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CHARACTERIZATION OF $PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$ IN AMBIENT AIR, YOKOHAMA, JAPAN
横浜における大気中 $PM_{2.5}$、$PM_{2.5\text{-}10}$、および $PM_{>10}$ の性状

○Khan Md. Firoz[1], Yuichiro Shirasuna[2], Koichiro Hirano[2] and Shigeki Masunaga [1]
([1]Graduate School of Environment & Information Sciences, Yokohama National University,
[2]Yokohama City Research Institute for Environmental Science)
○Khan Md. Firoz[1]、白砂裕一郎 [2]、平野耕一郎 [2]、益永茂樹 [1]（[1]横国大･院･環情、[2]横浜市･環境研）

Introduction: Deterioration of urban air quality has now become a prime issue both in developed and developing countries. Air pollution due to airborne Particulate Matter (PM) in the urban atmosphere has been identified to be severely harmful for human health[1]. Airborne particles are also largely responsible for reducing visibility in urban atmosphere[2], material decay, and global climate change. Particulate Matter by mass does not provide a clear understanding of a local PM pollution problem as well as its potential impact on human health. Therefore, current situation demands the need for further studies to explore the behavior of chemical species in PM. Present study aims to investigate the level of ambient $PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$ and study the characterization of carbonaceous aerosol and water soluble ions in the above size segregated PM, Yokohama, Japan.

Material and Methods

Sampling site: The main study area of the current research is focused on Yokohama, Japan. The city of Yokohama is located about 18 miles to the southwest of central Tokyo. Currently sampling site has been selected and operated at the rooftop of a three stored building of Yokohama National University campus.

Analysis of PM samples: MCI air sampler accommodated with a NILU impactor (Norwegian Institute for Air Research) has been used to collect $PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$. The air flow of the impactor has been maintained at 20 L/min during collection of samples with quartz fiber filter (PALLFLEX, 2500QAT-UP). The samples have been collected on 24 hours basis and twice in a week.

samples have been extracted into an ultrasonic bath and by a mechanical shaker to measure various water-soluble inorganic ions. Ion chromatography (Dionex, DX-320) is used to measure SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} ions.

Analysis of carbonaceous fraction: Elemental Carbon and Organic Carbon in particulate samples has been analyzed by thermal oxidation with CHN CORDER (Yanaco Co., Ltd, MT-3).

Results and Discussion

$PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$: A total of 58, 54 & 46 samples of $PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$ are collected in the current sampling location. The average concentration of $PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$ ranged from 3.63 to 47.77 ug/m^3, 2.07 to 46.14 ug/m^3 and 4.44 to 15.33 ug/m^3, respectively. The overall mean concentration has also been reported for the period of Sep 27, 2007 and Apr 26, 2008 as 20.18, 9.43 and 5.16 ug/m^3 for the above fractions. The overall mean concentration of $PM_{2.5}$ has shown significantly high concentration in the current study area. The current level of particle pollution is found above the US EPA (15 ug/m^3) and WHO (10 ug/m^3) annual ambient air

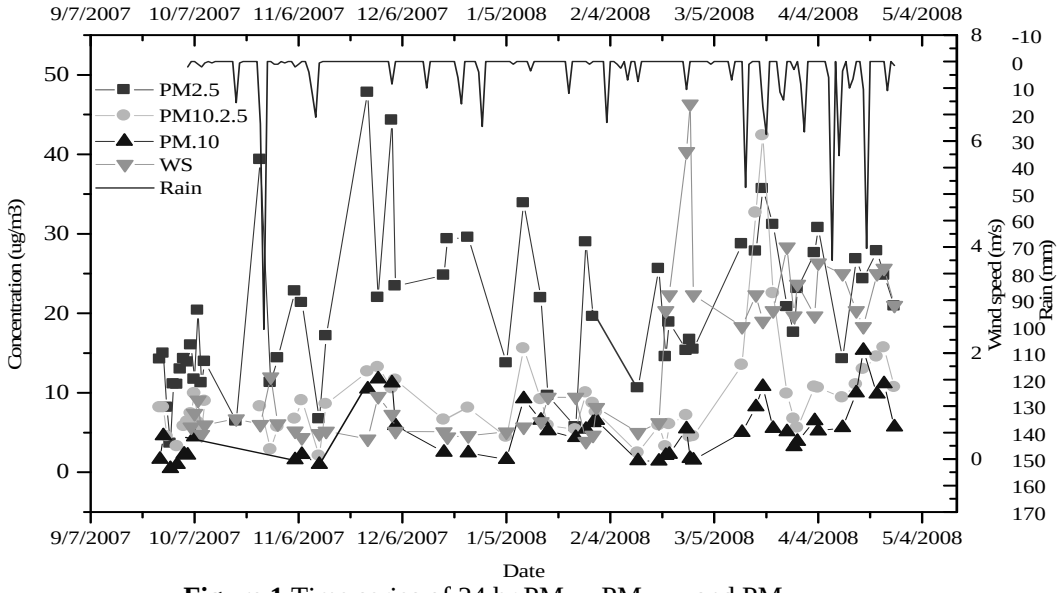

Figure 1 Time series of 24 hr $PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$

quality guidelines. Therefore, the current level of $PM_{2.5}$ has become significant and informative to the Ministry of Environment, Japan. It will help them out to include $PM_{2.5}$ as a criteria pollutant. The $PM_{2.5}$ shows a very good seasonal pattern with frequent sharp decrease as shown in Figure 1, because of the high frequency of rain events. The mean $PM_{2.5}$ has been found elevated in Dec, 2007 because the atmosphere is very stable due to low and steady wind speed during winter months. Temperature was also found lowest level with low relative humidity. Thus, stable, cold and dry meteorology in winter months favors the prolonged life of $PM_{2.5}$ in ambient air. However, there are some low concentration days due to several days of snowfalls in Yokohama (Jan 23, Feb 03 and Feb 9, 2008). Similar trend has been found for $PM_{10\text{-}2.5}$ and $PM_{>10}$. The concentration levels of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ are also shown high during Mar 13, 2008 and Apr 21, 2008. During the above period as exemplified in Figure 1, wind speed is reported highest in the whole sampling period. It is also assumed that the arrival of spring dust storm originated from East Asia has a suspected role to exhibit maximum concentrations[3].

Water soluble ions: The concentration of water soluble ions in $PM_{2.5}$ accounted for 34.9%. The concentration of sulfate, nitrate and ammonium found highest among all ions in $PM_{2.5}$. The mean level of ions in $PM_{10\text{-}2.5}$ accounted for 31.3% and major ions are shown Cl^-, NO_3^- and Na^+. The ions concentration in $PM_{>10}$ accounted for 23.6%. The individual ion concentration in $PM_{>10}$ is shown relatively low. The mean molar ratio of NO_3^-/SO_4^{2-} (autumn and winter) has been calculated as 0.80. The molar ratios of NO_3^-/SO_4^{2-} suggested that stationary and mobile emissions are equally important for $PM_{2.5}$ in Yokohama. In winter months, SO_4^{2-} level has shown significantly low due to low temperature and relative humidity. Although NO_3^- level had high episode during the end of Nov, 2007 and Feb, 2008. Therefore, the molar ratio of NO_3^-/SO_4^{2-} exhibited high during winter months and suggests that the contribution of mobile sources is predominant over stationary sources in winter months. The molar ratio of Cl^- and Na^+ has also been calculated in all three size fractions. $PM_{10\text{-}2.5}$ has a good agreement with the molar ratio of Cl^- and Na^+ for the pure sea salt (1.17). Therefore, Cl^- in $PM_{10\text{-}2.5}$ in the current study may originate from Tokyo Bay. The ratio of Cl^-/Na^+ for $PM_{2.5}$ has shown very high during winter. This fact can be explained that the consumption of coal contributed Cl^- of $PM_{2.5}$ into ambient aerosol since coal contains about 0.1% Cl^- [4]. Contribution of sea salt particles can be estimated by calculating the non-sea salt particles i.e. nss-SO_4^{2-} and nss–K^+ [5]. The contribution of nss-SO_4^{2-} and nss–K^+ ranged from 92 - 95% and 95 - 98% in $PM_{2.5}$.The contribution of nss-K^+ in $PM_{10\text{-}2.5}$ ranged 46 - 76% and 76% - 97% in $PM_{>10}$. The above fact suggests that the major sources of SO_4^{2-} and K^+ in $PM_{2.5}$ are non-marine sources. However, the dominant source of K^+ ion in $PM_{10\text{-}2.5}$ is marine sea salt.

Elemental Carbon (EC) and Organic Carbon (OC): The average OC and EC concentration found in $PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$ are 3.20 and 1.99 ug/m^3; 1.11 and 0.24 ug/m^3 & 0.49 and 0.23ug/m^3, respectively. The OC and EC have shown a clear seasonal pattern in $PM_{2.5}$; OC shows strong shifting in winter whereas EC level is found steady in $PM_{10\text{-}2.5}$ for the whole period. EC and OC level are shown very low in $PM_{>10}$ with maximum OC concentration in winter months. Strong linear and similar OC-EC correlations are found in $PM_{2.5}$ for autumn and winter giving an indication that the sources may be similar. OC-EC correlations in $PM_{10\text{-}2.5}$ and $PM_{>10}$ are varied markedly indicating the presences of various sources. The contribution of secondary organic carbon (SOC) concentration to total OC and their seasonal pattern has exhibited similar as the OC/EC ratio drops sharply in winter due to high EC level in $PM_{2.5}$. SOC in December and January are shown little high concentration compared with other months as the total OC is strongly shifted in that months for $PM_{10\text{-}2.5}$ and $PM_{>10}$.

Conclusion: The mean concentration of $PM_{2.5}$, $PM_{10\text{-}2.5}$ and $PM_{>10}$ and chemical compositions in the above size fractions have shown significant variation during autumn and winter in Yokohama, Japan. The overall mean concentration of $PM_{2.5}$ has exceeded USEPA and WHO annual guidelines. The $PM_{2.5}$ has accounted highest content of water soluble ions. The molar ratio of NO_3^-/SO_4^{2-} exhibited high during winter and concluded that the contribution of mobile sources predominant over stationary sources in winter months. Cl^- content in $PM_{10\text{-}2.5}$ of the current study may originate from Tokyo Bay and it is also concluded that the consumption of coal contributed Cl^- into ambient $PM_{2.5}$ aerosol. The major sources of SO_4^{2-} and K^+ in $PM_{2.5}$ are non-marine sources. However, large proportion of K^+ in $PM_{10\text{-}2.5}$ may originate from marine source. The concentrations of EC and OC are dominant in $PM_{2.5}$. It also suggests that the concentration OC and EC in $PM_{2.5}$ may originate from the similar type of sources whereas OC and EC in $PM_{10\text{-}2.5}$ and $PM_{>10}$ may have multiple sources.

Key words: Particulate matter, water soluble ions, carbonaceous aerosol.

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