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Short communication

Source identification of nickel in TSP and $PM_{2.5}$ in Tokyo, Japan

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Abstract

This study investigates the source identification of nickel in the aerosol of the Tokyo metropolitan area. TSP and $PM_{2.5}$ samples were collected daily from August to November 2004. The samples were examined by means of the water-extraction method, followed by elemental analysis and SEM/EDX analysis. We distinguished two types of atmospheric nickel sources in the studied area: (1) particles derived from heavy oil combustion, distributed mostly in fine particles such as $PM_{2.5}$, relatively water-soluble, and containing vanadium and (2) particles derived from mechanical abrasion/erosion of metallic surfaces, distributed in coarse particles such as TSP, relatively water-insoluble, and containing chromium.

Keywords: Aerosol; Chromium; Heavy metals; LA/ICP-MS; Nickel; $PM_{2.5}$; SEM/EDX; Trace elements; TSP; Vanadium; Water-soluble metals

1. Introduction

Many trace metals and metallic compounds are possibly harmful and carcinogenic to humans; therefore, atmospheric metal exposure represents a serious concern for human health. In particular, according to the International Agency for Research on Cancer (IARC, 2006), nickel compounds are classified into Group 1 (carcinogenic to humans), and metallic nickel is classified into Group 2B (possibly carcinogenic to humans). The effect of atmospheric nickel on human health depends on its chemical form and the diameter of the nickel-containing particles (WHO, 2000). Several previous reports have described the speciation of the chemical form of nickel in aerosols of different sizes (Fernandez Alvarez et al., 2004; Huggins et al., 2004). Sequential extraction methods were often used in these previous studies. Furuta et al. (2005) used a scanning electron microscope equipped with an energy dispersive X-ray microanalyzer (SEM/EDX) in order to identify the sources of trace elements in aerosols of different sizes. The wet-chemical sequential extraction method and SEM/EDX are useful for the speciation of atmospheric nickel; however, a study using both the wet-chemical method and SEM/EDX has not been reported heretofore. This study investigates the source identification of nickel in the aerosol of the Tokyo metropolitan area using a combined procedure consisting of (1) size separation of aerosol

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particles, (2) wet-chemical treatment followed by elemental analysis by ICP-MS equipped with a laser ablation system, and (3) SEM/EDX analysis.

2. Experimental

2.1. Sampling

The sampling site was located approximately 15 km in the south-southwesterly direction from the center of Tokyo. Aerosol samples were collected at the rooftop (approximately 30 m above the ground) of the building of Keio University, Yokohama, Japan. Total suspended particles (TSP) and $PM_{2.5}$ (particulate matter which passes through a size-selective impactor inlet with a 50% efficiency cut-off at an aerodynamic diameter of 2.5 μm) were collected on cellulose nitrate filters (AAWP04700, 0.8 μm of pore size, Millipore Corp.) using a low-volume air sampler. A multinozzle cascade impactor (MCI, NL-20-2.5A, Tokyo Dylec. Corp.) was used as the $PM_{2.5}$ impactor. TSP and $PM_{2.5}$ samples were collected daily from August to November 2004, 24 h a day, at an air flow rate of $20\,L\,min^{-1}$. Approximately 90 samples each of TSP and $PM_{2.5}$ were collected.

2.2. Water extraction

In order to identify the chemical form of nickel, we simply used a water-extraction procedure, which is often the first step in sequential extraction methods (Dabek-Zlotorzynska et al., 2005; Fujiwara et al., 2006; Kyotani and Iwatsuki, 2002; Wong et al., 1997). A portion of the sample filter was cut for further water-extraction treatment. Water-soluble metals were extracted from the filter by shaking 30 min with 10 mL of water. The treated filter was stored and dried in a desiccator for >48 h. The treated and dried filter sample was subjected to further elemental analysis.

2.3. Elemental analysis

Water-treated filter samples and non-treated (raw) filter samples were analyzed in order to determine the contents of trace metals. Trace metal concentrations were determined using an inductively coupled plasma mass spectrometer equipped with a laser ablation sample introduction system (LA/ICP-MS). The details of the experimental procedure used in the present study have been described elsewhere (Okuda et al., 2004, 2006, 2007; Tanaka et al., 1998). The precision of the replicated LA/ICP-MS measurements ($n = 8$) was within ~10% of the relative standard deviation. The detection limits of the trace metals analyzed by LA/ICP-MS were almost the same, and were slightly better than those obtained by instrumental neutron activation analysis (INAA) or X-ray fluorescence spectrometry (XRF; for Ni, Cd, and Pb determinations). The analytical results obtained by LA/ICP-MS were in good agreement with those obtained by INAA or XRF (Tanaka et al., 1998).

2.4. SEM/EDX analysis

SEM/EDX analysis was performed using a FEI SIRION field emission scanning electron microscope equipped with a BRUKER AXS energy-dispersive X-ray microanalyzer. The operating accelerating voltage was 15 kV.

3. Results and discussion

Fig. 1a shows the trace metal concentrations in TSP and $PM_{2.5}$, and Fig. 1b shows the ratio of the metal concentration in $PM_{2.5}$ to that in TSP for every trace metal tested. The arithmetic mean of the nickel concentration in TSP was $17.2 \pm 16.1\,ng\,m^{-3}$ ($n = 89$), and that in $PM_{2.5}$ was $9.0 \pm 8.5\,ng\,m^{-3}$ ($n = 91$). The $PM_{2.5}$/TSP ratio of nickel was 0.63 ± 0.47. The nickel concentration in both TSP and $PM_{2.5}$ showed good correlations with the vanadium and chromium concentrations ($0.74 < r < 0.83$, $p < 0.001$). The correlations between nickel and other metals (except for vanadium and chromium) were relatively low ($r < 0.6$ in most cases). The relationship between nickel and vanadium in $PM_{2.5}$ was $C_{Ni} = 1.26C_V$ ($r = 0.77$), which was similar to a result observed in the center of Tokyo ($C_{Ni} = 1.20C_V$ (winter of 2004) and $C_{Ni} = 1.77C_V$ (summer of 2004), Okuda et al., 2007). Almost all the vanadium in the air at the sampling site was contained in $PM_{2.5}$, because the $PM_{2.5}$/TSP ratio of vanadium was around 1.

The ratios of the concentrations of the water-insoluble metals (analytical results of water-treated filter samples) to that of the total metals (analytical results of non-treated (raw) filter samples) in TSP and $PM_{2.5}$ are shown in Figs. 1c and d, respectively. The maximum ratios of the concentrations of water-insoluble metals to that of the total metals were 0.75 for chromium in TSP and 0.65 for titanium in