# Study on Chemical Characterization of $PM_{10}$ Observed in Korean Peninsula, 1998 ~ 2001

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This study was conducted to investigate the chemical characteristics of $PM_{10}$ at Anmyeon-do during the periods from January 1998 to December 2001. The $PM_{10}$ samples ($PM_{10}$) were collected by High Volume Air sampler (HVAS). The measured items were mass concentration of $PM_{10}$ with the major ions ($Cl^-$, $SO_4^{2-}$, $NO_3^-$, $Mg^{2+}$, $Ca^{2+}$, $K^+$ etc.) and metallic elements (Al, Fe, Mn, Cr, Zn, Pb etc.). The chemical analysis of major ion components were made by Ion Chromatography (DX-500) and that of metallic elements were made by Inductively Coupled Plasma Spectrometer (ICP-AES, ICP-Mass). The average mass concentration of $PM_{10}$ increased substantially during the heavy dust periods (Asian Dust cases). For water-soluble ions, concentrations of $Ca^{2+}$, $SO_4^{2-}$ and $NO_3^-$ were remarkably enhanced. Concentrations and mass fraction of crustal elements such as Na, Mg, Ca, Fe, Mn were highly elevated, but those of pollution-derived heavy metals were appreciably decreased. The factor analysis was conducted in order to make the large and diverse data set as manageable levels and to qualitatively examine the relationship between the variables.

Key words : Chemical characteristic, $PM_{10}$, Major ion, Metallic element, Asian Dust

## 1. Introduction

Atmospheric particles are emitted from natural sources such as sea spray and volcanic emissions, and from anthropogenic processes such as fossil fuel combustion and industrial emissions. Some of the sources are neither purely natural nor purely anthropogenic. Soil dust is classified as natural source but with anthropogenic influence, and biomass burning is vice versa. Since the source of atmospheric particles is highly inhomogeneous and their atmospheric lifetime is short, concentrations and chemical composition of PM10s are widely variable in time and space. Furthermore, anthropogenic $PM_{10}$ have increased dramatically over the past century and implicated in global climate change through their direct and indirect role in Earth's radiation balance[1]. As a result, there is large uncertainty associated with estimating the climatic effect of $PM_{10}$.

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The main objective of Global Atmosphere Watch (GAW) is to provide data and other information on the chemical composition and related physical characteristics of the atmosphere and their trends, required to improve understanding of the behavior of the atmosphere of the atmosphere and its interactions with the oceans and the biosphere. Locations for GAW regional stations should be selected in such a way that the observations are representative for a significant portion of the region and are not unduly affected by nearby pollution sources or by significant land-use changes. Anmyeon-do represents clean background air as Korea Global Atmosphere Watch Observatory (KGAWO) station of World Meteorological Organization (WMO).

Soil dust is a major source for coarse $PM_{10}$ particles and its annual global emission amounts to ~1500 Tg, which is about 40 % of the total source[2]. Because of the large amounts involved, mineral dust is thought to have a considerable effect on the planetary radiation balance. They also affect human health and the life of terrestrial and aquatic ecosystems, after being deposited onto the soil and surface waters[3)]. Mineral dust originates mainly from desert and semi-desert regions in northern Africa and central Asia and is transported long distance to the North Atlantic and North Pacific[4)]. Arid and semi-arid regions in northern and northwestern China are major source for mineral $PM_{10}$ particles and for various trace elements including iron and aluminum in the air and water of the North Pacific region[5)]. A geochemically significant quantity of Asian dust, currently estimated to be 400~500 Tg, is deposited in the North Pacific each year[6)] In spring, dust storms take place in deserts and dry loess plateau (e.g. Gobi and Taklamakan in Mongolia and northwest China). These vast areas are located in the lee of the massive East Asian Mountains where a convergent airflow and a lee cyclone take place on a synoptic scale. The down-slope forms a very dry surface and annual rainfall in the majority of the desert and/or semi-desert area is less than 300 mm. In particular, a convergent flow in a lee cyclonic system enhances an upward motion and dust produced by mechanical and dynamic turbulence can be transported to the mid-troposphere. Hence the Asian Dust is typically observed in East Asian countries including China, Korea and Japan in springtime.

During Asian Dust period, several observations have been made in the eastern part of China[7)], Japan[8)], and the North Pacific Ocean[12),13)]. Cho[8)] and Kim et al[9)] reported that the number concentration of $PM_{10}$ in Korea was relatively higher in spring than other seasons. However, there are still very few sets of observed data in Korea, particularly for chemical compositions[10]. Thus it is required to carry out more research to investigate factors determining physical, optical, or chemical properties of $PM_{10}$, particularly during Asian Dust event in Korea. Since the concentration of different species in the atmospheric $PM_{10}$ has been significantly affected by human activities, the study of the elemental composition of the particles is of crucial for environmental management on local, regional and continental scales. In this study, particulate smaller than 10 μm were collected in Anmyeon-do. Through the chemical and statistical analysis of particulate composition, the attempt was made to elucidate the chemical characteristics and contributing sources of $PM_{10}$ in Anmyeon-do.

## 2. Experimental Methods

The particles with an aerodynamic diameter smaller than 10 μm ($PM_{10}$) were collected on cellulose membrane filters exposed for 24 hours (from 0010 to 0010 LST) using high volume samplers (Andersen) at the average flow rate of 1.1 $m^3min^{-1}$. Filters were pre-weighted and then dried in a desicator for at least 24 hours after being exposed to the air. Before the final weighing, filters were stored in an environmental chamber (HOTPACK model 305502, Customer & Technical Service, U.S.A.) for 24 hours at a constant humidity (50 % RH) and temperature between 20 and 23 ℃.

Chemical analysis was done for soluble ionic species such as $NO_3^-$, $SO_4^{2+}$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ and metallic elements such as Al, Ca, Mg, Na, Fe, Mn, Cr, Co, Ni, Cu, Zn, Cd, Pb and U. The filters were shaken for 30 minutes in deionized water and an extract was filtered through a 0.45 μm cellulose acetate membrane. The filtrate was then analyzed for water-soluble ionic species using ion chromatography(DX-500). Metal ions were extracted with 5 ml of mixed acids ($HF$:$HNO_3$: $HClO_4$=4:4:1) in 60 ml Teflon beaker. GR grade reagents were used after being refined employing quartz and Teflon sub-boiling reflux system. Al, Fe, Ca, Mg, Na, and Mn were determined using Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP/AES, Shimaz ICP-IV). Inductively Coupled Plasma Mass Spectrophotometer (ICP/MS, VG PQⅡ+) was used for the analysis of Cr, Co, Ni, Cu, Zn, Cd and Pb. ICP/AES system was calibrated for every 10 samples and internal standards were added to standards and samples for the analysis using ICP/MS. Meteorological parameters including air temperature, relative humidity, wind speed and direction, barometric pressure, and solar radiation were concurrently measured.

## 3. Results and Discussion

Figure 1 shows the time-series variation of monthly mean concentrations of $PM_{10}$ observed in Anmyeon-do from January 1998 to December 2001. For regular dust case(circule), average mass concentration was increased but not significantly. Particularly, the $PM_{10}$ concentration of $PM_{10}$ was far above the Korean air quality of 150 $\mu g/m^3$ (24-hour average).

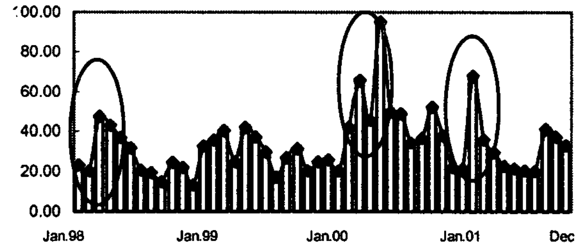


Fig.1. Time-series variation of monthly mean concentrations ($ug/m^3$) of $PM_{10}$ observed in Anmyeon-do from January 1998 to December 2001.

And the time trend of $PM_{10}$ was opposite to the trend of rainfall. Low $PM_{10}$ in summer was presented by dilution processing of a heavy rainfall.

Table 1 shows the annual mean concentrations of ion components and metallic elements in $PM_{10}$ from January 1998 to December 2001. A pattern of the monthly mean of major ion concentrations in $PM_{10}$, a pattern is similar to the trend of mass concentration. The mass concentration showed a top at 2000, the ion concentration showed the maximum price at 1999. Against this cause it is resaarching with Meteorological parameters including air temperature, relative humidity, wind speed and direction, barometric pressure, and solar radiation.

Among the major ions, $Na^+$ and $Cl^-$ was accounted of about 10% of the cation and anion value. Observed concentration of $Na^+$ and $Cl^-$ can be explained by a marine source. The contribution of observed $SO_4^{2-}$ and $NO_3^-$ on total anion concentration is approximately above about 45% and each year a distinctive two ions ($SO_4^{2-}$ and $NO_3^-$) contribution maximum occurred during the spring months and dropped to a summer.

Table 1. Annual mean concentrations of ion components and metallic elements in $PM_{10}$ from January 1998 to December 2001.

| | unit | 1998 | 1999 | 2000 | 2001 |
|---|---|---|---|---|---|
| mass | $\mu g/m^3$ | 27.30 | 31.04 | 40.70 | 31.60 |
| $Cl^-$ | $\mu g/m^3$ | 0.98 | 1.19 | 0.83 | 0.85 |
| $NO_3^-$ | $\mu g/m^3$ | 3.44 | 4.75 | 2.83 | 2.47 |
| $SO_4^{2-}$ | $\mu g/m^3$ | 3.46 | 5.60 | 3.22 | 2.74 |
| $Na^+$ | $\mu g/m^3$ | 0.71 | 0.95 | 0.68 | 0.70 |
| $NH^+$ | $\mu g/m^3$ | 1.74 | 2.87 | 2.61 | 1.81 |
| $K^+$ | $\mu g/m^3$ | 0.29 | 0.46 | 0.23 | 0.22 |
| $Mg^{2+}$ | $\mu g/m^3$ | 0.10 | 0.15 | 0.09 | 0.10 |
| $Ca^2+$ | $\mu g/m^3$ | 0.35 | 0.53 | 0.36 | 0.43 |
| s-$SO_4^{2-}$ | $\mu g/m^3$ | 0.18 | 0.24 | 0.17 | 0.18 |
| ns-$SO_4^{3-}$ | $\mu g/m^3$ | 3.28 | 5.36 | 3.05 | 2.56 |
| s-$Ca^{2+}$ | $\mu g/m^3$ | 0.03 | 0.04 | 0.03 | 0.03 |
| ns-$Ca^{2+}$ | $\mu g/m^3$ | 0.32 | 0.49 | 0.34 | 0.40 |

| | unit | 1998 | 1999 | 2000 | 2001 |
|---|---|---|---|---|---|
| Na | $\mu g/m^3$ | 27.30 | 30.58 | 40.70 | 31.60 |
| Mg | $\mu g/m^3$ | 141.65 | 115.23 | 97.61 | 64.80 |
| Al | $\mu g/m^3$ | 53.22 | 55.49 | 35.26 | 27.27 |
| Ca | $\mu g/m^3$ | 1.01 | 0.85 | 1.45 | 1.19 |
| Fe | $\mu g/m^3$ | 91.92 | 130.72 | 62.54 | 57.14 |
| Mn | $ng/m^3$ | 0.68 | 0.53 | 0.83 | 0.86 |
| Co | $ng/m^3$ | 24.55 | 18.43 | 19.25 | 10.68 |
| Ni | $ng/m^3$ | 0.80 | 0.39 | 0.38 | 0.49 |
| Cu | $ng/m^3$ | 3.07 | 3.28 | 3.12 | 4.03 |
| Zn | $ng/m^3$ | 92.01 | 85.96 | 33.88 | 32.83 |
| Cd | $ng/m^3$ | 70.85 | 71.45 | 66.01 | 78.63 |
| Pb | $ng/m^3$ | 1.16 | 1.48 | 1.53 | 1.84 |
| U | $ng/m^3$ | 41.05 | 54.47 | 51.82 | 47.95 |

This result caused by spring dust, the so-called Asian dust, transported across the North-

West China and by summer rainfall. On the other hand, the contribution of ns-$Ca^{2+}$ originate from crystal material, is calculated the highest value in the late autumn to early spring. But this reason is same that. Concentrations and mass fraction of crustal elements such as Na, Mg, Ca, Fe, Mn and Co were highly elevated, but those of pollution-derived heavy metals were appreciably decreased.

## 4. Conclusion

This study was conducted to investigate the chemical characteristics of $PM_{10}$ at Anmyeon, which represents clean background air as local Global Atmosphere Watch(GAW)/WMO station - during the periods from January 1998 to December 2001. The measured factors were mass concentration of $PM_{10}$ with the major ions ($Cl^-$, $SO_4^{2-}$, $NO_3^-$, $Mg^{2+}$, $Ca^{2+}$, $K^+$ etc.), metallic elements (Al, Fe, Mn, Cr, Zn, Pb etc.) and meteorological parameters. The average mass concentration and ion concentration of $PM_{10}$ increased during the Asian Dust case). Major ions concentrations of ns-$Ca^{2+}$, ns-$SO_4^{2-}$ and $NO_3^-$ were remarkably enhanced. Crustal elements such as Na, Mg, Ca, Fe, Mn were highly elevated, but those of pollution-derived heavy metals were appreciably decreased

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