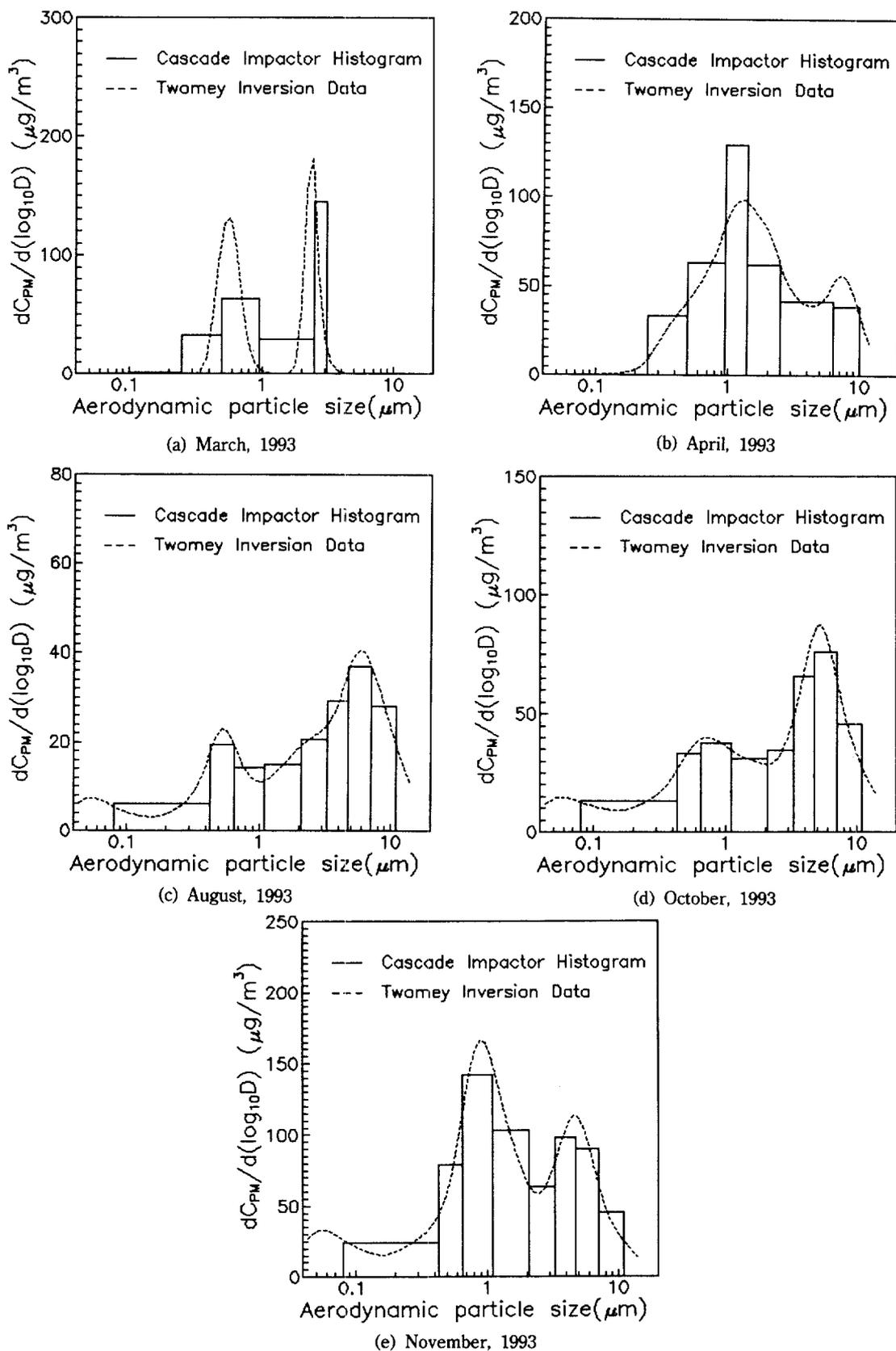


Fig. 3. (a)-(e). Seasonal variation of the particle size distribution.

Fig. 4 shows the relation between the optical properties (b_{ext} and b_{sp}) and PM-3 concentrations. The figure demonstrates the significance of fine particle fraction on visibility impairment. The

data were fitted by a linear regression. In Fig. 4, excluding the data for April, 1993 which is four day average, all data points were sampled at either 24 hr or 12 hr intervals. The PM-3 concen-

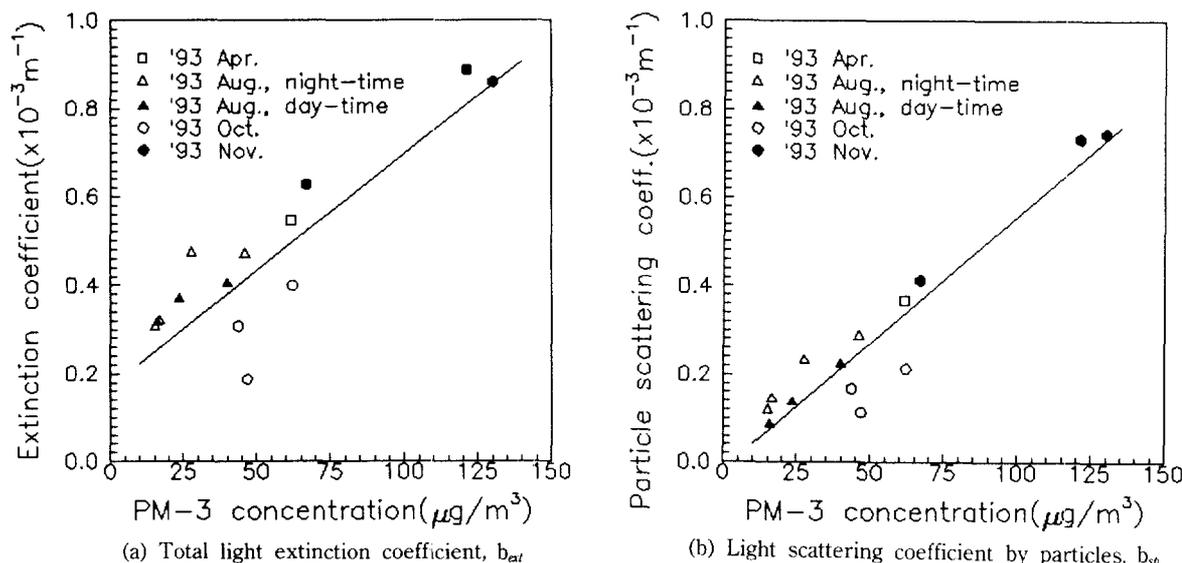


Fig. 4. (a), (b). Correlation between PM-3 concentration and optical properties.

Table 2. Size distributed ion concentrations measured during April, 1993¹⁾

Particle size (μm)	Concentration ($\mu\text{g}/\text{m}^3$)								
	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	Mass ²⁾
-0.25 ³⁾	-	-	-	-	-	-	-	-	16.6
0.25-0.50	0.39	N/D	N/D	0.37	0.16	1.54	0.48	0.04	7.8
0.50-0.96	0.95	N/D	N/D	N/D	0.04	2.85	1.39	0.09	16.8
0.96-1.40	0.35	N/D	N/D	0.68	0.27	2.42	1.26	0.07	15.6
1.40-2.50	0.08	N/D	N/D	0.19	N/D	1.20	1.27	0.07	21.2
2.50-6.30	0.05	N/D	N/D	0.81	0.09	0.58	0.83	0.09	17.9
6.30-10.0	0.05	N/D	N/D	0.25	0.05	0.22	0.27	0.02	10.1
Sum (0.25-2.5)	1.77	N/D	N/D	1.24	0.48	8.02	4.41	0.25	61.4
Sum	1.87	N/D	N/D	2.30	0.62	8.82	5.51	0.36	106.0

¹⁾Measurement period: Apr. 21, 11:40 a.m.-Apr. 24, 11:25 a.m. (about 72hr); Teflon 47mm diameter filter was used

²⁾Average TSP concentration during the sampling period measure by a Hi-Volume air sampler was $226.3 \mu\text{g}/\text{m}^3$

³⁾No ion analysis has been carried out for this size cut

tration is in close relationship with both b_{ext} and b_{sp} , but is better with b_{sp} . Note that b_{ext} is the sum of b_{sp} and other three terms in Eq. (2). A similar tendency has been widely observed at Denver [Groblicki et al., 1981], Los Angeles area [Larson and Cass, 1989], and Seoul [Baik et al., 1994].

The ion concentrations are shown in Tables 2, 3 and 4 for each measurement period. The size distributed ionic concentration results for the April measurement in Table 2 clearly show that most ions exist in the fine fraction of particles while the mass concentration of the fine fraction is only about 60%. The only exception for this trend is Ca^{2+} ion which originates from crustal materials. In Table 3, ionic compositions of daytime and nighttime are given for the summer measurement. The data show that sulfate concentration is higher during daytime than nighttime while nitrate and chloride show opposite trend. Ammonium concentration shows no such diurnal trend. The possible reason for this trend is currently under investigation. Table 4 shows ionic compositions of a clear period, October, and a severe smog period, November, respectively. While other ion concentrations for both periods do

Table 3. Ion concentrations of PM-3 measured during August, 1993¹⁾

Sampling period	Concentration ($\mu\text{g}/\text{m}^3$)					Mass
	NH_4^+	K^+	SO_4^{2-}	NO_3^-	Cl^-	
8/23 N ²⁾	2.06	N/D	8.38	2.94	1.06	46.0
8/24 N	0.26	N/D	2.51	0.16	1.21	5.2
8/25 D	1.51	N/D	9.35	0.42	0.57	39.9
8/25 N	0.41	N/D	3.85	0.29	0.66	16.4
8/26 D	0.52	N/D	4.80	N/D	0.53	15.8
8/26 N	0.80	N/D	2.35	0.16	1.11	27.6
8/27 D	1.24	7.75	7.99	0.12	0.24	23.3
8/27 N	0.56	N/D	4.93	0.33	1.58	15.0
Daytime average	1.09	-	7.38	0.27	0.45	26.3
Nighttime average ³⁾	0.82	-	4.04	0.78	1.12	22.0
	(0.96)	-	(4.88)	(0.93)	(1.10)	(26.3)
Total average	0.92	-	5.52	0.63	0.87	23.6

¹⁾Concentrations of Na^+ , Ca^{2+} , and Mg^{2+} ions are below the detection limits

²⁾Sampling time of each period is 12 hr;

N: 8:00 p.m.-8:00 a.m.; D: 8:00 a.m.-8:00 p.m.

³⁾When excluding 8/24 N data, it rained during the daytime on Aug. 24

Table 4. Ion concentrations of PM-3 measured during Oct. and Nov., 1993

Sampling period	Concentration ($\mu\text{g}/\text{m}^3$)								
	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	Mass
10/19	0.93	0.15	0.04	0.04	0.01	2.84	2.44	2.32	43.5
10/20	1.09	0.08	0.05	0.05	0.02	5.13	3.72	1.98	62.2
10/21	0.83	0.52	0.32	0.07	0.02	2.73	1.09	3.76	46.8
Average	0.95	0.25	0.14	0.05	0.02	3.57	2.42	2.69	50.8
11/3	3.90	0.09	0.08	0.06	0.02	20.97	16.06	2.34	121.2
11/4	3.03	0.10	0.06	0.05	0.01	11.80	6.06	2.06	66.8
11/5	3.57	0.12	0.07	0.13	0.02	14.32	14.28	4.28	130.0
Average	3.50	0.10	0.07	0.08	0.02	15.70	12.13	2.89	106.0

not differ significantly, concentrations of sulfate, nitrate, and ammonium ions differ significantly. It demonstrates the importance

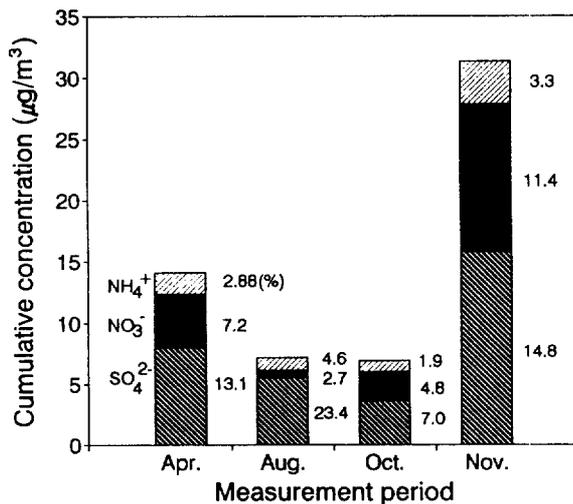


Fig. 5. Seasonal variation of the major PM-3 ionic species.

of these ions on visibility.

Ion balance of cations and anions shown in Tables 2 and 4 indicate that there were excess anions for all periods, i.e., PM-3 in Seoul are acidic. The amount of excess anion ranges between 8 to 400 nano-eq/m³. Also, metal cation concentrations (Na⁺, Ca²⁺, Mg²⁺, and K⁺) were generally very low, sometimes below the detection limits. Considering that the concentrations of these ions were reported to be significant [Shin and Kim, 1992], this trend clearly show that fine particles are mostly from non-crustal sources. Nitrate concentration in PM-3 was high for all periods except summer, Aug., 1993, more than 50% of sulfate mass concentration. The average nitrate and sulfate concentrations in PM-2.5 during 1985 were 0.2 µg/m³ and 9.7 µg/m³, respectively, with nitrate being only about 2% of sulfate mass concentration [Lee et al., 1986]. This trend reflects the drastic increase of the number of automobiles and the change of fuel from coal and heavy oils to natural gas and light oils in Seoul.

Since the distance from the Yellow sea to the sampling site was about 40 km and the prevailing wind was westerly, the effect of sea salt was expected to be noticeable. But chloride concentration is higher than sodium concentration, in molar base, two to seven times. Higher chloride concentration meant that there are chloride emission sources in and around Seoul other than from sea. Since Seoul metropolitan area is one of the most industrialized areas in Korea, the city contains many chloride emission sources.

The contribution of water activity to visibility impairment is twofold: (1) Water can associate with ionic species in fine particles of which the diameter is less than 0.1 µm and thus increase the size of fine particles to 0.1 µm-2.0 µm diameter which is effective in scattering visible light; and (2) Water itself is an effective light scattering species. Therefore, when the concentrations of ionic species are similar, as is the case for Aug. and Oct., 1993, water activity or relative humidity affects the optical properties, yielding higher optical coefficient values with higher RH value during Aug., 1993 than Oct., 1993.

CONCLUSIONS

Field studies of optical coefficients along with meteorological parameters and the fine particle mass concentration and composition have been carried out between March and November, 1993.

Variations of optical coefficients and relative humidity showed a strong diurnal variation pattern; high values during the night and low values during the day, implying visibility in Seoul is mainly governed by the diurnal variation of temperature and, thus, mixing height. Light scattering by particles was the dominant process, especially, during the smog episode periods, comprising about 70%-80%, comparing to 50%-60% during the clear period.

Occurrence of visibility impairment episodes is closely related to the concentration of fine particles and the fraction of ionic species in fine particles. The concentration of PM-3 and optical coefficients (b_{sp} and b_{ext}) show linear relationship. Sulfate concentration is higher than nitrate for all periods. Elevated sulfate and nitrate concentrations have been observed during the smog episode. When fine particle mass concentrations are similar for two periods, the fraction of sulfate, nitrate, and ammonium ions are critical to the occurrence and severeness of smog. The concentration of nitrate has drastically increased compared to the 1985 measurement data. A smog episode could be characterized by high mass loadings of PM-3 particles and larger fractions of sulfate, nitrate, and ammonium ions in the fine particles. Due to both the acidic nature and the size of fine particles, a smog episode may cause harmful effects on the human respiratory system. High relative humidity was one of the important factors for a smog episode to be a severe one.

ACKNOWLEDGEMENTS

This work was supported by the Korea Ministry of Science and Technology and the Korea Ministry of Environment under Project No. N10300 and N12140.

NOMENCLATURE

- VR : visual range [km]
 b_{ext} : extinction coefficient [$\times 10^{-3} \text{ m}^{-1}$]
 b_{sp} : scattering coefficient by particle [$\times 10^{-3} \text{ m}^{-1}$]
 b_{op} : absorption coefficient by particle [$\times 10^{-3} \text{ m}^{-1}$]
 b_{sg} : scattering coefficient by gas [$\times 10^{-3} \text{ m}^{-1}$]
 b_{og} : absorption coefficient by gas [$\times 10^{-3} \text{ m}^{-1}$]
 RH : relative humidity [%]
 $D_{p,50}$: 50% cut off particle diameter [µm]

REFERENCES

- Baik, N. J., Kim, Y. P. and Moon, K. C., "Visibility Study in Seoul, 1993", submitted to *Atmos. Environ.*(1994).
 Committee on Advances in Assessing Human Exposure to Airborne Pollutants, Board on Environmental Studies and Toxicology, Commission on Geosciences, Environmental, and Resources, and National Research Council, "Human Exposure Assessment for Airborne Pollutants", National Academy of Sciences, Washington, D.C., 1991.
 Groblicki, P. J., Wolff, G. T. and Countess, R. J., "Visibility-reducing Species in the Denver 'Brown Cloud' -I. Relationship between Extinction and Chemical Composition", *Atmos. Environ.*, **15**, 2473 (1981).
 Hodkinson, J. R., "Calculations of Color and Visibility in Urban Atmospheres Polluted by Gaseous NO₂", *Int. J. Air Wat. Pollut.*, **10**, 137 (1966).
 Larson, S. M. and Cass, G. R., "Characteristics of Summer Midday Low-Visibility Events in the Los Angeles Area", *Environ. Sci.*

- Technol.*, **23**, 281 (1989).
- Lee, M. H., Han, E. J., Han, J. S., Chung, H. D. and Han, J. K., "A Study on Characteristics of Aerosol in Atmosphere", Report of National Institute of Environmental Research, KOREA 86-04-170, **8**, 65 (1986).
- Shin, E. S. and Kim, H. K., "Influence of Yellow Sand on TSP in Seoul", *J. KAPRA*, **8**, 52 (1992).
- Sloane, C. S. and White, W. H., Visibility: "An Evolving Issue", *Environ. Sci. Technol.*, **20**, 760 (1986).
- Twomey, S., "Comparison of Constrained Linear Inversion and an Iterative Nonlinear Algorithm Applied to the Indirect Estimation of Particle Size Distribution", *J. Comput. Phys.*, **18**, 188 (1975).