PHYSICOCHEMICAL AND OPTICAL PROPERTIES OF ATMOSPHERIC AEROSOLS DURING ASIAN YELLOW DUST EVENTS AT THE PESCADORES ISLANDS, TAIWAN

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ABSTRACT

Asian yellow dusts could transport easterly to west pacific areas such as Korea, Japan, and Taiwan. Most surveys of Asian yellow dusts in Taiwan were conducted in urban areas and only a few have been conducted at its surrounding islands. The objective of this study was to investigate the physicochemical and optical properties of atmospheric aerosols at the Pescadores Islands located at the Taiwan Strait during Asian yellow dust events. Mass concentration, size distribution, and optical properties of atmospheric aerosols were measured in situ. The sampling protocol was conducted to collect sea-level atmospheric aerosols for further chemical analysis. An Asian yellow dust sampling site was established at Xiaumen, the northwest tip of Pescadores Islands, since February 2002. Atmospheric aerosols, including $PM_{2.5}$ and $PM_{2.5\text{-}10}$, were measured with a dichotomous sampler, while the size distribution (0.056-18.0μm) were measured with a 10-stage multi-orifice uniform deposition impactor (MOUDI). The mass concentration of atmospheric aerosols, particularly $PM_{2.5\text{-}10,}$ were 2-3 times higher than background levels. Water-soluble ionic species of atmospheric aerosols including SO_4^{-2}, NO_3^-, Cl^-, NH_4^+, K^+, Na^+, Mg^{+2}, and Ca^{+2} were measured with an ion chromatography (IC). The carbonaceous contents of atmospheric aerosols were analyzed with an elemental analyzer (EA). The metallic contents of atmospheric aerosols were analyzed with an inductively coupled plasma with atomic emission spectrometer (ICP-AES). The scattering and absorption coefficients were measured with an integrating nephelometer and an absorption photometer, respectively.

Key Words: Asian yellow dusts, atmospheric aerosols, physical properties, chemical composition, optical properties

INTRODUCTION

Asian yellow dusts transported frequently from Northwest China and Mongolia to the Pacific-Rim countries from late winter to late spring of each year [1,2]. It could cause environmental effects such as ambient air quality deterioration, atmospheric visibility impairment, radiation energy reduction, mineral deposition, and acid rain neutralization [3,4]. During Asian yellow dust events, significant increases of atmospheric aerosols, particularly PM_{10}, have been commonly observed in major cities of Taiwan [5-8]. Besides, a yellow rain episode has been reported both in Japan and Taiwan at the end of March 2000 [9,10]. Furthermore, source apportionment of atmospheric aerosols at an Asian dust episode in metro Kaohsiung indicated that the contribution of soil dusts increased from 8.5% (regular periods) to 26.2% (Asian yellow dust events) [6]. Asian yellow dusts were transported across the wet Pacific Ocean by strong monsoons prior to falling. Therefore, it might be important to sample Asian yellow dusts on their transportation route at oceanic sites. Asian yellow dusts have been sampled at Che-ju Island in the Yellow Sea and Tokchok Island in the Sea of Japan [1,11]. Measurement of Asian yellow dusts at these islands provides reliable

data for estimating the flux of Asian yellow dusts all over the ocean. The Pescadores Islands was selected in this study because it is located on the Asian dusts' transportation route to Taiwan. The Pescadores Islands can be treated as an air quality background site due to clean atmosphere and can be used to investigate the influence of Asian yellow dusts on the physicochemical properties of Taiwan's aerosols.

METHODOLOGIES

The Asian yellow dust sampling campaign was co-sponsored by Taiwan Academia Sinica and Taiwan Environmental Protection Administration (TEPA). The Pescadores Islands are located at the center of Taiwan Strait and are approximately 110 kilometers away from the West Coast of Taiwan Main Island. Asian yellow dusts were sampled at Xiaumen that is located at the northwestern tip of the Pescadores Islands (Figure 1). Surrounding by uncultivated grassland, the Xiaumen site was approximately half kilometers away from the coastline and about fifty meters above the sea level. In this study, both regular and intensive sampling protocols were conducted to collect atmospheric aerosols at the Pescadores Islands in the year of 2002. During the samply campaign, atmospheric aerosols were consecutively collected for twelve hours with a high-volume sampler (TSP) and two dichotomous samplers ($PM_{2.5}$ and $PM_{2.5-10}$). Daytime and nighttime samples were collected starting at 8:00 am and 8:00 pm, respectively. The size distribution of atmospheric aerosols was collected with a 10-stage micro-orifice uniform deposit impactor (MOUDI; 0.056-18.0 μm) for twenty-four hours starting at 8:00 am.

After sampling, filters were temporarily stored at 4^{o}C environment and then transfered back for weighing and chemical analysis within one week. Chemical analysis included water-soluble ionic species, carbonaceous content, and metallic content of aerosol samples. Water-soluble ionic species, including F^-, Cl^-, Br^-,NO_3^-, SO_4^{2-}, NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}, were measured with an ion chromatography (Dionex, Model DX100). Another half of the Teflon filter was extracted with perchloric and nitric acids for further analysis of metallic contents, including Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sn, Sr, Ti, and Zn, with an inductively coupled plasma with atomic emission spectrometer (Perkins Elmer, Model 400). Meanwhile, the carbonaceous contents including elemental, organic, and total carbons (EC, OC, and TC) of atmospheric aerosols were measured with an elemental analyzer (Carlo Erba, Model 1108). Moreover, the scattering and absorption coefficients were continuously measured with an integrating nephelometer and an absorption photometer, respectively.

RESULTS AND DISCUSSION

Mass Concentration of Atmospheric Aerosols

The highest monthly averaged concentration of particulate matter, particularly PM_{10} and $PM_{2.5-10}$, was observed in March, while the lowest concentration of particulate matter was observed in July (Figure 2). It concurred with previous findings that Asian dust storms invaded Pacific-Rim areas in the early months of each year [1,12]. During the sampling campaign, three Asian yellow dust episodes were observed on March 7th-10th and 17th-20th, and March 31st-April 2nd (Figure 3). Asian yellow dust episodes could last for approximately 2-3 days at the Pescadores Islands. The concentrations of TSP and PM_{10} during Asian yellow dust episodes were approximately 2-3 times higher than the background levels, however, the concentration of $PM_{2.5}$ did not vary much. The increase of PM_{10} concentration was mainly attributed to coarse particles ($PM_{2.5-10}$). The concentrations of PM_{10}, $PM_{2.5-10}$,

and $PM_{2.5}$ between Asian yellow dust events and regular periods were further compared in this study. In average, $PM_{2.5}$ accounted for approximately 44-47% of PM_{10}, while PM_{10} accounted for approximately 64-69% of TSP at Pescadores Islands. Besides, the ratios of $PM_{2.5-10}$ to $PM_{2.5}$ ranged from 0.64 to 3.32 with an average of 1.71 during Asian yellow dust events, which were higher than those ranged from 0.51 to 2.68 with an average of 1.38 during regular periods. The results indicated that the increase of PM_{10} was mainly attributed from coarse particles ($PM_{2.5-10}$) [5,6].

Size Distribution of Atmospheric Aerosols

The size distribution of atmospheric aerosols sampled at Asian yellow dust events (March 17^{th}-21^{st}) was compared with regular periods (April 12^{th}-18^{th}). Either single- or bi-mode distributions were observed. Particle sizes with the highest concentration in fine and coarse particle modes were 0.56-1.0 μm and 3.2-5.6 μm, respectively. The results indicated that, Asian yellow dusts contributed mainly from coarse particles rather than fine particles, which concurred with previous researches [6,13-15]. An increase of coarse particle concentration can be further applied to validate the invasion of Asian yellow dusts since it provided valuable information about particle size variation. Significant single-mode distributions with peak concentration up to180 $\mu g/m^3$ were observed during Asian yellow dust events (March 18^{th}-20^{th}), while bi-mode distributions were observed during regular periods (March 17^{th} and 21^{st}). However, in some cases, the mass concentration of aerosol particles was also raised. For instance, two Asian yellow dust events officially declared by Taiwan EPA during the period of April 12^{th}-18^{th}, 2002, were finally relinquished since there were no significant increase of coarse particles. The increase of coarse particles further validated three Asian dust storm episodes on March 7^{th}-10^{th}, March18^{th}-20^{th}, and March 31^{st}-April 2^{nd} at the Pescadores Islands in the year of 2002.

Chemical Composition of Atmospheric Aerosols

The highest concentrations of both anions and cations occurred in March (or April). Significant increases of Cl^-, Br^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} for both coarse and fine particles were observed in the springtime. The results suggested that not just natural soil dusts (Ca^{2+} and K^+) and oceanic spray (Cl^-, Br^-, Na^+, and Mg^{2+}), but anthropogenic pollutants (nss-SO_4^{2-}) could also associate with Asian yellow dusts and invaded the Pescadores Islands. Other ionic species including NO_3^- and NH_4^+ for both coarse and fine particles did not vary much all over the year. The overall equivalent concentration of both anions and cations in coarse particles versus $PM_{2.5-10}$ and PM_{10} was further compared. The variation of overall concentration of ionic species was consistent with $PM_{2.5-10}$ and PM_{10} during the sampling campaign (Figure 4). It suggested that the increase of $PM_{2.5-10}$ and PM_{10} was attributed to water-soluble ionic species of coarse particles during Asian yellow dust events.

The concentrations of water-soluble ionic species between Asian yellow dust events and regular periods were further compared. In general, the average concentrations of ionic species during Asian yellow dust events were approximately 1-2 times higher than regular periods except that the average concentration of Br^- during Asian yellow dust events was about four times higher than regular periods. During Asian yellow dust events, the most abundant ionic species of $PM_{2.5-10}$ were SO_4^{2-}, Cl^-, NO_3^-, Ca^{2+}, and Na^+, while the most abundant ionic species of $PM_{2.5}$ were SO_4^{2-}, NH_4^+, NO_3^-, Ca^{2+}. Moreover, Cl^-, NO_3^-, Na^+, and Ca^{2+} were more abundant in $PM_{2.5-10}$ than $PM_{2.5}$, while SO_4^{2-} and NH_4^+ were more abundant in $PM_{2.5}$ than $PM_{2.5-10}$. In average, the ionic species of $PM_{2.5-10}$ accounted for approximately 50.4% and

40.4% of PM_{10} for Asian yellow dust episodes and regular periods, respectively. The results indicated that Asian yellow dusts contributed ionic species to PM_{10}, particularly $PM_{2.5-10}$.

The concentrations of carbonaceous contents between Asian yellow dust events and regular periods were further compared. The average concentrations of carbonaceous contents during Asian yellow dust events were approximately 1-2 times higher than regular periods. In average, the total carbon of $PM_{2.5}$ accounted for approximately 57.8% and 63.5% of PM_{10} for Asian yellow dust episodes and regular periods, respectively. The results indicated that $PM_{2.5}$ contained more carbons than $PM_{2.5-10}$. Moreover, most carbons existed in the atmospheric aerosols were in the form of organic carbons since the ratios of organic carbon to elemental carbon (OC/EC) were generally greater than unity (1.17-1.86). A consistent variation of overall concentrations of carbonaceous contents with $PM_{2.5}$ and PM_{10} concentrations in the sampling campaign was observed (Figure 5). It suggested that carbonaceous contents existed mainly in fine particles, which concurred with previous studies [1,15,16].

The most abundant metals existed in the atmospheric aerosols for their concentrations greater than 1.0 $\mu g/m^3$ were Na, Ca, Fe, Mg, K, Al and Ti. Among them, Ca, Fe, Al, and Ti were crustal materials, while Na, Mg, and K came mainly from oceanic spray. During Asian yellow dust events, the concentrations of Na, Ca, Fe, Mg, Al, Ti, Sn, Sr, Ba, and Cr were generally higher than those during regular periods. The results indicated that both Asian yellow dusts and oceanic spray contributed to PM_{10} at the Pescadores Islands. On the contrary, the concentrations of other metals either declined or remained the same while Asian yellow dusts invaded. The ratio of metallic content of PM_{10} between Asian yellow dust episodes and regular periods ranged from 0.11 (Ni) to 4.58 (Ti). Among them, the concentration of lead (Pb) emitted mainly from local sources decreased from 0.32 to 0.07 suggested that the dilution effects of strong northward monsoons could diminish local emissions.

Optical Properties of Atmospheric Aerosols

The comparison of particle scattering coefficient with $PM_{2.5}$ is illustrated in Figure 6. Basically, the variation of scattering coefficient was consistent with the concentration of $PM_{2.5}$. The scattering coefficients measured at the Pescadores Islands ranged from 8.6 to 235.7 Mm^{-1}. The particle scattering coefficients (B_{sp}) accounted for approximately 72% of total light extinction by assumption that Rayleigh scattering (B_{sg}) is 10 Mm^{-1}, particle absorption equals to 10 m^2/g times the concentration of elemental carbon, gas absorption equals to 0.33 times the concentration of NO_2.

CONCLUSIONS

In this study, three Asian yellow dust episodes were observed at the Pescadores Islands on March 7^{th}-10^{th} 17^{th}-20^{th}, and March 31^{st}-April 2^{nd} in the year of 2002. It was found that Asian yellow dust events could last for approximately 2-3 days at the Pescadores Islands. Asian yellow dust invaded Taiwan from the northeast during the sampling campaign. The concentrations of atmospheric aerosols during Asian yellow dust episodes were 2-3 times higher than the background levels. Asian yellow dust storms could influence both physical and chemical properties of atmospheric aerosols collected at the Pescadores Islands. Size distribution results indicated that Asian yellow dusts contributed to the coarse particle mode rather than the fine particle mode of atmospheric aerosols collected at the Pescadores Islands. Moreover, significant increases of Cl^-, Br^-, SO_4^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+} for both coarse and fine particles were observed in the spring. It suggested that not just natural soil dusts and oceanic

spray, but anthropogenic pollutants could also associate with Asian yellow dusts and arrived at the Pescadores Islands. During the sampling campaign, this study revealed that Asian yellow dusts contained Ca^{2+} at both fine and coarse particle modes and contained SO_4^{2-} at coarse particle mode only.

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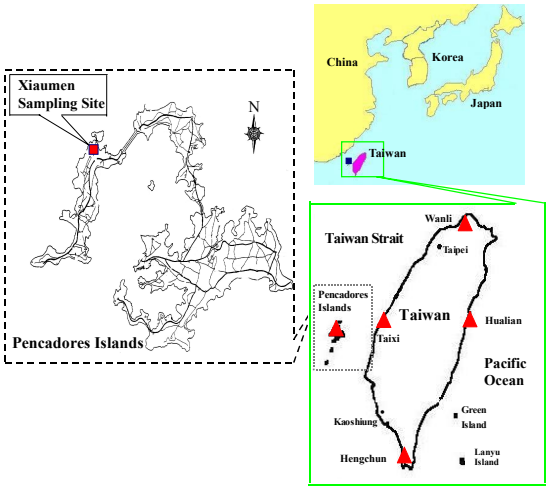

Figure 1. The location of Asian dust sampling sites located at Xiaumen, Pescadores Islands and in Taiwan over Taiwan Strait.

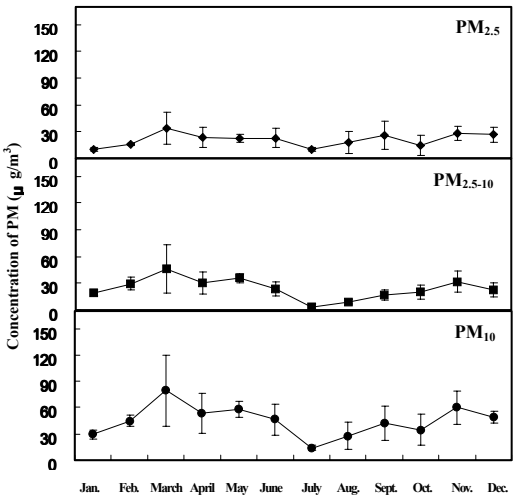

Figure 2. Monthly variation of $PM_{2.5}$, $PM_{2.5\text{-}10}$, and PM_{10} measured at the Pescadores Islands in the year of 2002.

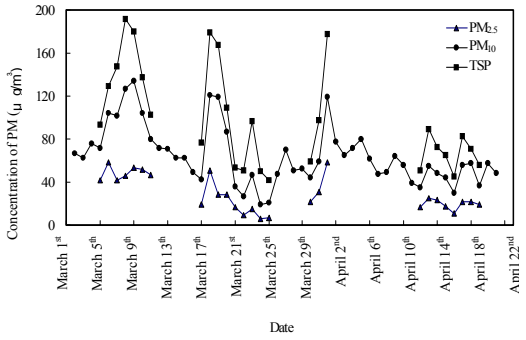

Figure 3. Daily variation of $PM_{2.5}$, PM_{10}, and TSP measured at the Pescadores Islands during intensive Asian dust sampling periods in the year of 2002.

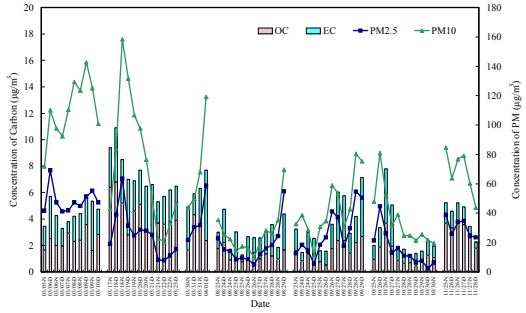

Figure 4. Comparison of $PM_{2.5\text{-}10}$ and PM_{10} with total water-soluble ionic species of atmospheric aerosols measured at the Pescadores Islands in the year of 2002.

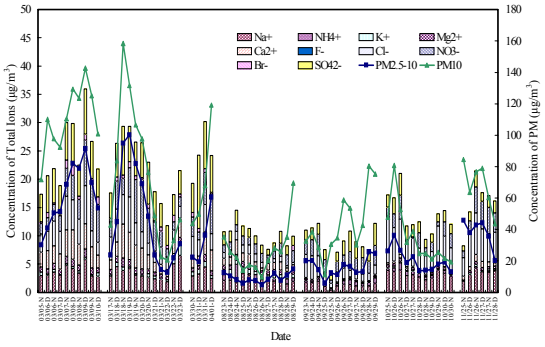

Figure 5. Comparison of $PM_{2.5}$ and PM_{10} with total carbonaceous contents of atmospheric aerosols measured at the Pescadores Islands in the year of 2002.

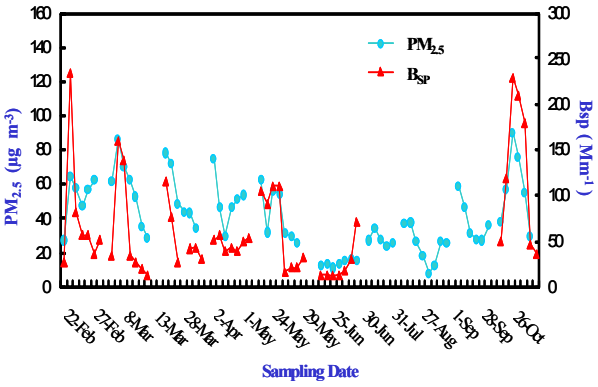

Figure 6. Comparison of scattering coefficient (B_{sp}) with $PM_{2.5}$.