



Different chemical properties of lead in atmospheric particles from urban roadside and residential areas

Kunihiro Funasaka¹, Toshiki Tojo¹, Satoshi Kaneco², Masaki Takaoka³

¹Osaka City Institute of Public Health and Environmental Sciences, 8–34 Tojo-cho, Tennoji, Osaka 543–0026, Japan

²Department of Chemistry for Materials, Graduate School of Engineering, Mie University, 1577 Kurimamachiya, Tsu, Mie 514–8507, Japan

³Environmental Engineering, Graduate School of Engineering, Kyoto University, Kyoto daigaku-Katsura, Nishikyo-ku, Kyoto 615–8530, Japan

ABSTRACT

Lead in atmospheric suspended particles was fractionized using simple acid extraction to assess differences in chemical properties of lead from roadside and residential areas. The Pb–LIII edge XANES measurement was also challenged to explore the possibilities of contamination from road dust into the air. Results suggest that 0.1 M–HCl extractable fractions of lead at the roadside area are significantly higher than those obtained at the residential area, especially for the coarse mode of the particulate samples. Moreover, the solubility characteristics of the roadside particulate lead have partially overlapped with those of the road dust samples. The XANES spectra for coarse mode of particulate lead also nearly correspond to that of the road dust collected around the roadside area. These results indicate effects by the re-suspension of road dust to the roadside air. However, it is difficult to clear the roadside contamination from specific lead material applied in this study. This might suggest that specific lead compounds do not exist exclusively in atmospheric particles but exist as mixtures or unknown complexes.

Keywords: Lead, atmospheric particles, fractionation, road dust, XANES



Corresponding Author:

Kunihiro Funasaka

☎ : +81-6-6771-3197

☎ : +81-6-6772-0676

✉ : k-funasaka@city.osaka.lg.jp

Article History:

Received: 18 March 2013

Revised: 24 June 2013

Accepted: 28 June 2013

doi: 10.5094/APR.2013.041

1. Introduction

In Japan, atmospheric particulate matter has decreased greatly since 1970 and has shown slight but continued reduction since 2000. Moreover, atmospheric particulate lead greatly decreased after complete abolition of leaded gasoline in 1986. The present lead concentration is less than one–500th of that in 1970. Nonetheless, the sources and health effects of lower level exposure to lead, such as neurotoxicity in children, persist as current topics (Pingitore et al., 2009). The World Health Organization Regional Office for Europe set annual guideline values for lead as 0.5 µg/m³ in 2000 (WHO, 2000). The US Environmental Protection Agency (EPA) has enforced the regulatory standard for airborne particulate lead as lower than 0.15 µg/m³ since 2008 (US–EPA, 2008).

In urban roadside areas, atmospheric particulate lead often shows higher concentrations than in residential areas, but the contamination source and mechanisms remain unclear. In a previous study, it was suggested that the lead compounds of various chemical forms are generated from various sources (Manceau et al., 1996; Takaoka et al., 2005). Therefore, we examined the characteristic differences of particulate lead between those obtained in roadside and residential areas in order to research possible candidates and possible sources which bring about the surplus Pb concentration at the roadside area with a chemical fractionation and XANES spectroscopy.

The chemical fractionation has been basically developed for the classification of metals in the solid matrix according to particle size and chemical bonding (Smichowski et al., 2005). Sequential extraction has become a widely accepted method that can fractionate sediment and soil samples into different specific phases based on the solubility characteristics of their constituent metallic species (Tessier et al., 1979). However, some limitations and drawbacks are pointed out because the selectivities of the chemical reagents towards specific forms of binding were not taken into account for most of the schemes reported (Smichowski et al., 2005). Therefore, modified chemical speciation techniques have been increasingly reported (Fernandez Espinosa et al., 2002; Canepari et al., 2006). In this study, a simple acid extraction that is applicable to atmospheric filter samples (Kyotani and Iwatsuki, 2002) is modified and applied to pursue chemical differences of the particulate lead between the roadside and residential area.

The XANES spectroscopy, which can detect metal chemical forms on the basis of electron states around the target element, has been widely used for the speciation of metallic particulates in environmental samples (Manceau et al., 1996; Takaoka, et al., 2005). However, application to the atmospheric particulate Pb is limited because of relatively lower sensitivity of the spectroscopy. In the previous study (Funasaka et al., 2008), enhancement of the particle density per filter unit by scaling and accumulation of the quartz filter pieces enabled to obtain Pb–LIII edge XANES spectra with a small amount of filter samples. Using this method, XANES spectroscopy was challenged to each coarse and fine modes of the particles and directly compared with that of the road dust samples.

This study was conducted (1) to investigate differences of chemical properties of particulate Pb between urban roadside and residential areas using a simple acid extraction procedure, and (2) to challenge physicochemical study using Pb–LIII edge XANES spectra for coarse and fine particles and road dust samples. (3) Finally, a ternary diagram of the Normalized Leaching Ratio (NLR), which means the non-dimensional ratio of the Pb concentration in a certain leaching fraction to the total, was compared among the coarse and fine particles, road dust samples and typical lead compounds. From these results, chemical and physicochemical characteristics of lead in the atmospheric particles have been discussed to assess the possibility of contamination by re-suspension of road dust into the air.

2. Methodology

2.1. Atmospheric particulate samples

Particulate samples were collected on quartz fiber filters (QR-100, 80 mm ϕ ; Advantec Toyo Kaisha Ltd.) using an Andersen Cascade Impactor (AN-200; Tokyo Dylec Corp.), which can collect particles size separately on nine filter sheets. Sampling was conducted continuously for 12–16 days from January through December 2010 at two monitoring sites in Osaka City, Japan. Site A (Nishiyodogawa Ward) is located at a point of heavy traffic flow with a large volume of diesel vehicles (34°42'N, 135°26'E). Site B (Hirano ward) is located in a general suburban residential area (34°37'N, 135°32'E). Site A faces the Route 43 roadside and the overhead Hanshin Expressway. The sampler was set at 7 m from the R43 roadside and 3 m above the ground. Sampling at site B was conducted on a rooftop 16 m above the ground.

2.2. Simple acid extraction procedure for atmospheric particulate samples

The atmospheric particulate sample collected on the filter was used for a simple acid extraction procedure. It was divided into water-soluble, 0.1 M–HCl soluble, and residual fractions in accordance with a previous study (Kyotani and Iwatsuki, 2002). In the final step, we applied aqua regia (HNO₃:HCl=1:3) decomposition for the residue (Birmili et al., 2006) instead of XRD analysis conducted in the original paper. A portion of the 25 mm ϕ circle area of the sample filter was cut and attached directly to a PTFE filter holder. First, 5 mL of distilled water was added to the filter samples. This procedure was repeated four times. The suction pressure was adjusted to 0.05 MPa using a vacuum pump (MDA-015; Ulvac Riko, Inc.). The filtrates were gathered as a water-soluble fraction. Second, 5 mL of 0.1 M–HCl was added sequentially. This procedure was repeated four times. Each filtrate was heated on a hotplate until dry. Then 5 mL of 0.2 M–HNO₃ was added after cooling to room temperature. The sample solution was placed into a polypropylene test tube (62.554.001, 15 ml; Sarstedt AG and Co.).

The residual filter was removed from the holder, transferred into a glass beaker and decomposed with 10 mL of aqua regia and heated for 1 h with a glass cover. Then, after removing the cover, heating was continued until dry. After cooling to room temperature, 5 mL of 0.2 M–HNO₃ was added and then filtered (16555, 26 mm ϕ , cellulose acetate, pore size 0.45 μ m; Sartorius AG). Finally, the sample solution was placed into the polypropylene test tube.

Three fractionized solutions were used for the analysis of Pb by Zeeman Electro Thermal Atomic Absorption Spectrometry (ET–AAS, AAnalyst 600; PerkinElmer Inc.). In order to calculate atmospheric Pb concentration in each fraction, the sample concentration was corrected by the blank and then divided by the sampling air volume. In this way, lead in the filter sample was fractionized to water-soluble, 0.1 M–HCl extractable, and residue.

Before experiment for the atmospheric filter samples, 15 blank filters were used for the calculation of detection limits (DLs), which correspond to 3 times the standard deviation. DLs were 0.24 for water-soluble, 0.37 for 0.1 M–HCl extractable, and 0.74 ng/m³ for the residual fraction. Half of DL was also used when the sample Pb concentration was lower than the DL.

2.3. Simple acid extraction for Pb compounds

To check the possibility that specific lead compound gets mixed in the particulate samples, 10 kinds of Pb compounds were applied to the simple acid extraction procedure and the results were compared to those of the atmospheric particulate samples. As listed in Table S1 of Supporting Material (SM), Pb(NO₃)₂, PbCl₂, PbCO₃, Pb(OH)₂, PbO, Pb (free), PbSO₄, PbSiO₃, PbS and PbO₂ were powdered with a Teflon mortar and pestle; then they were passed through a polyethylene 25 μ m sieve in order to replicate the real atmospheric particulate samples. Portions of 0.10, 0.20, 0.50, 1.0, 2.0, and 5.0 mg of each powder were weighed (Supermicro, S4; Sartorius AG) and placed directly on the center of a quartz fiber filter before simple acid extraction (n=3 for each dose). In this experiment, however, considering the lower limit of the microbalance and relatively higher concentration of the added Pb samples than the above atmospheric particulate samples, it is not realistic to use an ET–AAS technique. Therefore, lead in the extracted solutions was analyzed using a Flame AAS (AA640; Shimadzu Corp.).

2.4. Road dust sampling and application to simple acid extraction

To compare NLRs obtained for atmospheric particulate samples, road dust around the Site A was collected and used for simple acid extraction. Dusts accumulated on a Route 43 roadway curbstone was swept by a brush. Then it was collected on a paraffin paper. Sampling was done when 10 days of prior fair weather had continued. Road dust samples, collected at four points of the R43 roadside, were passed through a 25 μ m sieve. The filtrates were collected in a sealed glass vial and stored at 20°C and 50% relative humidity before use. Each 0.2 mg of road dust sample was also weighed and put directly on the center of a quartz fiber filter on the PTFE filter holder and simple acid extraction was applied (each n=3).

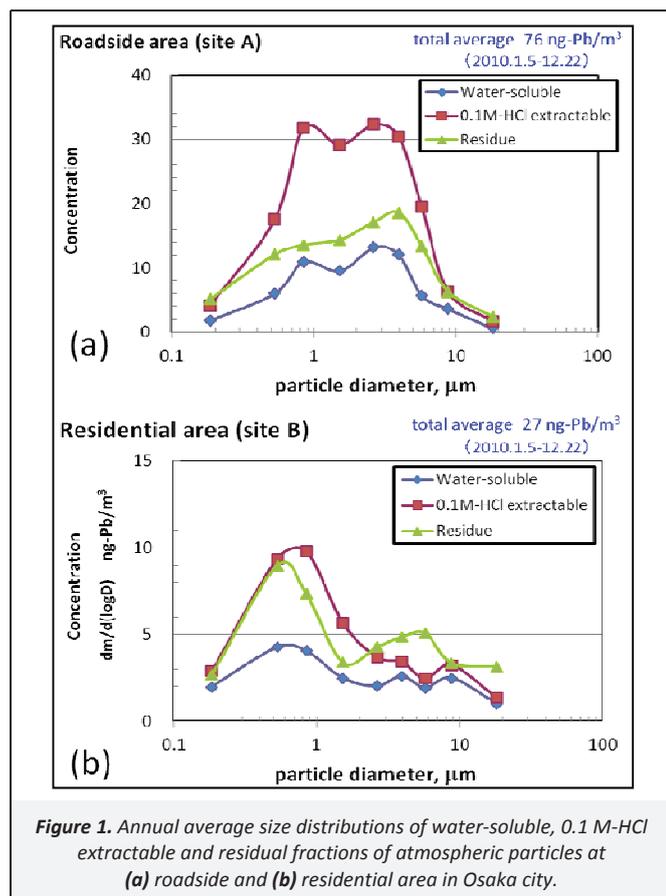
2.5. Pb–LIII edge XANES spectra

The Pb–LIII edge XANES experiments were conducted on Beamline BL01B1 at SPring-8 (Hyogo, Japan), which operates at a ring energy of 8 GeV and with stored current at 99 mA. The main optics is a standard SPring-8 bending magnet system. The Pb–LIII edge XANES spectra were measured using a Si(111) two-crystal monochromator (Takaoka et al., 2005). In this experiment, the quartz fiber filters were divided into two groups of coarse and fine particles collected by the Andersen Cascade Impactor, which respectively correspond to greater than 2.1 μ m and less than 2.1 μ m of aerodynamic diameter. To enhance the particle density per filter unit, the filter was cut into small pieces (25×25 mm). Then the surface layers of the filter pieces were scaled and accumulated. The XANES spectra of the filter samples and foregoing road dust samples were recorded in fluorescent mode with a 19-element SSD to facilitate the high-resolution, high-sensitivity measurement of the fluorescence signal of the filter samples as described in a previous study (Funasaka et al., 2008).

3. Results

3.1. Simple acid extraction for atmospheric particulate samples

Annual average size distribution curves for lead in water-soluble, 0.1 M–HCl extractable, and residual fractions in the roadside and residential areas are presented respectively in Figure 1.



Lead in the samples at the roadside area is superior in the 0.1 M-HCl extractable fractions, fundamentally indicating a bimodal size distribution curve. However, the samples at the residential area mainly show a single size distribution of water-soluble and 0.1 M-HCl extractable fractions.

Monthly lead concentrations and NLRs in each fraction of coarse (more than 2.1 μm) and fine (less than 2.1 μm) particles are presented in Tables 1 and 2. Overall, it is shown that coarse and fine lead concentration at the roadside area is often higher than that of the residential area. Annual average fractional concentration in Table 3 also shows statistical significances for the roadside comparing to the residential area.

Samples with more than five times the ratio of coarse mode of lead at the roadside to residential area are 9 for 22 sample datasets, as shown in Table 1: February 2–16, March 1–16, March 16–26, May 27–June 11, September 15–30, September 30–October 14, October 14–29, November 12–26, and November 26–December 9, 2010. The maximum NLR in 0.1 M-HCl extractable fractions in the coarse particles were 0.76 and 0.66, respectively, at the roadside and residential sites, obtained for samples collected on April 28–May 13, 2010.

Table 2 shows that the lead concentrations in fine particles at the roadside area were not so high compared to those of the coarse one. Samples with more than five times the ratio of fine mode of lead at the roadside to residential area were 4 of 22 sample datasets: February 2–16, March 16–26, May 13–27, and May 27–June 11, 2010. These terms are almost overlapped with those of the coarse one.

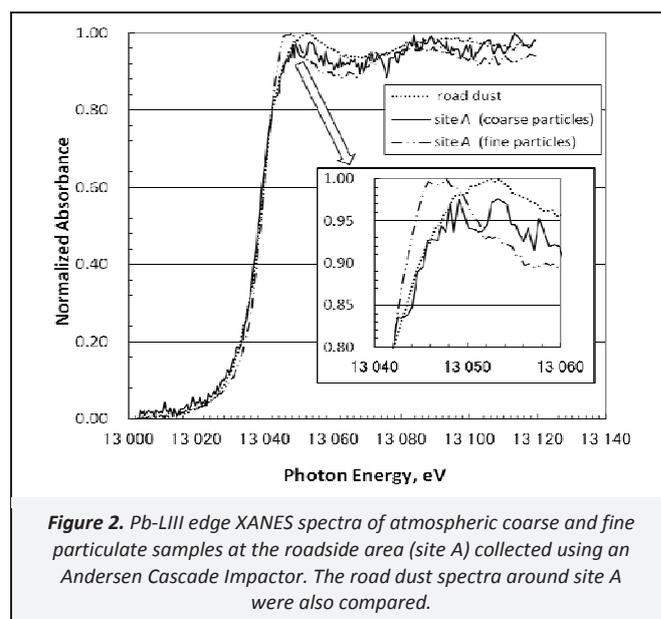
As shown in Tables 1 and 2, monthly sum of the Pb concentration at the roadside area during September to early December, is seasonally high adding to the spring term. This reason is not clear but the possibility of stagnation of atmospheric

pollutants is undeniable because monthly average wind velocity (2.0–2.4 m/sec) from September to November 2010 in Osaka city was relatively low according to the Japan Meteorological Agency.

Table 3 also summarizes annual average concentrations of coarse and fine particles for roadside and residential areas. Total lead concentration at the roadside area, 76 ng/m³, was 2.8 times higher than in the residential area, 27 ng/m³. This fact is more apparent in the coarse particulate samples: the ratio was 3.5. Significant differences between roadside and residential areas were also found in coarse and fine mode.

3.2. Pb-LIII edge XANES spectra for the samples at roadside area

To supplement lead chemical properties from through simple acid extraction, Pb-LIII edge XANES spectra for the coarse and fine particulate samples and road dust samples were directly compared. The spectra pattern is depicted in Figure 2. Although the XANES spectra for the particulate sample are noisy because of the limit of filter loading on the measuring spot, there are apparent differences of the spectra, especially for 13 042–13 049 eV. Moreover, the XANES spectra for coarse mode of particulate lead within this range of photon energy nearly correspond to that of the road dust collected around site A. These results show different physicochemical properties of Pb between coarse and fine mode of particulate samples, and it also shows the similarities between coarse particles and road dust.



3.3. Simple acid extraction for Pb compounds

For the 10 chemical forms of Pb compounds, the relation between NLR and loading amount of the chemicals was investigated. Figure 3 (upper side) represents examples of extraction characteristics for PbCO₃ and Pb(NO₃)₂. Although PbCO₃ is mainly recovered in 0.1 M-HCl fraction as presented in Figure 3(a), Pb(NO₃)₂ is almost fractionized to the water-soluble fraction in Figure 3(b). For instance, 0.1 mg of PbCO₃ gives 0.97±0.042 of NLR for 0.1 M-HCl fraction, but the 5.0 mg loading amount reduces the NLR of 0.1 M-HCl fraction to 0.89±0.061. In contrast, NLR in the water-soluble fraction by the loading amount of 0.1 mg and 5.0 mg of Pb(NO₃)₂ were, respectively 0.98±0.0080 and 0.97±0.013. The bottom figures, (c) and (d), also showed the maximum fraction ratio of these chemicals, which represents the ratio of the concentrations in the main fraction to that of the next leaching fraction. The maximum fraction ratio confirms the stability of leaching procedure with amplification. The maximum fraction ratio over 0.5 mg of PbCO₃, which corresponds to the 0.1 M-HCl fraction

to the next residual fraction, dropped to less than half of the initial quantity (i.e. 0.1 mg of PbCO_3). In contrast, the maximum fraction ratio for 0.1 mg of $\text{Pb}(\text{NO}_3)_2$ was stable up to 2.0 mg of loading amount. Therefore, at least, up to 0.2 mg of loading amount of Pb compounds, which is equivalent to 100 L/g of the L/S ratio, suggests inherent leaching characteristics depending on the chemical form of Pb compounds in the simple acid extraction procedure.

Table 4 presents NLR for typical 10 Pb compounds examined in this study when 0.2 mg of each powder was applied to the simple acid extraction procedure. Characteristics of NLRs for Pb compounds are representatively divisible into three groups. First, $\text{Pb}(\text{NO}_3)_2$ and PbCl_2 are highly dissolved in water. Second, PbCO_3 , $\text{Pb}(\text{OH})_2$ and PbO belong to 0.1 M-HCl extractable group. Thirdly, $\text{Pb}(\text{free})$, PbSO_4 , PbSiO_3 , PbS and PbO_2 are mainly extracted in the residual fraction. The recovery rate for Pb compounds tested here was in the range of 86–130%.

4. Discussion

4.1 Differences of chemical and physicochemical properties of lead in atmospheric particulate samples between roadside and residential areas

According to the simple acid extraction procedure, different chemical properties of lead in atmospheric particles between roadside and residential sites were investigated. Although strict identification of chemical species in the particulate samples in this simple manner is difficult, chemical fractionation of Pb in the particulate samples is expected to be interesting to offer insight into what chemical forms are available in the atmospheric environment by comparing Pb reference compounds.

Table 1. Monthly fractionated coarse lead concentrations and the ratio of the sum at the site A to the site B. The number in parenthesis shows Normalized Leaching ratio (NLR) of each fraction to the sum of concentration

| Sampling date | Roadside area (site A), ng-Pb/m ³ | | | | Residential area (site B), ng-Pb/m ³ | | | | Ratio of the sum (site A)/(site B) |
|---------------|--|-----------|---------|-------|---|-----------|---------|-------|------------------------------------|
| | Water | 0.1 M-HCl | Residue | Sum | Water | 0.1 M-HCl | Residue | Sum | |
| 2010.1.5 to | 10 | 16 | 17 | 43 | 10 | 10 | 12 | 32 | 1.3 |
| 2010.1.19 | (0.23) | (0.37) | (0.39) | (1.0) | (0.32) | (0.30) | (0.38) | (1.0) | |
| 2010.1.19 to | 4.1 | 13 | 6.0 | 23 | 5.0 | 7.6 | 12 | 25 | 0.92 |
| 2010.2.2 | (0.18) | (0.56) | (0.26) | (1.0) | (0.20) | (0.30) | (0.50) | (1.0) | |
| 2010.2.2 to | 3.4 | 18 | 14 | 36 | 1.0 | 0.92 | 1.8 | 3.8 | 9.4 |
| 2010.2.16 | (0.10) | (0.51) | (0.39) | (1.0) | (0.27) | (0.24) | (0.49) | (1.0) | |
| 2010.2.16 to | 3.3 | 15 | 15 | 32 | 3.0 | 0.92 | 3.0 | 7.0 | 4.7 |
| 2010.3.1 | (0.10) | (0.45) | (0.45) | (1.0) | (0.44) | (0.13) | (0.43) | (1.0) | |
| 2010.3.1 to | 6.7 | 21 | 8.0 | 35 | 0.61 | 0.92 | 4.0 | 5.5 | 6.5 |
| 2010.3.16 | (0.19) | (0.58) | (0.23) | (1.0) | (0.11) | (0.17) | (0.72) | (1.0) | |
| 2010.3.16 to | 17 | 11 | 8.6 | 36 | 0.61 | 0.92 | 1.8 | 3.4 | 11 |
| 2010.3.26 | (0.46) | (0.30) | (0.24) | (1.0) | (0.18) | (0.27) | (0.55) | (1.0) | |
| 2010.4.28 to | 1.4 | 17 | 4.0 | 22 | 1.3 | 6.0 | 1.8 | 9.2 | 2.4 |
| 2010.5.13 | (0.061) | (0.76) | (0.18) | (1.0) | (0.14) | (0.66) | (0.20) | (1.0) | |
| 2010.5.13 to | 0.85 | 11 | 5.5 | 18 | 0.61 | 1.3 | 1.8 | 3.7 | 4.8 |
| 2010.5.27 | (0.048) | (0.64) | (0.31) | (1.0) | (0.16) | (0.34) | (0.50) | (1.0) | |
| 2010.5.27 to | 2.0 | 15 | 9.0 | 26 | 0.61 | 0.92 | 1.8 | 3.4 | 7.7 |
| 2010.6.11 | (0.079) | (0.57) | (0.35) | (1.0) | (0.18) | (0.27) | (0.55) | (1.0) | |
| 2010.6.24 to | 2.5 | 3.0 | 3.8 | 9.2 | 3.4 | 1.2 | 4.4 | 8.9 | 1.0 |
| 2010.7.7 | (0.27) | (0.32) | (0.41) | (1.0) | (0.38) | (0.13) | (0.50) | (1.0) | |
| 2010.7.7 to | 0.61 | 3.0 | 3.5 | 7.1 | 0.61 | 0.92 | 1.8 | 3.4 | 2.1 |
| 2010.7.21 | (0.087) | (0.42) | (0.49) | (1.0) | (0.18) | (0.27) | (0.55) | (1.0) | |
| 2010.7.21 to | 3.9 | 5.3 | 4.8 | 14 | 3.1 | 4.9 | 4.5 | 13 | 1.1 |
| 2010.8.6 | (0.28) | (0.38) | (0.34) | (1.0) | (0.25) | (0.39) | (0.36) | (1.0) | |
| 2010.8.6 to | 4.6 | 0.92 | 1.8 | 7.3 | 1.1 | 1.3 | 1.8 | 4.2 | 1.8 |
| 2010.8.18 | (0.63) | (0.12) | (0.25) | (1.0) | (0.26) | (0.30) | (0.44) | (1.0) | |
| 2010.8.18 to | 1.5 | 3.7 | 2.2 | 7.5 | 1.7 | 2.6 | 1.8 | 6.1 | 1.2 |
| 2010.9.2 | (0.20) | (0.50) | (0.30) | (1.0) | (0.27) | (0.43) | (0.30) | (1.0) | |
| 2010.9.2 to | 2.8 | 12 | 6.0 | 20 | 0.78 | 1.9 | 1.8 | 4.5 | 4.5 |
| 2010.9.15 | (0.14) | (0.57) | (0.29) | (1.0) | (0.17) | (0.42) | (0.41) | (1.0) | |
| 2010.9.15 to | 12 | 29 | 23 | 63 | 2.8 | 1.5 | 1.8 | 6.1 | 10 |
| 2010.9.30 | (0.19) | (0.45) | (0.36) | (1.0) | (0.45) | (0.25) | (0.30) | (1.0) | |
| 2010.9.30 to | 9.3 | 32 | 17 | 58 | 1.2 | 1.6 | 2.2 | 5.0 | 12 |
| 2010.10.14 | (0.16) | (0.54) | (0.30) | (1.0) | (0.23) | (0.31) | (0.45) | (1.0) | |
| 2010.10.14 to | 12 | 27 | 22 | 62 | 2.1 | 4.2 | 5.6 | 12 | 5.2 |
| 2010.10.29 | (0.20) | (0.44) | (0.36) | (1.0) | (0.18) | (0.35) | (0.47) | (1.0) | |
| 2010.10.29 to | 13 | 31 | 20 | 65 | 2.3 | 3.0 | 13 | 18 | 3.6 |
| 2010.11.12 | (0.21) | (0.48) | (0.32) | (1.0) | (0.13) | (0.17) | (0.71) | (1.0) | |
| 2010.11.12 to | 14 | 36 | 17 | 67 | 1.0 | 3.8 | 6.8 | 12 | 5.8 |
| 2010.11.26 | (0.20) | (0.54) | (0.26) | (1.0) | (0.089) | (0.33) | (0.58) | (1.0) | |
| 2010.11.26 to | 12 | 30 | 20 | 62 | 1.3 | 5.0 | 5.8 | 12 | 5.1 |
| 2010.12.9 | (0.20) | (0.48) | (0.32) | (1.0) | (0.11) | (0.42) | (0.48) | (1.0) | |
| 2010.12.9 to | 3.0 | 11 | 8.6 | 23 | 0.92 | 3.0 | 6.7 | 11 | 2.1 |
| 2010.12.22 | (0.13) | (0.49) | (0.38) | (1.0) | (0.086) | (0.28) | (0.63) | (1.0) | |

Table 2. Monthly fractionated fine lead concentrations and the ratio of the sum at the site A to the site B. The number in parenthesis shows Normalized Leaching Ratio (NLR) of each fraction to the sum of concentration

| Sampling date | Roadside area (site A), ng-Pb/m ³ | | | | Residential area (site B), ng-Pb/m ³ | | | | Ratio of the sum (site A)/(site B) |
|--------------------------|--|------------|------------|-----------|---|------------|------------|-----------|------------------------------------|
| | Water | 0.1 M-HCl | Residue | Sum | Water | 0.1 M-HCl | Residue | Sum | |
| 2010.1.5 to 2010.1.19 | 12 (0.23) | 29 (0.55) | 12 (0.23) | 53 (1.0) | 7.6 (0.24) | 13 (0.40) | 11 (0.36) | 32 (1.0) | 1.7 |
| 2010.1.19 to 2010.2.2 | 8.5 (0.12) | 53 (0.74) | 10 (0.14) | 72 (1.0) | 11 (0.23) | 20 (0.43) | 15 (0.33) | 45 (1.0) | 1.6 |
| 2010.2.2 to 2010.2.16 | 6.6 (0.12) | 38 (0.69) | 11 (0.19) | 56 (1.0) | 2.7 (0.36) | 2.8 (0.37) | 2.1 (0.27) | 7.6 (1.0) | 7.3 |
| 2010.2.16 to 2010.3.1 | 8.0 (0.19) | 27 (0.64) | 7.3 (0.17) | 43 (1.0) | 2.5 (0.13) | 6.9 (0.35) | 10 (0.52) | 20 (1.0) | 2.2 |
| 2010.3.1 to 2010.3.16 | 4.0 (0.13) | 22 (0.72) | 4.5 (0.15) | 30 (1.0) | 0.74 (0.060) | 6.5 (0.53) | 5.0 (0.41) | 12 (1.0) | 2.5 |
| 2010.3.16 to 2010.3.26 | 7.0 (0.14) | 35 (0.69) | 8.9 (0.17) | 51 (1.0) | 1.2 (0.13) | 4.2 (0.47) | 3.6 (0.40) | 9.0 (1.0) | 5.7 |
| 2010.3.26 to 2010.4.28 | 9.4 (0.21) | 24 (0.55) | 10 (0.23) | 44 (1.0) | 3.9 (0.17) | 9.7 (0.43) | 9.1 (0.40) | 23 (1.0) | 1.9 |
| 2010.4.28 to 2010.5.13 | 9.8 (0.21) | 28 (0.55) | 17 (0.23) | 55 (1.0) | 1.2 (0.17) | 5.7 (0.43) | 3.8 (0.40) | 11 (1.0) | 5.2 |
| 2010.5.13 to 2010.5.27 | 7.5 (0.18) | 15 (0.51) | 12 (0.31) | 34 (1.0) | 0.49 (0.11) | 1.2 (0.53) | 1.5 (0.36) | 3.1 (1.0) | 11 |
| 2010.5.27 to 2010.6.11 | 8.7 (0.22) | 7.4 (0.43) | 4.6 (0.35) | 21 (1.0) | 5.8 (0.16) | 14 (0.38) | 6.2 (0.47) | 26 (1.0) | 0.79 |
| 2010.6.11 to 2010.6.24 | 8.7 (0.42) | 7.4 (0.36) | 4.6 (0.22) | 21 (1.0) | 5.8 (0.22) | 14 (0.54) | 6.2 (0.24) | 26 (1.0) | 2.4 |
| 2010.6.24 to 2010.7.7 | 2.5 (0.12) | 10 (0.51) | 7.4 (0.37) | 20 (1.0) | 2.0 (0.24) | 4.8 (0.58) | 1.5 (0.18) | 8.2 (1.0) | 1.1 |
| 2010.7.7 to 2010.7.21 | 6.1 (0.31) | 8.9 (0.45) | 4.7 (0.24) | 20 (1.0) | 6.5 (0.37) | 5.9 (0.33) | 5.3 (0.30) | 18 (1.0) | 1.1 |
| 2010.7.21 to 2010.8.6 | 4.5 (0.59) | 1.2 (0.15) | 1.9 (0.25) | 7.6 (1.0) | 3.3 (0.57) | 1.1 (0.18) | 1.5 (0.25) | 5.9 (1.0) | 1.3 |
| 2010.8.6 to 2010.8.18 | 3.6 (0.30) | 4.7 (0.39) | 3.7 (0.31) | 12 (1.0) | 3.1 (0.27) | 5.2 (0.46) | 3.0 (0.27) | 11 (1.0) | 1.1 |
| 2010.8.18 to 2010.9.2 | 7.1 (0.25) | 16 (0.57) | 5.0 (0.18) | 28 (1.0) | 1.8 (0.26) | 3.6 (0.53) | 1.5 (0.22) | 6.8 (1.0) | 4.1 |
| 2010.9.2 to 2010.9.15 | 4.3 (0.14) | 19 (0.61) | 7.6 (0.25) | 30 (1.0) | 1.8 (0.20) | 4.9 (0.56) | 2.1 (0.24) | 8.8 (1.0) | 3.5 |
| 2010.9.15 to 2010.9.30 | 10 (0.23) | 20 (0.45) | 15 (0.32) | 45 (1.0) | 4.1 (0.28) | 6.9 (0.46) | 3.9 (0.26) | 15 (1.0) | 3.0 |
| 2010.9.30 to 2010.10.14 | 13 (0.28) | 23 (0.49) | 11 (0.23) | 47 (1.0) | 4.2 (0.18) | 12 (0.51) | 7.3 (0.31) | 23 (1.0) | 2.0 |
| 2010.10.14 to 2010.10.29 | 7.1 (0.14) | 23 (0.44) | 22 (0.42) | 52 (1.0) | 5.7 (0.24) | 9.7 (0.42) | 7.9 (0.34) | 23 (1.0) | 2.2 |
| 2010.10.29 to 2010.11.12 | 8.5 (0.18) | 24 (0.51) | 15 (0.31) | 47 (1.0) | 3.4 (0.18) | 7.4 (0.40) | 7.8 (0.42) | 19 (1.0) | 2.5 |
| 2010.11.12 to 2010.11.26 | 13 (0.19) | 35 (0.51) | 20 (0.30) | 68 (1.0) | 4.9 (0.17) | 13 (0.47) | 10 (0.36) | 29 (1.0) | 2.4 |
| 2010.11.26 to 2010.12.9 | 5.1 (0.16) | 16 (0.50) | 11 (0.34) | 31 (1.0) | 6.9 (0.23) | 13 (0.41) | 11 (0.36) | 31 (1.0) | 1.0 |
| 2010.12.9 to 2010.12.22 | | | | | | | | | |

Table 3. Annual average fractionated concentrations of lead in coarse, fine and total particles. The number in parenthesis shows Normalized Leaching Ratio (NLR) of each fraction to the sum of concentration

| | Roadside area (site A), ng-Pb/m ³ | | | | Residential area (site B), ng-Pb/m ³ | | | |
|-----------|--|-----------------|-----------------|-----------------|---|-----------|---------|-------|
| | Water | 0.1 M-HCl | Residue | sum | Water | 0.1 M-HCl | Residue | sum |
| Average | 6.4 ^a | 16 ^a | 11 ^a | 34 ^a | 2.1 | 2.9 | 4.5 | 9.5 |
| Coarse Pb | (0.20) | (0.48) | (0.33) | (1.0) | (0.22) | (0.31) | (0.48) | (1.0) |
| Average | 7.6 ^a | 22 ^a | 13 ^a | 42 ^a | 3.8 | 7.6 | 6.2 | 18 |
| Fine Pb | (0.22) | (0.51) | (0.28) | (1.0) | (0.23) | (0.44) | (0.34) | (1.0) |
| Average | 14 ^a | 38 ^a | 24 ^a | 76 ^a | 5.9 | 11 | 11 | 27 |
| Total Pb | (0.21) | (0.49) | (0.30) | (1.0) | (0.22) | (0.39) | (0.38) | (1.0) |

^ap<0.001 (n=22)

Figure 1 and Tables 1 and 3 show that the NLRs of 0.1 M-HCl extractable fractions obtained for the roadside particulate samples are prominent compared to those of residential area especially in coarse mode of particulate samples. Moreover, Pb-LIII edge XANES spectra for particulate samples collected at the roadside area show different shapes of the spectra between coarse and fine particles

as shown in Figure 2, and it also shows that the spectra for the coarse particles partially resemble those of the road dust.

In a previous study, atmospheric lead particles were found out to be extractable to 0.1 M-HCl fractions in winter, but they were water-soluble in summer (Kyotani and Iwatsuki, 2002). Such seasonality is also shown in this study. This means that basic

chemical characteristics of atmospheric particulate lead are essentially common in urban and suburban areas in Japan.

Generally, in the East Asia including Japan, yellow sand dust and advection current of the particles by westerly winds cause a significant effect on the atmospheric environment during the spring term, and such a long-range transport of particulate matter has a possibility to force up 0.1 M-HCl extractable fraction of lead particles. Therefore, the surplus 0.1 M-HCl extraction amount of lead at the roadside area more than that of the residential area might be discharged from urban traffic relations adding to the common existence of lead particles including long-range transport.

Table 4. Average Normalized Leaching Ratios (NLRs) and standard deviations for 10 lead compounds ($n=3$, each)

| Lead compounds | (i) Water soluble | (ii) 0.1 M-HCl soluble | (iii) Residual |
|-----------------------------------|-------------------|------------------------|-----------------|
| Pb(NO ₃) ₂ | 0.99±0.0024 | 0.012±0.0024 | ND ^a |
| PbCl ₂ | 0.74±0.040 | 0.19±0.015 | 0.072±0.035 |
| PbCO ₃ | 0.0013±0.0023 | 0.98±0.024 | 0.020±0.025 |
| Pb(OH) ₂ | 0.0030±0.0020 | 0.97±0.0092 | 0.029±0.0083 |
| PbO | 0.0075±0.0037 | 0.89±0.0070 | 0.099±0.011 |
| Pb, free | 0.023±0.011 | 0.38±0.036 | 0.59±0.041 |
| PbSO ₄ | 0.020±0.010 | 0.34±0.030 | 0.64±0.038 |
| PbSiO ₃ | 0.0021±0.0025 | 0.28±0.0088 | 0.72±0.0071 |
| PbS | 0.0040±0.0058 | 0.18±0.016 | 0.81±0.018 |
| PbO ₂ | 0.025±0.0033 | 0.057±0.0079 | 0.92±0.011 |

^aND means <0.0010 of NLR.

4.2. Relation between atmospheric particulate samples, road dust and typical Pb compounds

For the excess 0.1 M-HCl extractable concentration of particulate lead at the roadside area discussed above, re-suspension

of road dust is a plausible candidate for the contribution to particulate lead (Kauhaniemi et al., 2011; Deocampo et al., 2012). For that reason, we compared the ternary diagram of atmospheric particulate lead with that of road dust samples and typical 10 Pb compounds. Here, triangle NLR plots for the coarse and fine mode of atmospheric particulate samples are shown respectively in Figures 4a and 4b. The plots for road dust samples and reference Pb compounds are also presented in Figure 4c.

The NLR diagram for coarse particulate Pb suggests different distribution between roadside and residential areas almost distinguished near the line of 0.4 for 0.1 M-HCl extractable fraction when one exception (NLR of Water soluble: 0.1 M-HCl extractable: Residue=0.14:0.66:0.20, April 28–May 13, 2010, at site B) is excluded. On the other hand, the differences between roadside and residential areas with fine mode samples are unclear compared to the coarse one. Only 6 points over the range of 0.6 of NLR in 0.1 M-HCl extractable fraction of fine mode at the roadside are clearly distinguished from those for the residential one. Figure 4c also shows that the NLR distribution of road dust samples is widely dispersed and the NLRs in water-soluble fractions are limited to within 0.25.

These results suggest that solubility distribution of the roadside coarse particulate Pb is basically different from that of the residential one, and the solubility distributions of the coarse particulate Pb at the roadside area has partially overlapped with those of the road dust samples.

Road dust, in general, is comprised of various particle sizes, mainly originates from exhaust gas, tire abrasion, asphalt eroding, sand, and silt transported by wind and other means (Aryal and Lee, 2009). Moreover, deterioration and weathering in the open air and local source might affect the road dust chemistry. Therefore, NLR of the road dust samples fundamentally show wide dispersion of the ternary plot.

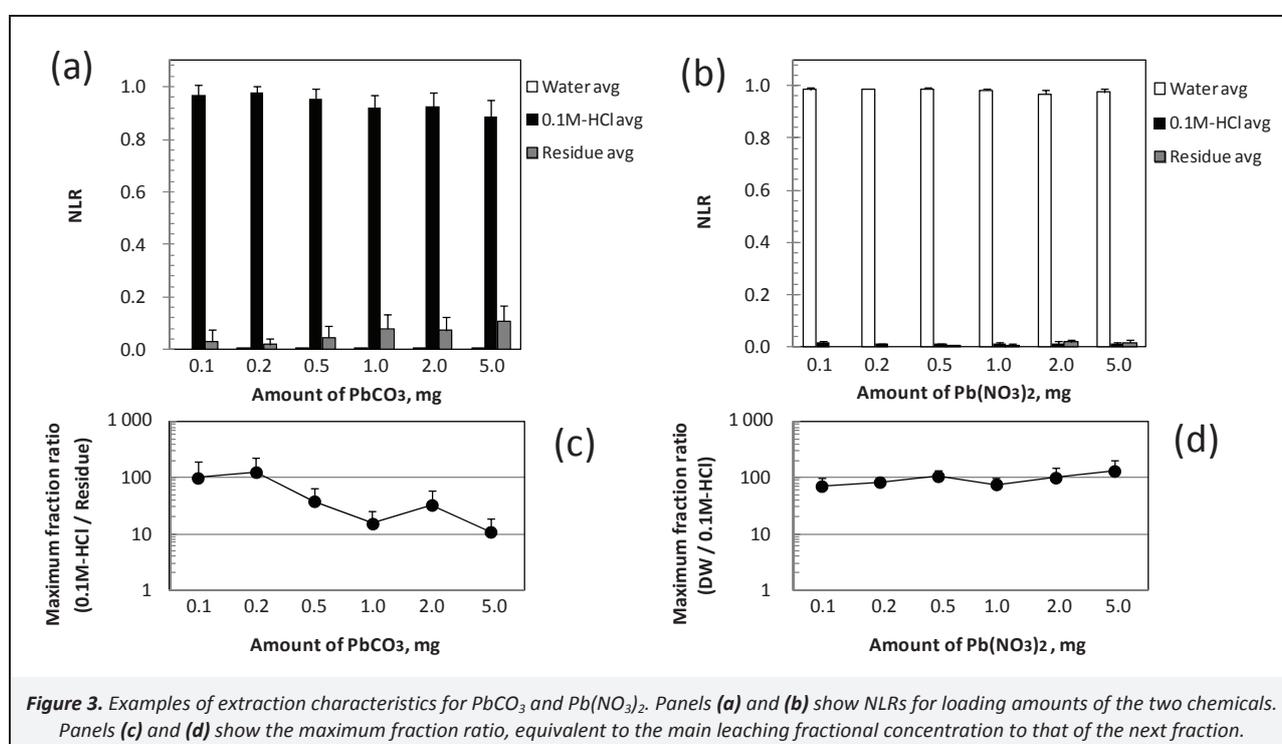


Figure 3. Examples of extraction characteristics for PbCO₃ and Pb(NO₃)₂. Panels (a) and (b) show NLRs for loading amounts of the two chemicals. Panels (c) and (d) show the maximum fraction ratio, equivalent to the main leaching fractional concentration to that of the next fraction.

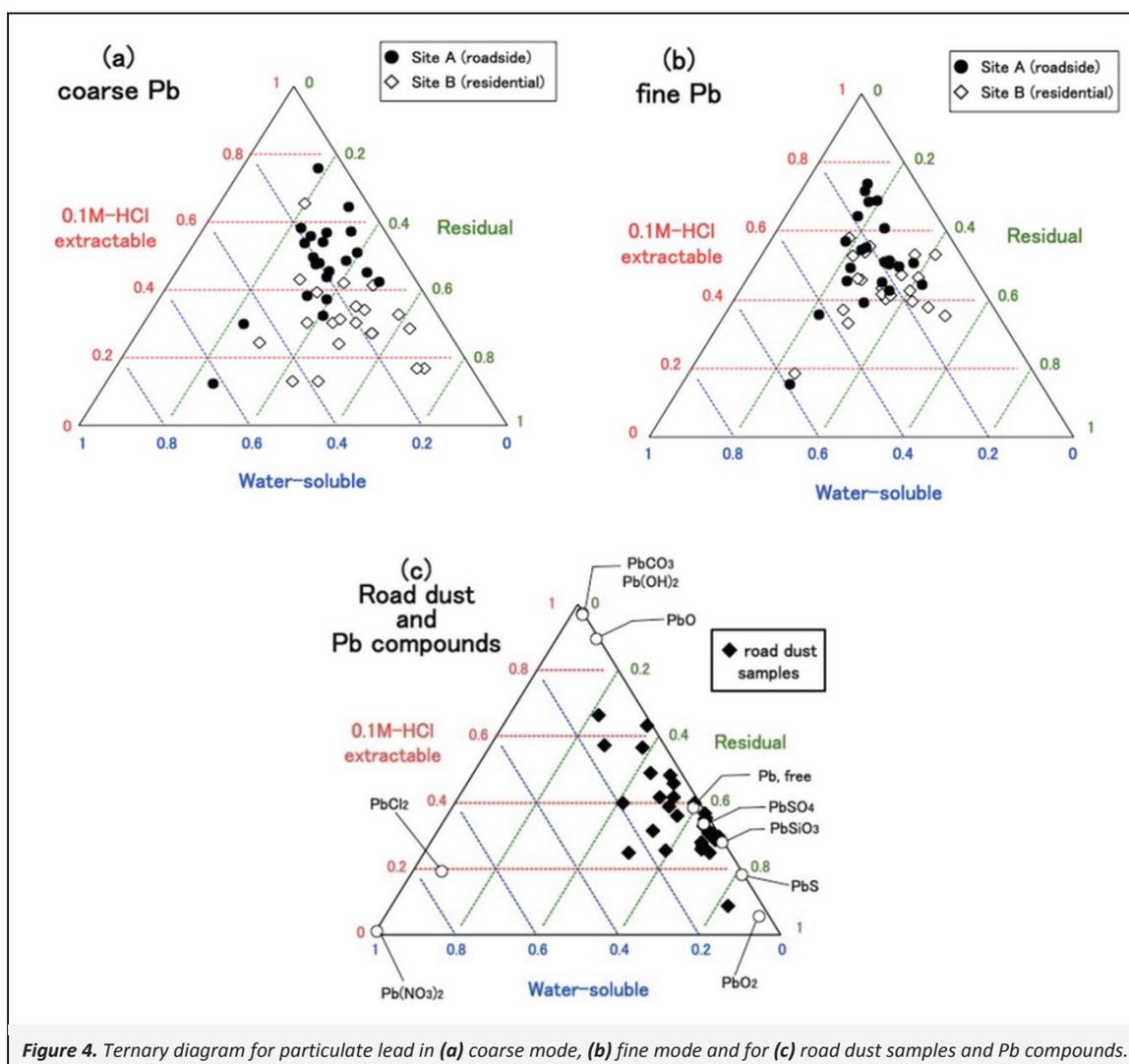


Figure 4. Ternary diagram for particulate lead in (a) coarse mode, (b) fine mode and for (c) road dust samples and Pb compounds.

Also, we applied the simple acid extraction to the typical Pb compounds, and the results suggested that they are located around each corner or near each side of the triangle in Figure 4c. These plots are far from that for coarse and fine particulate samples as shown in Figure 4a and 4b. Hence, specific lead compounds do not exist solely in atmospheric particulate samples, although the lead compounds examined in this study are limited.

EXAFS and XANES spectroscopy is a valuable physicochemical technique for analysis. Recently, some studies have been directed to the lead chemical species in various environmental samples such as soil particles, sediments, solid and liquid wastes, and fly ash samples. For instance, an XANES analysis showed predominant $PbSiO_3$, $PbCl_2$, or $Pb_2O(OH)_2$ in fly ash samples (Funatsuki et al., 2012). Barrett et al. (2010) also reported possible presence of Pb-sorbed goethite in urban road dust sediment with XAFS study. Furthermore, Deocampo et al. (2012) suggested the possibilities of transport of particulate Pb to the urban air other than from road dust with a different neighborhoods investigation. Therefore, atmospheric particulate lead might be directly or indirectly affected by the contamination from various original sources including unknown long-range transport mechanisms other than the road dust contamination as shown in this study.

5. Conclusion

Differences of chemical properties of atmospheric particulate lead between roadside and residential areas were investigated using simple acid extraction and XANES spectroscopy. Results

suggested that 0.1 M-HCl extractable fractions of lead at the roadside area are significantly higher than those obtained at the residential area, especially for the coarse mode of the particulate samples. The XANES spectra for coarse Pb were partially overlapped with that for the road dust samples. These results might indicate effects by the re-suspension of road dust into the roadside air. Further studies on the confirmation of chemical states of lead in atmospheric particles and the relations with original sources including long-range transport would be also expected in order to identify unknown sources other than road dust.

Acknowledgements

This research is supported as a prioritized study (11-01) at the Osaka City Institute of Public Health and Environmental Sciences. Special thanks are extended to Mr. Mamoru SAKAI Ph.D, Mr. Akira OSHIMA, and Mr. Masaaki KITANO. We also appreciate assistance for experiments provided by Ms. Ayu IKEMOTO.

Supporting Material Available

List of Pb compounds tested in this study (Table S1). This information is available free of charge via the internet at <http://www.atmospolres.com>

References

- Aryal, R.K., Lee, B.K., 2009. Characteristics of suspended solids and micropollutants in first-flush highway runoff. *Water, Air & Soil Pollution* 9, 339–346.
- Barrett, J.E.S., Taylor, K.G., Hudson-Edwards, K.A., Charnock, J.M., 2010. Solid-phase speciation of Pb in urban road dust sediment: a XANES and EXAFS study. *Environmental Science & Technology* 44, 2940–2946.
- Birmili, W., Allen, A.G., Bary, F., Harrison, R.M., 2006. Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic. *Environmental Science & Technology* 40, 1144–1153.
- Canepari, S., Cardarelli, E., Perrino, C., Catrambone, M., Pietrodangelo, A., Strincone, M., 2006. Two-stage chemical fractionation method for the analysis of elements and non-volatile inorganic ions in PM₁₀ samples: application to ambient samples collected in Rome (Italy). *Atmospheric Environment* 40, 7908–7923.
- Deocampo, D.M., Reed, P.J., Kalenuik, A.P., 2012. Road dust lead (Pb) in two neighborhoods of urban Atlanta, (GA, USA). *International Journal of Environmental Research and Public Health* 9, 2020–2030.
- Fernandez Espinosa, A.J., Ternero Rodriguez, M., Barragan De La Rosa, F.J., Jimenez Sanchez, J.C., 2002. A chemical speciation of trace metals for fine urban particles. *Atmospheric Environment* 36, 773–780.
- Funasaka, K., Tojo, T., Katahira, K., Shinya, M., Miyazaki, T., Kamiura, T., Yamamoto, O., Moriwaki, H., Tanida, H., Takaoka, M., 2008. Detection of Pb–LIII edge XANES spectra of urban atmospheric particles combined with simple acid extraction. *Science of the Total Environment* 403, 230–234.
- Funatsuki, A., Takaoka, M., Oshita, K., Takeda, N., 2012. Methods of determining lead speciation in fly ash by x-ray absorption fine-structure spectroscopy and a sequential extraction procedure. *Analytical Sciences* 28, 481–490.
- Kauhaniemi, M., Kukkonen, J., Harkonen, J., Nikmo, J., Kangas, L., Omstedt, G., Ketzler, M., Kousa, A., Haakana, M., Karppinen, A., 2011. Evaluation of a road dust suspension model for predicting the concentrations of PM₁₀ in a street canyon. *Atmospheric Environment* 45, 3646–3654.
- Kyotani, T., Iwatsuki, M., 2002. Characterization of soluble and insoluble components in PM_{2.5} and PM₁₀ fractions of airborne particulate matter in Kofu city, Japan. *Atmospheric Environment* 36, 639–649.
- Manceau, A., Boisset, M.C., Sarret, G., Hazemann, R.L., Mench, M., Cambier, P., Prost, R., 1996. Direct determination of lead speciation in contaminated soils by EXAFS spectroscopy. *Environmental Science & Technology* 30, 1540–1552.
- Pingitore, N.E., Clague, J.W., Amaya, M.A., Maciejewska, B., Reynoso, J.J., 2009. Urban airborne lead: x-ray absorption spectroscopy establishes soil as dominant source. *Plos One* 4, art no. e5019.
- Smichowski, P., Polla, G., Gomez, D., 2005. Metal fractionation of atmospheric aerosols via sequential chemical extractions: a review. *Analytical and Bioanalytical Chemistry* 381, 302–316.
- Takaoka, M., Yamamoto, T., Tanaka, T., Takeda, N., Oshita, K., Uruga, T., 2005. Direct speciation of lead, zinc and antimony in fly ash from waste treatment facilities by XAFS spectroscopy. *Physica Scripta* T115, 943–945.
- Tessier, A., Cambell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51, 844–851.
- U.S. EPA (U.S. Environmental Protection Agency), 2008. National Ambient Air Quality Standards for Lead: Final Rule, Federal Register: 40 CFR Parts 50, 40 CFR Parts 51, 40 CFR Parts 53, and 40 CFR Parts 58.
- WHO, 2000. Air Quality Guidelines for Europe World Health Organization Regional Office for Europe, European Series No. 91, WHO Regional Publications, 273 pages.