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Present and long-term pollution status of airborne copper in major urban environments

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HIGHLIGHTS

- The pollution status of metals from anthropogenic sources has been worsened over the past decades.
- There is a strong imbalance in the amount of quantitative data between different airborne metal species.
- Although Cu data are abundant in soil media, its direct measurement data are scant in ambient air.
- This work aims to elucidate the factors underlying the spatiotemporal distribution of airborne Cu.

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ABSTRACT

The concentrations of many harmful metals in air have been continuously decreasing around the world especially in North America and Western Europe, although deviations from such trend have been observed elsewhere such as East Asia. To help understand spatiotemporal factors governing the environmental behavior of hazardous metals, the concentrations of copper (Cu) in total suspended particulate (TSP) fractions were analyzed in the seven major cities in South Korea over a two decadal period (1991 through 2012). Unlike other metal species, there was no distinctive seasonal trend (e.g., spring/winter maximum and summer minimum) in the Cu levels in most South Korean cities. The long-term trend of Cu, if assessed by its annual mean values, recorded two contrasting trends for each decade: the earlier period (from 1991 to early 2000) is characterized by high variabilities with a maximum concentration of 243 ng m^{-3} (in 2003), while the later period showed an appreciable (several-fold) reduction to the latest (2012) available concentration level of 35.7 ng m^{-3}. As such, the present Cu levels in Korea should approach those commonly seen in moderately clean urban environments elsewhere. The overall results suggest that South Korean regulatory efforts to control particulate matter (PM) emissions have greatly influenced the present Cu levels consistent with the observed temporal trends of airborne PM.

1. Introduction

The uptake of trace metals by ecological systems has long been the subject of environmental concern due to their potential human health hazards (Charlesworth et al., 2012). Their presence in all types of environmental media (e.g., water, air, and soil) is the consequence of diverse natural/anthropogenic sources and processes. Although the extent of relative contributions from two source types can differ greatly across diverse metal species, the main sources of most toxic components are generally explained by man-made processes such as industry, agriculture, sewage sludge, waste incineration, and road traffic (Song and Gao, 2011).

The pollution status of metals from anthropogenic sources has been worsened over the past decades because of unrestrained (or unregulated) industrialization/urbanization lacking efficient integrated control efforts (e.g., environmental legislation plus pollution abatement measures) to effectively reduce their emissions. In spite of the increasing relevance of metallic pollution, detailed knowledge concerning their sources, impacts, and remedies is still very limited. Consequently, the significance of environmental monitoring has been acknowledged, as it allows to properly evaluate the degree of contamination derived by diverse factors and processes (Barrett et al., 2013; Steinle et al., 2013).

An accurate quantification of airborne pollutants is considered one essential step to diagnose the health of air quality. In this respect, a number of airborne toxics are often selected as the means to judge their harmful effects on human health or ecological

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systems (Astel et al., 2008). However, as most of previous efforts have been directed heavily to some well-publicized species such as Pb, Cd, and Hg, there is a poor balance in the amount of quantitative data for certain metal species. Note that the concentration data of such publicized species are abundant in all different media (water, air, and soil), while those of others are lacking significantly in relative terms. For instance, concentration levels of Cu in soil media have been reported in numerous studies; however, data for Cu in ambient air is scant. Ironically, atmospheric pollution of Cu has been assessed rather frequently and indirectly through the monitoring of certain biological (trees, moss, soil microorganisms, etc. (Cao et al., 2008; Marx et al., 2010; Guttov et al., 2011; State et al., 2012)) or geochemical indicators (e.g., peat bog, sediment, etc. (Mighall et al., 2002, 2009)). Such efforts have been helpful to provide the descriptive basis for explaining the environmental behavior of Cu at various time scales (e.g., prehistoric period to present). Evaluation of long-term monitoring data has been in fact advantageous to judge various factors involved in regulation efforts and the response of those target pollutants. However, the low availability of its concentration data can restrict the direct diagnosis of the fundamental factors underlying its source/sink processes.

In South Korea, the pollution levels of most important airborne metal species have been routinely monitored from air quality monitoring network connecting most major cities and highly urbanized areas (e.g., Nguyen and Kim, 2008). The vast amount of data accumulated via such efforts allowed us to explore the long-term behavior of metals in each strategic location and the associated effectiveness of emission control strategy with respect to discrete metal species such as Pb (Kim, 2007a), Cd (Kim, 2007b), Cr (Nguyen and Kim, 2008), Mn (Myeong et al., 2009), and Ni (Kim et al., in press). In this study, efforts were extended further by conducting an in-depth analysis on the distribution of airborne Cu using the data sets collected from seven major cities in South Korea, especially over a two decadal period (1991–2012). The results of this study are expected to widen our understanding of the metal pollution in urban environments and to increase the database of airborne Cu in East Asia.

2. Materials and methods

From the early 1990s, heavy metal monitoring stations were established in most urbanized locations throughout the Korean peninsula and operated by Korean Ministry of Environment (KMOE). As the operation of this monitoring network has been constantly adjusted throughout the years, the locations of individual monitoring stations for a given city have been changed on many occasions. In this study, the pollution status of Cu in air was evaluated based on extensive data sets collected from seven major cities in South Korea over a two decadal period from 1991 to 2012 (Fig. 1).

Although all measurements were conducted to obtain representative monthly data, all the data were reported/calculated on a cumulative annual basis until 1997. The management scheme for the data changed as of 1998 so that all the monthly metal data are recorded in line with the actual monitoring interval set for the monitoring network. The basic information concerning the number and operational conditions of these stations has been described elsewhere (Kim, 2007a,b). Because of a procedural difference in data management between the two periods, all the detailed analysis of Cu behavior has generally been made using the monthly data sets collected since 1998. However, to explore the long-term variability of Cu, its annual mean data available for the entire study period (1991–2012) were also examined for each city for simple comparison.

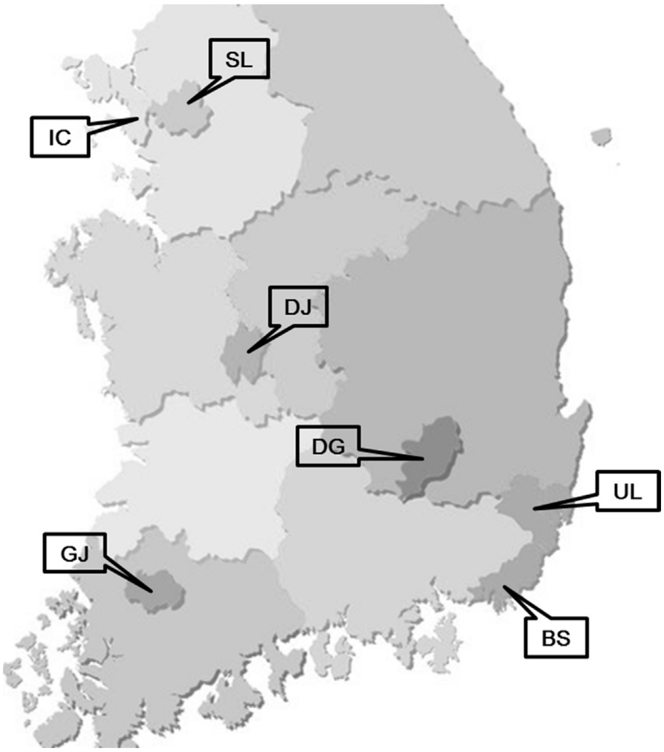

Fig. 1. Geographical locations of the seven major cities in South Korea for routine monitoring of airborne Cu levels.

For the determination of heavy metal concentration levels, PM as TSP were collected and analyzed on a monthly basis from each monitoring station according to standard procedures for metal analysis recommended by KMOE (Kim, 2007a,b). For instance, the total number of the stations amounted to 13 in Seoul and 6 in Busan (KMOE, 2006). However, due to the unavailability of the original TSP data, evaluation of Cu data was made occasionally in relation to the PM_{10} data collected concurrently from each station since 1995. The general information concerning the analytical procedures and basic QA has been described in our previous work (Kim et al., 2004). The collection of TSP samples was made at a flow rate of 1.5 $m^3\ min^{-1}$ (a total volume of 2100 m^3) using Whatman PM2000 glass fiber filters (0.1 µm pore-size and 99.9% collection efficiency). Pre-treatment of samples (a total sample area of $25 \times 20\ cm^2$) was done by immersing 23% of the filter cut into several pieces in 35 mL of acid solution prepared by mixing 6:1 ratio of concentrated HNO_3 (after 50% dilution) and H_2O_2 solution. This procedure was completed by repetitive treatments of heating, filtering, and resolubilization of this mixture. The concentrations of target metals were then analyzed using Atomic Absorption Spectrometry (AAS). Detection limits (DL) of Cu were typically found in 0.2 µg (in absolute mass (AM)) or 0.1 ng m^{-3}.

3. Results

In light of the format differences of data availability between prior to and after 1998, a detailed analysis of the Cu behavior can only be made using its monthly data sets obtained after 1998. However, to explore the long-term distribution trend, the analysis of the Cu data was made by directly taking the annual data (between 1991 and 1997) and by converting monthly data into annual ones (between 1998 and 2012). Hence, a descriptive analysis on the long-term trend of Cu data monitored from each of all seven major