Lead isotope ratios in urban road runoff

M. Shinya*, K. Funasaka*, K. Katahira*, M. Ishikawa and S. Matsui*****

*Osaka City Institute of Public Health and Environmental Sciences, 8-34 Tojo-cho, Tennoji-ku, Osaka 543-0026, Japan (E-mail: *m.shinya@iphes.city.osaka.jp*)

**Department of Civil Engineering, Osaka Institute of Technology, 5-16-1 Ohmiya, Asahi-ku, Osaka 535-8585, Japan

***Graduate School of Global Environmental Studies, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Abstract Lead isotopic analyses of road runoff and airborne particulate matter have been carried out to elucidate sources of lead pollution at urban and suburban sites. While lead is often observed in road runoff in suspended form, suspended particle size had no relation to the lead isotopic distribution, as a result of comparison between runoff samples with total suspended solids and those with minute particles passed through a 75 μm sieve. Lead isotope ratios in airborne particulate matter in urban areas fell within a wider range than those in road runoff. Since there was little difference of the ratios between a heavy traffic-flow site and residential sites, airborne lead derived from vehicle exhaust was found to make little contribution to the contamination of road runoff. On the other hand, the ratios in road runoff at a suburban site showed the same range as those at an urban site. Lead in road runoff was therefore suggested to be produced on site by traffic related substances, such as tire wear, other than vehicle exhaust.

Keywords Road runoff; airborne particulate matter; lead isotope ratio; inductively coupled plasma mass spectrometry (ICP-MS)

Water Science & Technology **Vol 53 No 2 pp 185–191** © IWA Publishing 2006

Introduction

Lead pollution in urban environment has been widely studied because of its ubiquitous distribution and serious effects on human health (Nriagu, 1988). The amount of anthropogenic lead emitted into the atmosphere has declined as a result of the phasing out of leaded gasoline products (Mukai *et al.*, 1993). However, although unleaded gasoline has been in use for several decades in Japan, runoff from the road surface contains significant loads of hazardous lead, especially in urban areas. Lead in runoff water is mainly particulate-bound and its concentration is highest in the initial phases of runoff water regardless of rainfall conditions (Shinya *et al.*, 2000), often reaching values 10 to 100 times above the Japanese environmental water quality standard ($0.01\,mg\,L^{-1}$). The source of lead in urban road runoff has however not been identified.

Many studies have sought to determine the source of lead in the urban atmosphere. The potential anthropogenic sources of airborne lead, such as mining, smelting, coal combustion, waste incineration, and the use of lead additives in petrol, exceed the contribution of natural sources on a global scale (Nriagu, 1996). Atmospheric deposition of lead has led to pollution of surface soils (Hansmann and Koppel, 2000; Prohaska *et al.*, 2000) and lake sediments (Renberg *et al.*, 2002).

Measurement of stable lead isotopes in atmospheric aerosols gives valuable information about their sources, since different sources often have a dissimilar lead isotope signature. This variation derives from the use of many different ore bodies in the various industrial uses of lead. For lead isotopic analysis, an alternative to thermal ionization mass spectrometry (TIMS), which is the traditional technique for determining isotope

doi: 10.2166/wst.2006.052

ratio, is provided by inductively coupled plasma mass spectrometry (ICP-MS), which offers ease of operation, high sample throughput, and widespread availability, although with limited precision compared to TIMS. The use of ICP-MS in source determination by isotopic analysis has been increasing year by year in the field of environmental research.

The objective of the present study was to identify the source of lead in urban road runoff by isotopic analysis using ICP-MS and to elucidate the contribution to road runoff of airborne particulate matter by comparing the lead isotope ratio of the two.

Methodology

Sampling sites

The urban sampling site, located in Osaka city, was the same as in the previous study (Shinya *et al.*, 2000). As a suburban control a site in Ritto city was selected, which has several heavily trafficked routes including Route 1, along which are located many factories and warehouses, but which is sparsely populated and has a large area of fields away from the roads. Runoff samples in Ritto were collected at the side of Route 1.

Airborne particulate matter samples were also collected for the purpose of comparison with runoff samples. Collection was performed on filters with a high-volume air sampler at six monitoring sites in Osaka City: one site, Dekijima, was located at the roadside of Route 43, which has heavy traffic flow with a large volume of diesel vehicles, and the others in commercial and residential areas. The sampling sites are shown in Figure 1.

Sampling methods

At the Osaka site, five different runoff events were investigated in 1999 and three in 2000, and at the Ritto site ten events in 2002. Runoff samples were collected in the same manner as described in the previous study (Shinya *et al.*, 2003). All runoff samples were passed through a 2 mm-mesh stainless sieve then stored in a refrigerator at 4°C until analysis. In the 2000 study, a 75 μm-mesh sieve was also used to examine the behavior of the minute particles that are easily flushed out even by lower levels of rainfall and may be transported by air. These particles are rich in lead, and the cumulative runoff load derived from them accounts for half of the total load (Shinya *et al.*, 2002).

Using a high-volume air sampler (Model-120, Kimoto Electric) without impactor, airborne particulates were collected monthly from October 2002 to March 2004 on a quartz fiber filter (QR-100, Advantec) at a flow rate of 1,000 L min^{-1}. The sampling period was

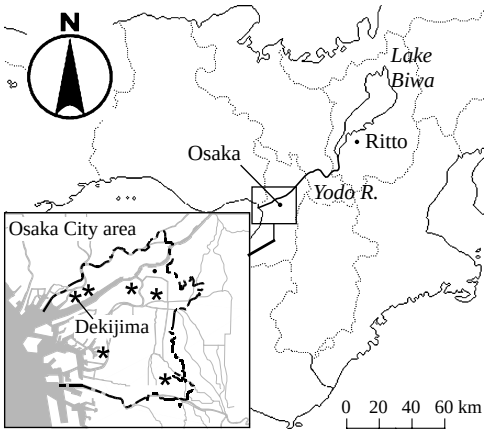

Figure 1 Sampling site for road runoff (•) and airborne particulate matter (★); the Dekijima site is a roadside site with heavy traffic-flow while the others are located in commercial and residential areas

24 h for each sample. After collection, the filters were stored in a freezer at −20°C until analysis.

Analytical procedures

Runoff samples were digested with nitric acid and perchloric acid by heating on a commercially available hot plate and filtered (5C, Advantec). The filtrate was reheated until almost dry and finally dissolved in 0.1 mol l^{-1} HNO_3. The filter samples with airborne particulates were prepared using the same procedure as in the previous study (Funasaka *et al.*, 2003).

Lead determination of these samples was performed with an electrothermal atomic absorption spectrometer (4100ZL, Perkin-Elmer) for lower concentration or an inductively coupled plasma emission spectrometer (IRIS 1000, Nippon Jarrel-Ash) for higher concentration. After determination, the lead concentration in the sample solution was adjusted to around 100 μg L^{-1}, as this concentration allowed isotopic analysis with satisfactory precision (Shinya *et al.*, 2005).

Lead isotope analysis of the solution was performed by quadrupole ICP-MS (HP4500, Yokogawa Analytical Systems). Operating conditions have been described in detail elsewhere (Shinya *et al.*, 2005). Four stable isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, were monitored; only ^{204}Pb is non-radiogenic, ^{206}Pb, ^{207}Pb, and ^{208}Pb are continuously formed by the radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. Each sample was measured ten times, and the average lead isotope ratio and the relative standard deviation of the sample were calculated. NIST SRM981 was used as a reference to determine the mass bias correction factors of the lead isotope ratios.

Results and discussion

Lead isotope ratios of road runoff samples in Osaka

The lead isotope composition of urban road runoff has been described in detail (Shinya *et al.*, 2005), with typical values for each lead isotope ratio in the road runoff indicated for the duration of all runoff events regardless of sampling season. Obtained by averaging the lead isotope ratio of runoff samples from five events in Osaka in 1999, the typical values for the ratios of $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, and $^{206}Pb/^{204}Pb$ were 0.8656 ± 0.0034, 2.108 ± 0.007, and 18.02 ± 0.07, respectively.

Average lead isotope ratios of runoff samples from three events in 2000 are shown in Table 1, in which maximum lead concentration refers to the concentration in the first flush sample. The observed isotope ratios of runoff samples passed through a 2 mm-mesh sieve, which included total suspended solids (TSS), were very close to those observed in 1999. Lead isotope ratios of runoff samples passed through a 75 μm-mesh sieve, which included minute particles only, are also shown in Table 1. In all events, the average value in samples with minute particles was very close to that in a sample with TSS.

Table 1 Average lead isotope ratios of road runoff in Osaka

Event date	Mesh size*	No. of samples	Range of Pb concentration [mg L^{-1}]	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
9/Jun/00	2 mm	9	0.007–0.211	0.8650 ± 0.0015	2.110 ± 0.002	18.08 ± 0.10
	75 μm	9	0.007–0.149	0.8617 ± 0.0015	2.106 ± 0.004	18.10 ± 0.07
25/Jul/00	2 mm	7	0.023–1.616	0.8678 ± 0.0018	2.115 ± 0.002	18.03 ± 0.07
	75 μm	7	0.021–0.298	0.8669 ± 0.0020	2.114 ± 0.005	18.04 ± 0.09
8/Sep/00	2 mm	5	0.019–1.638	0.8648 ± 0.0016	2.108 ± 0.002	18.07 ± 0.04
	75 μm	5	0.012–0.354	0.8648 ± 0.0018	2.109 ± 0.004	18.03 ± 0.06

*Mesh size of the sieve through which the samples passed

Geochemists prefer to use lead isotope ratios incorporating ^{204}Pb due to the mathematical simplicity of using a non-radiogenic isotope. However, environmental scientists tend to use $^{206}Pb/^{204}Pb$ vs. $^{206}Pb/^{207}Pb$ or $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{206}Pb$ because of their better analytical precision (Monna *et al.*, 1997). Here we use $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ for comparability with recent studies conducted using ICP-MS. We also present conventional $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagrams.

Figure 2 illustrates diagrams of $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ in road-runoff samples collected in Osaka in 2000. It is clear that the plotted area of the samples with minute particles is very close to that of the samples with TSS in both diagrams. Larger-sized particles are flushed out when it rains heavily in what is called the first flush phenomenon, so that most particles larger than 75 μm are flushed out within the first 10 min even with a runoff duration of 60 min, as in the event of 25th July, 2000 (Shinya *et al.*, 2002). In other words, very few larger-sized particles are observed after the first flush. As described above, runoff characteristics differed according to particle size, but lead-isotopic characteristics were almost the same. This suggests that runoff water includes particles of various size derived from a specific source of lead.

Comparison of lead isotope ratios of first-flush samples between urban and suburban areas

Lead isotope analysis was carried out with runoff samples from Ritto, a site with suburban location but heavy traffic flow. Since analytical results from the Osaka samples showed that the values for isotope ratio were almost constant for the duration of all events, only the first flush samples with the highest concentration of lead were measured because of their superior analytical precision. Table 2 shows lead isotope ratios of first flush samples from eight events in Osaka in 1999 and 2000 and from ten events in Ritto in 2002. First flush samples contained the richest lead, but, as shown in Table 2, the average lead concentration was one order lower in the Ritto samples than in the Osaka samples as the former location is less polluted. The mean values for lead isotope ratios at the Ritto site were closely similar to those at the Osaka sites.

The lead isotope ratio diagrams shown in Figure 3 indicate that lead isotope compositions for Ritto overlapped fully with those for Osaka. The specific lead isotope compositions observed at both urban and suburban sites, therefore, suggest that traffic is a source of lead in road runoff.

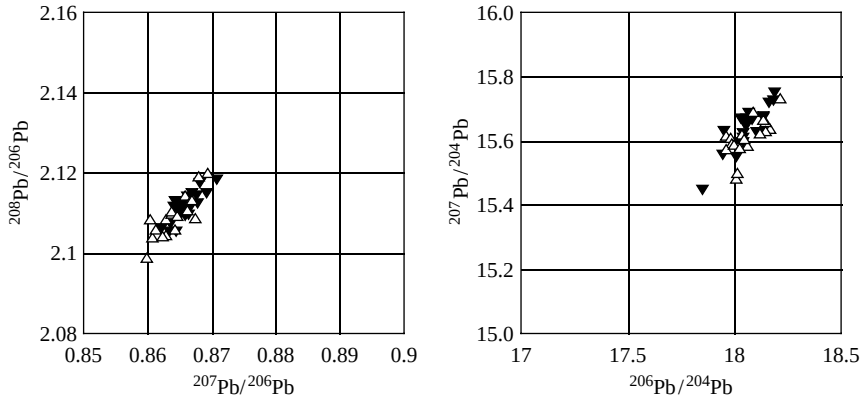

Figure 2 $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ of road runoff in Osaka, (▼) runoff samples passed through 2 mm-mesh sieve (including total suspended solids), (△) particles passed through 75 μm-mesh sieve (including minute particles)

Table 2 Average lead concentration and isotope ratios of first flush samples of road runoff

Site	Category of site	Year	No. of samples	Mean Pb concentration [mg L^{-1}]	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
Osaka	Urban	1999–2000	8	0.745	0.8647 ± 0.0027	2.108 ± 0.007	17.99 ± 0.14
Ritto	Suburban	2002	10	0.084	0.8644 ± 0.0033	2.109 ± 0.006	18.04 ± 0.07

Lead isotope ratios in airborne particles

Lead isotope ratios were also measured in airborne particulate matter collected in Osaka. The results are shown in Table 3. The ratio of both $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ in airborne particulates showed somewhat larger values than in road runoff samples at the Osaka site. The isotopic characteristics of airborne lead from the heavy-traffic roadside site, Dekijima, were not distinct from those at commercial and residential sites, with no evident difference in lead isotope ratio, although higher lead concentration was observed at Dekijima (Funasaka *et al.*, 2003). Although the airborne samples at each site were taken during different seasons, no large variation in isotope ratio was observed.

Road runoff samples were not collected from January to April, as the region is affected during this season by yellow sand dust from China (Funasaka *et al.*, 2003) and continental lead could therefore be present in airborne particulate samples. However, even when samples collected during this season were excluded, lead isotope ratio did not vary between the Dekijima and the others. Mukai *et al*. state that there is no large seasonal variation in isotope ratios of airborne lead in Japan because industrial emissions also do not show seasonal variation (Mukai *et al.*, 1993).

Diagrams of isotope ratios of airborne lead are shown in Figure 4. Compared with the road runoff in Figures 2 and 3, lead isotope ratios of airborne particulate matter fell within a wider range which included the isotope ratio range of road runoff. This finding suggests that the source of airborne lead included not only the sources of lead in road runoff but other various sources. In other words, lead in airborne particulate matter does not contribute greatly to lead in road runoff. It is concluded that lead in road runoff is produced on site as a consequence of traffic.

Characterization of the lead source in urban road runoff

Figure 5 was obtained by comparing the lead isotope ratios in the present study to those in the literature, focusing on the radiogenic lead isotope ratio of $^{207}Pb/^{206}Pb$, which is generally measured in various studies. Examination of the figure leads to the inference

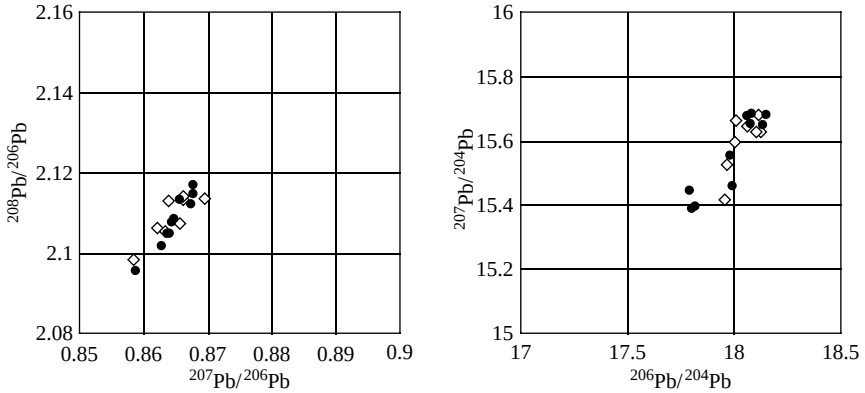

Figure 3 $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ in first-flush samples of road runoff in Osaka (◇) and Ritto (•)

Table 3 Average lead isotope ratios of airborne particulate matter collected in Osaka

Category of site	Season	No. of samples	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
Heavy traffic roadside	All	18	0.8710 ± 0.0060	2.118 ± 0.011	17.91 ± 0.16
	except for winter–spring*	11	0.8700 ± 0.0052	2.118 ± 0.012	17.98 ± 0.08
Residential and commercial	All	90	0.8706 ± 0.0072	2.117 ± 0.014	17.91 ± 0.17
	except for winter–spring*	55	0.8689 ± 0.0063	2.116 ± 0.015	17.97 ± 0.13

*January, February, March and April

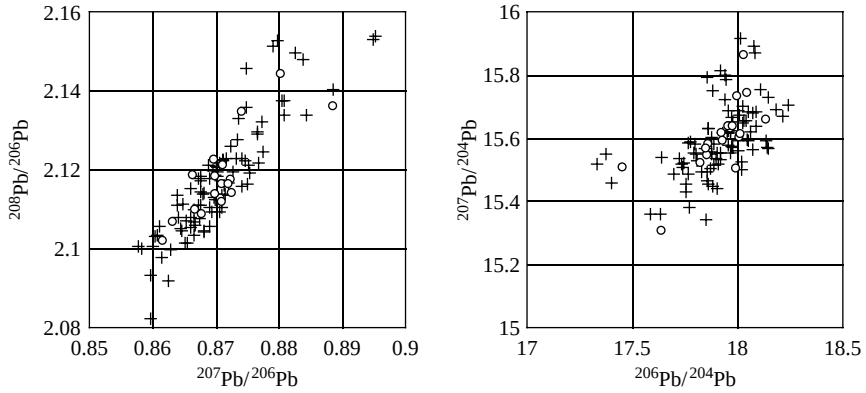

Figure 4 Lead isotope ratios ($^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$) in airborne particulate matter collected in Osaka; (○) heavy traffic-flow roadside site, (+) residential and commercial sites

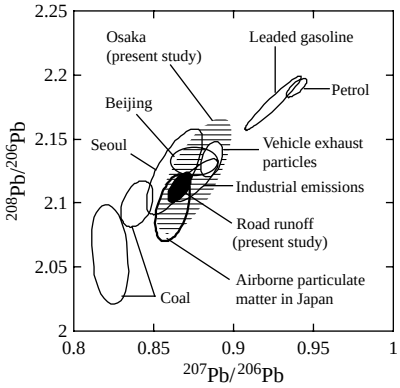

Figure 5 Comparison of lead isotope ratios from other environmental samples and sites; airborne particulate matter in Japan (Mukai *et al.*, 1993), in Beijing (Mukai *et al.*,1993), in Seoul (Mukai *et al.*,1993), coal (Bacon, 2002; Mukai *et al.*,1993), industrial emissions (Bacon, 2002; Monna *et al.*, 1997), vehicle exhaust particles (Mukai *et al.*, 1993; Zheng *et al.*, 2004), leaded gasoline (Monna *et al.*, 1997; Mukai *et al.*,1993) and petrol (Bacon, 2002).

that the source of lead in road runoff could be airborne particulate matter or industrial emissions. While it is likely that industrial emissions have a widely varying lead isotopic composition due to the multiple sources of lead (as shown in several studies), lead in incinerator ashes is generally considered to be an acceptable surrogate as incinerated wastes represent all the sources of industrial lead (Bacon, 2002). Even though incinerator fly ash may well be deposited on the road surface by way of the atmosphere, it is difficult

to determine whether it is the source of the lead in road runoff because of the small contribution of airborne particulate matter to road runoff, as described above.

Traffic as a potential lead source was mentioned above, but the lead isotope ratio of vehicle exhaust particles is quite far removed from that of road runoff, as shown in Figure 5. These particles are therefore not proposed as the source of the lead. Leaded gasoline had not been in use for several decades in Japan. Lead in road runoff is therefore suggested to be produced by wear of other traffic-related substances, for example tires and asphalt. Further study is necessary to clearly explain the lead source of road runoff.

Conclusions

Lead isotopic measurement of road runoff and airborne particulate matter in the Osaka urban area was applied to investigate the contribution of airborne lead to lead in urban road runoff and to estimate the source of lead in urban road runoff. The following conclusions could be drawn:

The lead isotope composition of road runoff was specific regardless of the particle sizes included in the samples and of the sampling sites, urban or suburban. They fell within a narrower range than airborne lead isotopes, suggesting little contribution of airborne particulate matter to road runoff. While no definite lead source for urban road runoff was determined, it appeared to be produced on site by traffic-related substances other than vehicle exhaust.

References

Bacon, J.R. (2002). Isotopic characterization of lead deposited 1989–2001 at two upland Scottish locations. *J. Environ. Monit.*, **4**, 291–299.

Funasaka, K., Sakai, M., Shinya, M., Miyazaki, T., Kamiura, T., Kaneko, S., Ohta, K. and Fujita, T. (2003). Size distributions and characteristics of atmospheric inorganic particles by regional comparative study in urban Osaka, Japan. *Atmos. Environ.*, **37**, 4597–4605.

Hansmann, W. and Koppel, V. (2000). Lead isotopes as tracers of pollutants in soils. *Chem. Geol.*, **171**, 123–144.

Monna, F., Lancelot, J., Croudace, I.W., Cundy, A.B. and Lewis, J.T. (1997). Pb isotopic composition of airborne particulate material from France and the southern United kingdom; implication for Pb pollution sources in urban areas. *Environ. Sci. Technol.*, **31**, 2277–2286.

Mukai, H., Furuta, N., Fujii, T., Ambe, Y., Sakamoto, K. and Hashimoto, Y. (1993). Characterization of sources of lead in the urban air of Asia using ratios of stable lead isotopes. *Environ. Sci. Technol.*, **27**, 1347–1356.

Nriagu, J.O. (1988). A silent epidemic of environmental metal poisoning? *Environ. Pollut.*, **50**, 139–161.

Nriagu, J.O. (1996). A history of global metal pollution. *Science*, **272**, 223–224.

Prohaska, T., Watkins, M., Latkoczy, C., Wenzel, W.W. and Stingeder, G. (2000). Lead isotope ratio analysis by inductively coupled plasma sector field mass spectrometry (ICP-SMS) in soil digests of a depth profile. *J. Anal. At. Spectrom.*, **15**, 365–369.

Renberg, I., Brannvall, M.-L., Bindler, R. and Emteryd, O. (2002). Stable lead isotopes and lake sediments – a useful combination for the study of atmospheric lead pollution history. *Sci. Total Environ.*, **292**, 45–54.

Shinya, M., Tsuchinaga, T., Kitano, M., Yamada, Y. and Ishikawa, M. (2000). Characterization of heavy metals and polycyclic aromatic hydrocarbons in urban highway runoff. *Wat. Sci. Technol.*, **42**(7–8), 201–208.

Shinya, M., Konishi, T., Miyanishi, H. and Ishikawa, M. (2002). Characterization of urban highway runoff. *Jpn J. Water and Waste*, **44**, 207–213 (in Japanese).

Shinya, M., Tsuruho, K., Konishi, T. and Ishikawa, M. (2003). Evaluation of factors influencing diffusion of pollutant load in urban highway runoff. *Wat. Sci. Technol.*, **47**(7–8), 227–232.

Shinya, M., Katahira, K., Ishikawa, M. and Matsui, S. (2005). Determination of stable lead isotope ratios in urban highway runoff by inductively coupled plasma mass spectrometry, submitted.

Zheng, J., Tan, M., Shibata, Y., Tanaka, A., Li, Y., Zhang, G., Zhang, Y. and Shan, Z. (2004). Characteristics of lead isotope ratios and elemental concentrations in PM10 fraction of airborne particulate matter in Shanghai after the phase-out of leaded gasoline. *Atmos. Environ.*, **38**, 1191–1200.