Transboundary and Local Air Pollutants in Western Japan Distinguished on the Basis of Ratios of Metallic Elements in Size-Segregated Aerosols

Yuta Taniguchi1, Kojiro Shimada2, Akinori Takami3, Neng-Huei Lin2,4, Chak K. Chan5, Yong Pyo Kim2,6, Shiro Hatakeyama1,2,7*

1Graduate School of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan
2Global Innovation Research Organization, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8538, Japan
3National Institute for Environmental Studies, Tsukuba, Ibaraki 305-0053, Japan
4Department of Atmospheric Science and Department of Chemistry, National Central University, Chung-Li, Taoyuan 32001, Taiwan
5School of Energy and Environment, City University of Hong Kong, Hong Kong, China
6Department of Chemical Engineering and Materials Science and Department of Environmental Science and Engineering, Ewha Womans University, Seoul 03760, Korea
7Center for Environmental Science in Saitama, Kazo 347-0115, Saitama, Japan

ABSTRACT

Trace metals in aerosols were observed at an urban site (Kumamoto, Kyushu, Japan) and a rural site (Cape Hedo, Okinawa, Japan) to investigate the relative contributions of transboundary air pollutants from mainland Asia and local air pollutants in western Japan. We used a cascade impactor to collect aerosols in five size classes. We apportioned the sources of the air masses on the basis of elemental components. Transboundary and local air pollutants were distinguished by use of the Pb/Cu and V/As ratios in selected size fractions of aerosols. The contribution of Pb (primarily from coal combustion in China) to total anthropogenic elements was greatest in spring, autumn, and winter in the 0.5–1 µm size fraction at both collection sites. The atmospheric environment at both sites was affected by this transboundary air pollutant. The contribution of Cu (primarily from local vehicle traffic) to total anthropogenic elements was greatest in all seasons in Kumamoto. Local air pollutants such as road dust, automobile brake abrasion, and waste incineration affected ambient air quality in Kumamoto. Because these pollutants resided mainly in the coarse aerosol fraction (> 2.5 µm), most of them were not transported to Cape Hedo in air bodies that we were able to trace to Kumamoto by backward projection. Based on our data the ambient air quality at Cape Hedo was little affected by local air pollutants emitted in the Kumamoto area.

Keywords: Size-segregated aerosol analysis; Chemical composition of metallic elements; Difference in transboundary and local pollution; Elemental ratios.

INTRODUCTION

Severe air pollution has been caused by rapid economic growth in Asia (Chan and Yao, 2008; Deng et al., 2012). Emissions of gaseous pollutants and particulate matter (PM) from both industries and residents have increased in this area (Ohara et al., 2007), while the emission of SO2 and NOx in China have decreased since 2006 and 2011, respectively (Xia et al., 2016). PM is transported from East Asian countries to Japan and Korea with prevailing westerly winds in the winter and spring (Kaneyasu and Takada, 2004; Kim et al., 2009; Itahashi et al., 2010; Hatakeyama et al., 2014). Many studies have reported on the occurrence of transboundary air pollution in western Japan (Kaneyasu et al., 2014). Coal combustion is a major source of fine particulate matter (PM) in China (Han et al., 2005). Concentrations of PM smaller than 2.5 µm (PM2.5) derived from coal combustion are highest during the winter heating period in China. PM2.5 has significant impacts on climate and human health (Shaheen et al., 2005).

Toxic trace elements are often contained in PM (Shah et al., 2006). In PM2.5, these can cause lung and cardiopulmonary injuries in humans (Shaheen et al., 2005; IARC, 2012). The concentrations and size distributions of
trace elements in PM are mainly governed by the natural and anthropogenic emission sources in the atmosphere (Samara and Voutsa, 2005). Major natural emission sources are sea salt, soils, and forest fires. Major anthropogenic emission sources are fuel combustion, waste incineration, and road traffic. In particular, traffic emissions consist of various sources such as combustion products from fuel and lubricating oil, abrasion products from brake pads and tires, and resuspension of road dust (El-Fadel and Hashisho, 2001).

The objective of this study was to determine the contribution of transboundary air pollution transported from China to western Japan. In order to investigate the contributions of transboundary air pollutants and local air pollutants in western Japan, we conducted observations simultaneously at an urban site and a remote site, more than 1500 km southeast of Beijing. The urban site was at Kumamoto University in Kumamoto City, on Kyushu Island, and the remote site was the Cape Hedo Atmosphere and Aerosol Monitoring Station (CHAAMS) on Okinawa Island. Takami et al. (2007) reported that the ambient air quality at Cape Hedo is influenced by air pollutants transported by the northwest winter monsoon and the prevailing westerlies. Cape Hedo usually receives air masses directly transported from eastern China, which pass over the East China Sea. At times air masses from China that pass over the city of Kumamoto and its vicinity are affected by locally emitted air pollutants on their way to Cape Hedo (Tatsuta, 2017).

This study focused on distinguishing between local pollutants and pollutants transported across national boundaries. This was done by conducted measurements of toxic metallic elements in different aerosol size fractions with four objectives: (1) to evaluate seasonal variation of trace elements at Kumamoto and Cape Hedo; (2) to evaluate the size distribution of anthropogenic trace elements in aerosols at the two sites; (3) to use of elemental ratios to determine the contribution of transboundary and local air pollutants at both sites; and (4) to compare the elemental compositions of aerosols transported directly to Cape Hedo from China and aerosols transported to Cape Hedo from China by way of Kumamoto.

**METHODS**

**Observations**

Sampling at Kumamoto City was conducted at the top of a nine-story building (32.81°N, 130.73°E) in Kumamoto University. Kumamoto is a city of 740,000 inhabitants on Kyushu Island in western Japan, approximately 1500 km southeast of Beijing (Fig. 1). The city contains no heavy industries; however, the sampling site was adjacent to a central arterial road with heavy traffic. Furthermore, the location is in the eastern part of the city. We collected a total of 38 daily samples during spring (13–17 March 2015 and 1–7 March 2016), summer (27 July–2 August 2015), fall (14–21 October 2014 and 26–31 October 2015) and winter (17–21 December, 2014).

In Okinawa, sampling was conducted at CHAAMS (26.87°N, 128.25°E; 60 m above sea level), located at the northern end of Okinawa Island, approximately 100 km north of Naha, the largest city on the island, and approximately 1800 km southeast of Beijing (Fig. 1; details of the station are reported in Takami et al., 2007). There are no large industrial or residential areas nearby. Air masses reaching Cape Hedo are transported from China, Korea, Japan, Southeast Asia, or the Pacific Ocean, depending on weather conditions. We collected a total of 33 daily samples during spring (13–17 April 2014 and 12–16 March 2015), fall (17–21 October 2014 and 26 October–7 November 2015) and winter (13–17 December 2013).

Sampling was carried out by a five-stage cascade impactor (Nanosampler Model 3180, Kanomax, Japan) operated with 40 L min⁻¹ air flow at 1 atm air pressure (Otani et al., 2007). Each sample was collected for 24 h from 10:00 am to 10:00 am the next day. Aerosols of particle diameter (Dp) > 10 µm, 10 > Dp > 2.5 µm, 2.5 > Dp > 1 µm, 1 > Dp > 0.5 µm and 0.5 µm > Dp were collected on PTFE filters 55 mm in diameter (PF020, Advantec, Japan). After
sampling, filters were cut into two pieces for analyses of trace metal elements and ionic components.

**Size-Segregated Aerosol Analysis**

The metallic elements in the aerosol samples were quantitatively analyzed after digestion of the samples with a mixture of 1.5 mL hydrofluoric acid, 2.5 mL nitric acid, and 0.5 mL hydrogen peroxide in a Teflon vessel in a microwave oven operated at 200 W for 10 min. After digestion, the hydrofluoric acid was removed by evaporation at 200°C on a hot plate in a hood. Sample solutions were prepared by the addition of nitric acid solution and filtration. The atomic species 23Na, 24Mg, 27Al, 39K, 51V, 55Mn, 57Fe, 63Cu, 75As, 82Se, 88Sr, 111Cd, 121Sb, 137Ba, 208Pb and 209Bi were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500, Agilent Technologies, USA). Ionic components were measured by the method described in Tatsuta et al. (2017, this volume).

**Backward-Trajectory Analysis**

To identify the transport pathways of air masses, backward trajectories for 72 hours starting from a height of 500 m above sea level were calculated using the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model (Stein et al., 2015) from the U.S. National Oceanic and Atmospheric Administration (http://ready.arl.noaa.gov/hysplit-bin/trajtype.pl) based on GDAS (Global Data Assimilation System) global weather data by 1 degree.

**RESULTS AND DISCUSSION**

**Source Identification of Metallic Elements Based on Enrichment Factors**

To determine the extent to which aerosols were emitted from natural or anthropogenic sources, enrichment factors (EFs) for elements in each aerosol size fraction were calculated (Tables S1 and S2). The sea salt enrichment factor (EF_{sea salt}) and the crustal enrichment factor (EF_{crust}) are defined by

\[
EF(X)_{\text{sea salt}} = \frac{(X/Na)_{\text{aerosol}}}{(X/Na)_{\text{sea salt}}} \quad (1)
\]

and

\[
EF(X)_{\text{crust}} = \frac{(X/Al)_{\text{aerosol}}}{(X/Al)_{\text{crust}}} \quad (2)
\]

respectively, where X is the target element. EF < 10 typifies mainly natural sources, and EF > 10 suggests strong enrichment from non-natural sources (Waheed et al., 2011). In this study, we assumed that all Na originated from sea salt and all Al originated from the crust. In these equations, we used the average chemical profile of sea salt from Chester (2009) and of continental crust from Taylor and McLennan (1995).

The average EF_{sea salt} values for Mg in all size ranges at both sites were lower than 10, indicating a source in sea salt. The average EF_{crust} values for Fe, Sr, and Ba in all size ranges at both sites were lower than 10, indicating a crustal source. Average EF_{sea salt} and EF_{crust} values were much higher than 10 for Cu, As, Cd, Sb, Pb and Bi in all size ranges, indicating emission from anthropogenic sources. Enrichment factors for K, V, Mn and Se had mostly anthropogenic values (> 10) in fine particles (< 2.5 μm), but mostly crustal values (< 10) in coarse particles (> 2.5 μm).

From the resulting EF values, we determined the proportional contributions to total elements from sea salt, crustal, and anthropogenic sources (Fig. 2). Here, total elements mean the sum of mass concentrations of 16 elements in all size fractions sampled in this study in each season. At Kumamoto, sea salt, crustal, and anthropogenic sources accounted for roughly 45%, 45%, and 10% of total elements in aerosols in spring, autumn and winter, respectively; however, these percentages were about 73%, 21%, and 6%, respectively, in summer (Fig. 2(a)). At Cape Hedo, sea salt, crustal, and anthropogenic sources accounted for about 86%, 12%, and 2%, respectively, in the three seasons we took samples (Fig. 2(b)).

The influence of sea salt at Cape Hedo was greater than at Kumamoto, because Cape Hedo is surrounded by the sea. At Kumamoto, the contribution of sea salt sources was much greater in summer than in other seasons. Backward-trajectory analyses for the days on which we took samples showed clearly that most air masses in summer were transported to

![Fig. 2. Average proportions of sea salt, soil, and anthropogenic sources in total metallic elements for each season at Kumamoto (a) and Cape Hedo (b).](image-url)
Kumamoto primarily over the ocean (Fig. S1). These results suggest that the contribution of natural sources to the total elements was dominant at both sites. The annual average contribution of anthropogenic sources was small, although it was greater at Kumamoto (8%) than at Cape Hedo (2%).

**Seasonal Variation of Anthropogenic Trace Elements**

Total concentrations of eight elements (V, Cu, Cd, As, Se, Sb, Pb, and Bi) are shown for each aerosol size class in Fig. 3. Their EF values show that all of these elements, except V and Se, were derived from anthropogenic sources in all size ranges at both sites (Table S1 and S2). Concentrations were higher at Kumamoto than at Cape Hedo in all size ranges and seasons (Fig. 3). At both sites, the highest concentration was observed in the 0.5–1 µm fraction. At Cape Hedo, the highest concentrations in the 0.5–1 µm, 1–2.5 µm, and 2.5–10 µm fraction were observed in winter, indicating greater transboundary air pollutants in winter (Takami et al., 2007).

As for anthropogenic sources, Waheed et al. (2011) attributed high metal concentrations in the Dp = 0.2–1 µm fraction of Shanghai aerosols to coal and fuel oil combustion. Other studies have attributed high metal concentrations in the Dp = 2–4 µm fraction at other localities to mechanical abrasion of brake pads and tires (Gietl et al., 2010; Oakes et al., 2016). We show the proportions of the eight anthropogenic elements at our sites in the 0.5–1 µm and 2.5–10 µm fractions for each season in Fig. 4.

In the 0.5–1 µm fraction at both sites, Pb was the greatest contributor to total anthropogenic elements in spring, autumn, and winter. Shimada et al. (2015) inferred that the source of Pb, As, Se, and Cd in PM$_{2.5}$ at Cape Hedo may have been coal combustion in China on the basis of a statistical analysis using positive matrix factorization. Tian et al. (2010, 2012) reported that trace elements such as Pb, As, Se, and Cd in emissions from China were mainly derived from coal combustion. Among these four elements, Cd made the smallest contribution to total anthropogenic elements in 0.5–1 µm aerosols at Kumamoto and Cape Hedo were derived from coal combustion in China.

In the 2.5–10 µm fraction at Kumamoto, Cu was the greatest contributor to total anthropogenic elements in all seasons (Fig. 4(a)); however, this was not the case at Cape Hedo (Fig. 4(b)). This indicates that Cu in the coarse particles was a local pollutant, mainly derived from abrasion of vehicle brake pads (Sternbeck et al., 2002).

The contribution of V to total anthropogenic elements in the 0.5–1 µm fraction was greatest in summer at Kumamoto, where summer air masses were usually transported from the East China Sea (Fig. S1). According to Eyring et al. (2010), the activity at large Chinese ports creates a very high density of shipping traffic in the East China Sea, and Celo et al. (2015) reported that V in fine particles is a
Identification of Transboundary and Local Air Pollutants Based on Metallic Element Ratios

The next task was to characterize air sources on the basis of ratios of metal concentrations in aerosols. We evaluated two ratios: Pb/Cu and V/As.

The Pb/Cu ratio was used as a means of identifying transboundary air pollution, using the Pb concentration in the fine (0.5–1 μm) fraction and Cu in the coarse (2.5–10 μm) fraction. Coal combustion in China is the predominant source of Pb in aerosols. Annual coal consumption in China increased by 2.4 times from 2000 to 2010, at which time it amounted to 50% of worldwide coal combustion (BP Statistical Review of World Energy, 2016). Coal combustion is the main source of toxic elements such as Pb, Cd, As, and Se in aerosols. In particular, the concentration of Pb emitted from coal combustion is larger than that of any other toxic element (Li et al., 2012). On the other hand, Fe, Ba, Cu, and Sb are derived from abrasion of vehicle brake pads and tires (Hulskotte et al., 2014). Among these, Fe and Ba are not suitable tracers of vehicle-brake abrasion, because they are also abundant in soil; therefore Cu was used as a tracer of vehicle abrasion at Kumamoto. Cu in coarse particles is emitted from abrasion of vehicle brakes (Sternbeck et al., 2002), whereas Cu in fine particles is derived from combustion (Font et al., 2015). Cu concentrations in the coarse size range were considerably higher at Kumamoto than at Cape Hedo, because Kumamoto had much more vehicle traffic. Furthermore, because PM₁₀
has a much shorter residence time in the atmosphere than PM$_{2.5}$ (Shin et al., 2009), we can expect that little or no Cu in coarse particles emitted in Kumamoto reached Cape Hedo.

The size distribution of Cu concentrations at Kumamoto differed from that at Cape Hedo (Fig. 5(b)). At Kumamoto, Cu concentrations were highest in the coarse fraction owing to the contribution of vehicle abrasion in Kumamoto. At Cape Hedo, Cu concentrations were lowest in the coarse fraction and highest in the fine fraction. We attributed this difference to the more rapid deposition of coarse particles than fine particles during long-range transport (Allen et al., 2001).

Pb/Cu ratios were higher in all seasons at Cape Hedo (Fig. S2(a)). The ratio in winter was particularly high at both sites. Similar to the results of Shimada et al. (2014), the contribution of coal combustion at Cape Hedo is greater in winter than in other seasons. V/As ratios were also used as a means of distinguishing among transboundary pollutants. Fuel oil combustion releases V in aerosols (Viana et al., 2014), and concentrations of V are often used as a tracer of ship emissions. Coal combustion releases As (Tian et al., 2010), and almost all As observed in western Japan originates from China (Sakata et al., 2014) as coal is little used in Japan. Therefore the V/As ratio should effectively distinguish ship emissions from coal emissions. Because particles derived from fossil fuel combustion dominate the 0.2–1 µm aerosol fraction (Waheed et al., 2011), we used the elemental concentrations of the 0.5–1 µm fraction to determine V/As (Fig. S2(b)).

The V/As ratio at Kumamoto was particularly high in summer (Fig. S2(b)), when air masses are transported to Kumamoto from the East China Sea (Fig. S1), indicating large contributions of V from ship emissions. The ratio was low at both sites in spring, autumn, and winter, but was particularly low in winter. This is attributed to the large contribution of As from coal combustion in China, because air masses reaching Kumamoto in winter were largely derived from China (Fig. S1).

**Comparisons of Aerosols in the Same Air Masses at Kumamoto and Cape Hedo**

In two cases, backward-trajectory analysis showed that the same air mass was observed at both Kumamoto and Cape Hedo (Fig. S3). The air mass reaching Cape Hedo on 17 October 2014 passed over Kumamoto on 16 October, and the air mass reaching Cape Hedo on 31 October 2015 passed over Kumamoto the same day. Fig. S4 compares the mass proportions of the 16 metallic elements in coarse particles at our two measurement sites. The correlation between sites was very strong ($r^2 = 0.97$, $p < 0.05$), and the regression-line slope was 0.93. That most of the elements plotted on the 1:1 line indicated that they did not increase or decrease during transport from Kumamoto to Cape Hedo. However, percentages of Cu, Sb, and K departed greatly from the 1:1 line, with Cu and Sb being higher at Kumamoto and K being higher at Cape Hedo.

Looking in detail at Sb (Fig. 5(a)) and Cu (Fig. 5(b)), we found the highest concentrations in the 0.5–1 µm fraction at Cape Hedo, but at Kumamoto, Cu had its peak concentration in the 2.5–10 µm fraction, and Sb had a bimodal distribution, with peaks in the 0.5–1 µm and 2.5–10 µm fractions. Sb and Cu are found in coarse particles emitted from the abrasion of vehicle brakes (Hulskotte et al., 2014), as brake pads contain 1–5% Sb$_2$S$_3$ (Varrica et
**Fig. 6.** Correlation between Cl⁻ and K in fine particles (< 2.5 µm) at Kumamoto (a) and Cape Hedo (b). Correlation between Na⁺ and Cl⁻ in coarse particles (> 2.5 µm) at Kumamoto (c) and Cape Hedo (d). Correlation between Na⁺ and Cl⁻ in fine particles (< 2.5 µm) at Kumamoto (e) and Cape Hedo (f).
al., 2013), and brake linings contain Cu (Stembeck et al., 2002). Furthermore, particles produced by mechanical abrasion are mainly in the 2–4 μm size range (Gietl et al., 2010). According to Pio et al. (2013), Cu/Sb ratios in material derived from vehicle abrasion range from 7.1 to 12.1, and in our results the annual average Cu/Sb ratio at Kumamoto was in the same range (10.3). The sum of the evidence indicates that Cu and Sb are enriched in coarse aerosols at Kumamoto that settle out from air bodies before reaching Cape Hedo.

Conversely, the content ratio of K at Kumamoto was smaller than at Cape Hedo (Fig. S4), meaning that the K content in fine particles was larger at Kumamoto than at Cape Hedo. Concentrations of K were highest in the coarse (2.5–10 μm) fraction at both sites (Fig. 5(c)). Our analysis of EF values showed that particles in this size range originated from sea salt or soil dust (Tables S1 and S2). Because the EF values showed that particles in this size range originated from sea salt and/or soil dust, the EF values of K at Kumamoto were much higher than at Cape Hedo during the observation period. As expected, Na+ in fine particles (Figs. 6(e) and 6(f)) at Kumamoto and Cape Hedo during the observation period. As expected, Na+ in fine particles (Figs. 6(e) and 6(f)) at Kumamoto and Cape Hedo were higher at Kumamoto (0.91 neq m−3) than at Cape Hedo, but was appreciable at Kumamoto (0.0038) at Cape Hedo, but was appreciable at Cape Hedo, and K is an indicator of local emissions from vehicle brake abrasion. In other words, K is an indicator of local emissions.

In sum, our results showed that Cu and Sb in coarse aerosols can be tracers of local emissions from vehicle brakes and tires, and K in fine aerosols can be a tracer of local emissions from waste incineration or biomass burning.

CONCLUSIONS

At the Kumamoto site, local air pollutants, including elements derived from abrasion of vehicle brakes, affected ambient air quality. However, because these pollutants resided mainly in coarse aerosol particles, most of them were not transported long distances, and air quality at the Cape Hedo site was relatively unaffected by them. This means that in air masses from China that arrive at Cape Hedo after passing over Kumamoto, almost all trace elements in the fine aerosol particles were from China. Our results show that the contribution of most anthropogenic elements in transboundary air pollutants, particularly in fine particles, is greater than that of local air pollutants at Kumamoto. Therefore, transboundary air pollutants are of special concern when assessing the effects of ambient trace elements on human health in western Japan. Trace element concentrations and their ratios, specifically Pb/Cu and V/As, are effective in distinguishing transboundary air pollutants from local air pollutants. In particular, Cu and Sb are useful indicators of local emissions from vehicle brake abrasion, and K is an indicator of local emissions from waste incineration or biomass burning.

ACKNOWLEDGMENTS

This research was supported by the Global Environment Research Fund (5-1452 and 2-1403) of the Ministry of the Environment of Japan.

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Tatsuta, S., Shimada, K., Chan, C.K., Kim, Y.P., Lin, N.H.,


Received for review, December 29, 2016
Revised, July 11, 2017
Accepted, July 21, 2017