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A review of atmospheric fine particulate matter and its associated trace metal pollutants in Asian countries during the period 1995–2005

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Abstract

Many studies have monitored atmospheric particulates and gaseous phases of $PM_{2.5}$ in Asia over the past 10 years. This work also compared and discussed different sample collection, pretreatment and analytical methods in Asia countries in past decade. The results indicated that the main $PM_{2.5}$ sources are traffic exhausts. $PM_{2.5}$ concentrations are also ranked highest in the areas of traffic, followed by the urban sites, and lowest in rural sites in Asian countries. This work elucidates the sources, analytical tools, and the average concentrations for $PM_{2.5}$ and related metallic elements during 1995–2005. The results indicated that the average highest concentrations order of metallic elements for $PM_{2.5}$ were Fe > Mg > Zn, and the average concentrations of lowest metallic elements was Pb > Cu > Mn > Cr > Cd. The results also indicated that the concentration of metallic element Cu increased as the averaged concentrations of metallic element Zn and Mn increased during the past 10 years in Asian countries.

Keywords: Asia; $PM_{2.5}$; Cu; Zn; Mn

1. Introduction

There are quite a few ambient air pollution related studies in Asian countries during the past decade. The motivation of this study was focus on the ambient air pollutants related studies in Asian area during the past 10 years. Especially the comparison those sampling techniques, sampling instruments, and ambient air pollutants concentrations were also widely discussed in this study. The detail descriptions were listed as follows.

1.1. Comparison with other sampling sites in Asian countries

1.1.1. Singapore

The study was made by Orlic et al. [1] in Singapore. The sampling period was from 1996 January to 1997 November and 12 h sampling period was proceeded in this study. In addition, Singapore's population has been increased from 3.53 to 4.43 million, and the vehicles have been increased from 0.51 to 0.62 million and gross domestic product (GDP) have also been increased from 83.93 to 116.78 billion dollars during the past decade [2].

These were two sampling sites: one site was the Civil Service College (CSC) located within the campus of the National University of Singapore (NUS) at Kent Ridge, and the other at the Anderson Junior College (AJC) located in the central part of Singapore. The aim of this study was to determine the average elemental concentrations in fine and coarse aerosol fractions as well as to identify major pollution sources and their impact. During the period of 2 years more than 700 aerosol samples were collected and analyzed using PIXE (particle induced X-ray emission) and RBS (Rutherford backscattering spectrometry) techniques. All samples were analyzed for 18 elements ranging between sodium (Na), magnesium (Mg), aluminum (Al), etc., up to arsenic (As) and lead (Pb). The main objective was to find the average concentrations of aerosols in Singapore and to identify major pollution sources and their impact.

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Table 1
Summary of $PM_{2.5}$ in Asia countries during 1995–2005

Country	Sampling site	Sampling device	Analytic methods	Major source
Singapore [1]	NUS, AJC NTU, RLH	$PM_{2.5}$ ANSTO PM_{10} SFU	PIXE, RBS PIXE, RBS	Heavy-traffic roads, highways Industrial zone
China [3]	OT, NB, BJ, XY, CH (Beijing)	–	GC/MS	Heavy-traffic, shop, restaurants
China [6]	Tongji University Campus and Hainan Road (Shanghai)	GT22001 for $PM_{2.5}$, USA	TC, IC, TOC	Scenery district, small residential area
China [7]	SY, FZ, RJ, ZS, YZ (Nanjing)	KC-2000 for PM_{10}, China	TC, IC, TOC	Heavy-traffic, downtown, residential area
Korea [12]	Chongju	Teflon filters	IC	City
Japan [14]	Busy roadside (Tokyo)	Low-volume sampler	IC, ICP-AES, XRF	Busy roadside
Taiwan [15]	Urban, country region (Taichung)	Teflon filters	AA	Urban and country region

1.2. China

1.2.1. Beijing

Beijing, the capital of China, is facing very serious air pollution problems including extremely high concentrations of suspended particles in the atmosphere. $PM_{2.5}$ samples were collected from five sites in Beijing with samplers fabricated from commercial sampler components that have been extensively used in the past [3]. These sampling sites were OT (Ming Tombs site), NB (airport), BJ (Peking University site), XY (Beijing Environmental Protection Bureau), CH (Yong Le Dian site), respectively and samples were collected in January, April, July, and October 2000 simultaneously at five sampling sites in Beijing including rural and urban areas were analyzed by GC/MS to obtain the detailed information of particle-phase and solvent-extractable organic compounds in Beijing $PM_{2.5}$, which were used as tracers for source apportionment of $PM_{2.5}$. In addition, Beijing's population has been increased from 12.51 to 14.93 million, and the vehicles have been increased from 0.72 to 3.08 million and GDP have also been increased from 18.60 to 90.86 billion dollars during the past decade [4] (Tables 1–3).

In this study, one microliter of each derivatized sample was injected into the GC/MS on a Hewlett-Packard GC/MSD (6890 GC and 5973N MSD) for identification and quantification of organic compounds. The column used was a HP 5 MS capillary column (coated with 5% phenyl methyl siloxane). The GC conditions were: isothermal hold at 65 °C for 10 min, temperature ramp of 10 °C/min −300 °C, isothermal hold at 300 °C for 22 min, and He as carrier gas with a flow rate of 1.0 mL/min. The GC/MS interface temperature was 300 °C. Organic compounds passing the interface were ionized by electron impact (70 eV) and scanned from 50 to 500 amu.

1.2.2. Shanghai

Shanghai and Beijing are two of the largest cities in China. Shanghai has populations of over 10 million. The urban areas had experienced a rapid increase in the use of vehicles, concurrent with large increases in energy consumption. Particulate pollution has become a major problem. In addition, Shanghai's population has been increased from 14.15 to 17.42 million, and the vehicles have been increased from 0.32 to 1.15 million and GDP have also been increased from 29.76 to 121.92 billion dollars during the past decade [4]. A year-long field study to characterize the ionic species in $PM_{2.5}$ was carried out in Shanghai, China, in 1999–2000. Weekly samples of $PM_{2.5}$ were collected using a special low flow rate (0.4 L/min) sampler in this study.

$PM_{2.5}$ sampling in Shanghai was conducted by Tongji University. The two sampling sites in Shanghai were both downtown and were 5 km apart. One was inside the Tongji University campus and the other was on Hainan Road. The sampler at the Tongji University campus was placed on the roof of a three-story building, 16 m above ground level. About 150 m northwest from this site is a heavily trafficked road. The sampler at the Hainan Road site was also placed on the roof of a building, 18 m above the ground level, and 150 m from a main road. The Hainan site was next to an air quality monitoring station, where the meteorological conditions and the concentrations of sulfur dioxide (SO_2), Nitrogen oxides (NO_x), and Ozone (O_3) were measured. The sampler and chemical analyses employed in this study were the same as described by He et al. [5]. Concurrent weekly (7 days) samples were collected at these two sampling sites in each city. The sampler was a special low flow rate sampler equipped with three cassettes for collecting $PM_{2.5}$, each at a flow rate of 0.4 L/min (Aerosol Dynamics, USA). The low flow rate enables continuous sampling during a week without overloading the filters so that a year-long data set could be readily obtained [6].

Table 2
Comparison of metallic elements concentrations in $PM_{2.5}$ around Asian areas during 1995–2005 (ng/m^3)

Country	Sampling site	Cu	Mn	Zn	Pb	Cr	Mg	Fe	Cd
Singapore [1]	CSC (Pre-Haze)	5.2	7.2	43	29	–	52	105	–
Singapore [1]	CSC (Haze)	6.5	6.2	68	31	–	40	123	–
Singapore [1]	AJC (Pre-Haze)	26.6	5.2	41	42	-	207	115	–
Singapore [1]	AJC (Haze)	27	4.7	56	21	–	40	117	–
China [7]	Nanjing	21.719	33.851	132.494	12.99	1.789	337	17.088	–
Taiwan [17]	Taichung Harbor	87.425	20.6	136.075	5.4	41.275	174.025	249.05	–
Taiwan [18]	Taichung	11.5	19.1	177.8	283.1	33.5	37.9	162.8	4.3

Table 3
The source and pollution characteristic category of the metallic elements around the world

Source	The pollution characteristic category of the metallic elements around the world
Sea salt [11,29]	Na, Ca, Mg and K
The industry processes [19,21]	Mn, Zn and K
Soils and dusts [19-25]	Ca, Mg, Al, Si, Fe and Mn
The vehicle exhaust [20–23,25–27]	Cr, Pb, Cu, Zn, Cd, Sb, Br, Fe and Ba
Construction site [22]	Al, Fe, Si, Mn and Ti
Industrial oil combustion [22,31]	Ni and V
Incinerator [27,28]	K, Ze and Pb
Metals industry [27,28]	Fe, Mn and Pb
The coal combustion [30]	Cr

1.2.3. Nanjing

High ambient suspended particulate loading has been a persistent problem in Nanjing, a typical metropolitan in China. For identification of atmospheric species in Nanjing, a campaign was carried out from February to May 2001 [7]. In addition, Nanjing's population has been increased from 70.06 to 74.33 million, and the vehicles have been increased from 0.51 to 1.61 million and GDP have also been increased from 7.79 to 32.17 billion dollars during the past decade [4].

Many studies have concerned about the organic fraction and heavy metals of aerosols. However, they have mainly focused on the water-insoluble fractions of the particulate matter. Five sites were chosen for this study: 1) Suyuan hotel (SY); 2) Fuzi temple (FZ); 3) Ruijin village (RJ); 4) Zhongshan mausoleum (ZS) and 5) Yangzi school (YZ). SY is located Nanjing. RJ is a big residential area and located in FZ, a downtown, in the southern areas of the city. ZS is a nearby Zhujiang highway, a heavy traffic center of scenery district and located in the east of Nanjing. YZ is a small residential area and lies in a large-scale petrochemical district, which is located in the northwestern Nanjing city. Two kinds of samplers have been used during the campaign. KC-2000 for PM_{10} (made in China) and Anderson GT22001 for $PM_{2.5}$ (made in USA) are high volume air samplers, the flow rates of which are 1.05 and 1.12 m^3/min, respectively. The glass fiber filters (200–250 mm^2) was baked at 500 °C for 2 h in order to eliminate organic species, conditioned in a dessicator for 24 h, and then weighted with Mettler AE240 electronic balance (limit of detection 10 mg). After sampling, the filters were also equilibrated in the desiccators for 24 h prior to weight, and stored at −18 °C before analysis. And then, determination for pH, conductivity, total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), elements and ions of water-soluble species of the aerosols.

1.2.4. Hong Kong

The results from a year-long monthly (October, 1996–September, 1997) study of the solvent extractable organic compounds (SEOC) in $PM_{2.5}$ of the ambient aerosols in Hong Kong are reported [8]. In addition, Hong Kong's population has been increased from 6.16 to 6.97 million, and the vehicles have been increased from 0.50 to 0.54 million and GDP have also been increased from 14.17 to 17.77 billion dollars during the past decade [9].

A total of 18 samples were analyzed. The extracted organic compounds were separated into four major fractions (*n*-alkanes, fatty acids, alkanols and PAHs (polycyclic aromatic hydrocarbons)) and identified with GC (gas chromatography)–MS (mass spectrometry). Samples were collected on glass fiber filters using a high-volume sampler (Graseby GMWT 2200) with a Graseby 10 μm inlet (Model 1200). A single impactor stage F (Graseby, Model 231-F) (2.5 μm cut-point) allowed the collection of particles smaller than 2.5 μm.

1.3. Korea

The concentrations of ionic constituents associated with both $PM_{2.5}$ and PM_{10} were measured at 24-h intervals from the two study sites selected in the Seoul and Busan areas of Korea during the winter period of 2002. In addition, Korea's population has been increased from 44.61 to 47.28 million, and the vehicles have been increased from 8.47 to 15.03 million and GDP have also been increased from 517.12 to 787.50 billion dollars during the past decade [10].

From both locations, the collection of PM samples was made using the identical PM sampling systems developed by URG Inc. (USA). The analysis of ionic components was conducted by extracting them from the filter sample using deionized water. These ionic components were then analyzed by ion chromatography (IC) with a detection limit of about 10 ng/g [11].

Fine particles were collected over four seasons from October 1995 to August 1996 to evaluate the chemical characteristics of principal $PM_{2.5}$ components in Chongju, South Korea.

The Teflon filter (1 μm pore size; Gelman Science) was used to collect $PM_{2.5}$ mass. All filters were extracted with 10 mL of double-distilled water (DDW; Barnstead). Ion chromatography (Dionex DX-100) was used for the analysis of anion and cation concentrations from the filter extracts [12].

1.4. Japan

Long-term measurements of suspended particulate matter (SPM, <7 μm), PM_{fine} (<2.1 μm), and PM_{coarse} (2.1–7 μm) were obtained from a traffic-dominated site in Tokyo, Japan for the period 1994–2004 to evaluate the effects of emission reduction measures for motor-vehicle emissions. These samples at Yamanashi University, Kofu, located at 351400N, 1381340E in Central Japan. This area locates at the northern edge of the Kofu Basin and motor-cars are the major means of transport there. Aerosol samples were collected for 7–20 days on membrane filters by a low-volume air sampler with a satellite unit (Rupprecht and Patashnick Co., Partisol Model 2000). In addition, Japan's population has been increased from 125.57 to 127.76 million, and the vehicles have been increased from 70.11 to 78.28 million and GDP have also been increased from 4247.20 to 4560.5 billion dollars during the past decade [13].

Materials and properties of collection media influence the succeeding analytical methods of aerosol particles collected. Therefore, some commercially available membrane filters were examined as collection media for the systematic characterization, which consists of the fractional determination of soluble and insoluble components by ICP-AES, IC and XRF [14].

1.5. Taiwan

Samples of atmospheric aerosol and these metallic elements concentrations of calcium (Ca), iron (Fe), manganese (Mn), lead (Pb), copper (Cu), zinc (Zn) and chromium (Cr) were collected from June to August in 1998 at a four-story building (12 m height) at Thunghai University (THU). Sampling time was divided into daytime and night-time [15]. In addition, Taiwan's population has been increased from 21.36 to 22.77 million, and the vehicles have been increased from 5.03 to 6.4 million, and GDP have also been increased from 264.93 to 345.90 billion dollars [16].

Daily average concentrations of fine and coarse, and TSP samples have been measured simultaneously at daytime and night-time periods by using Universal and PS-1 sampler in a suburban area of central Taiwan from June to August 1998. The samples were analyzed by atomic absorption spectrometry to determine the fine and coarse particulate concentrations of metallic elements (Ca, Fe, Mn, Pb, Cu, Zn and Cr).

Air aerosol samples for TSP (total suspended particulate), coarse particulate (particle matter with aerodynamic diameter 2.5–10 μm, $PM_{2.5-10}$), fine particulate (particle matter with aerodynamic diameter <2.5 μm, $PM_{2.5}$) and metallic elements were collected during March 2004 to January 2005 at TH (Taichung Harbor) in central Taiwan [17].

The sampler has a designed inlet sampling flow rate of 300 L/min. It is provided with an omni-directional inlet, a PM_{10} (10 μm cut) virtual impact classifier, and either a $PM_{2.5}$ or PM_{10} virtual impact classifier, or a fine particle filter. This allows the sampler to be operated as a high volume dichotomous sampler for size fractionation of airborne particles in the fine (0–2.5 μm) and coarse (2.5–10 μm) aerodynamic size ranges.

2. Summary

The average Cu concentration of $PM_{2.5}$ in Taichung Harbor (Taiwan, 87.425 ng/m^3) which was higher than other sampling sites such as Taichung (Taiwan), CSC Pre-Haze (Singapore), CSC Haze (Singapore), AJC Pre-Haze (Singapore), AJC Haze (Singapore), Nanjing (China). And the average Mn concentration of $PM_{2.5}$ in Nanjing (China) was 33.851 ng/m^3. This value which was 1.6, 1.8, 4.7, 5.5, 6.5 and 7.2 times as those of Taichung Harbor, (Taiwan, 20.6 ng/m^3), Taichung (Taiwan, 19.1 ng/m^3), CSC Pre-Haze (Singapore, 7.2 ng/m^3), CSC Haze (Singapore, 6.2 ng/m^3), AJC Pre-Haze (Singapore, 5.2 ng/m^3), AJC Haze (Singapore, 4.7 ng/m^3), respectively. As for the element Zn, the highest average concentration of $PM_{2.5}$ was Taichung (Taiwan, 177.8 ng/m^3). This values which was 1.30, 1.34, 2.61, 3.18, 4.13 and 4.34 times as those of Taichung Harbor (Taiwan, 136.075 ng/m^3), Nanjing (China, 132.494 ng/m^3), CSC Haze (Singapore, 68 ng/m^3), AJC Haze (Singapore, 56 ng/m^3), CSC Pre-Haze (Singapore, 43 ng/m^3) and AJC Pre-Haze (Singapore, 41 ng/m^3), respectively. In general, the concentrations ratios of Pb for $PM_{2.5}$ in Taichung, Taiwan to those of AJC Pre-Haze (Singapore), CSC Haze (Singapore), CSC Pre-Haze (Singapore), AJC Haze (Singapore), Nanjing (China), Taichung Harbor (Taiwan) was 6.74, 9.13, 9.76, 13.48, 21.79 and 52.425, respectively. As for the element Cr, the average Cr concentration for $PM_{2.5}$ in Taichung Harbor (Taiwan, 41.275 ng/m^3) which was higher than other sampling sites. And the average Mg concentration in $PM_{2.5}$ was Nanjing (China, 337 ng/m^3). This value which was 1.63, 1.94, 6.48, 8.43, 8.43 and 8.89 times as those of AJC Haze (Singapore, 207 ng/m^3), Taichung Harbor (Taiwan, 174.025 ng/m^3), CSC Pre-Haze (Singapore, 52 ng/m^3), CSC Haze (Singapore, 40 ng/m^3) and AJC Pre-Haze (Singapore, 40 ng/m^3), Taichung (Taiwan, 37.9 ng / m^3), respectively. As for the element Fe, the average highest Fe concentration in $PM_{2.5}$ was Taichung Harbor (Taiwan, 249.05 ng/m^3). This values which was 1.52, 2.02, 3.12, 2.16, 2.37 and 14.57 times as those of Taichung (Taiwan), CSC Haze (Singapore), AJC Haze (Singapore), AJC Pre-Haze (Singapore), CSC Pre-Haze (Singapore) and Nanjing (China), respectively. To sum up, the average highest concentrations order of metallic elements for $PM_{2.5}$ were Fe (126.99 ng/m^3) > Mg (126.85 ng/m^3) > Zn (93.48 ng/m^3). And the average concentrations of lowest metallic elements was Pb (60.64 ng/m^3) > Cu (26.56 ng/m^3) > Mn (13.84 ng/m^3) > Cr (10.93 ng/m^3) > Cd (0.61 ng/m^3).

In general, the previous study indicated that the concentration of metallic element Cu increased as the averaged concentration of metallic element Zn and Mn increased during the past 10 years. In general, metallic elements Ca, Mg, Al, silicon (Si), Fe and Mn were riched in soils and dust. And the vehicle exhaust is the source for metallic elements Cr, Pb, Cu, Zn, Cd, stibium (Sb), bromine (Br), Fe and Ba. As for the industry processes, metallic elements Mn, Zn and K were tended to be associated with it. Incinerator is the source for metallic elements K, Zn and Pb. However, sea salt was the source for elements of Na, Ca, Mg, and K. And element Cr is likely to be found in the coal combustion process. As for the metals industry, metallic elements Fe, Mn and Pb were tended to be associated with it. The previous research also indicated that the industrial oil combustion was the source for metallic elements nickel (Ni) and vanadium (V). Finally, construction site was the source for metallic elements Al, Fe, Si, Mn and titanium (Ti).

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