Stable Lead Isotopic Ratios as Indicator of Urban Geochemical Processes

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Abstract. The study is aimed to apply the Pb isotope fingerprinting technique for tracing pollution of urban surface deposited sediment (USDS). USDS reflect changes in the geochemical conditions occurring in the environment. USDS samples were collected in residential areas with multistory buildings in Russian cities: Magnitogorsk, Nizhny Tagil, Tyumen, Ufa, and Chelyabinsk. Elements concentrations and stable Pb isotopic ratios were measured in the samples. The reconstruction of the initial geochemical baseline (IGB) relationship between potentially harmful element (PHE) Pb and conservative lithogenic element (CE) Fe was carried out for USDS sample populations in the cities. The IGB reconstruction divided USDS sample populations into the groups of ‘polluted’ and ‘unpolluted’ with Pb samples. Analysis of elements concentrations and Pb isotope ratios in the groups of USDS samples showed different trends in altering geochemical conditions for metals in the surveyed cities. The USDS is characterized by a decrease in the isotope ratios of 206Pb/204Pb and 208Pb/204Pb as a result of soil pollution by vehicles during the period of using leaded gasoline.

1. Introduction
Stable Pb isotopes 206Pb, 207Pb, and 208Pb are the products of radioactive decay of 238U, 235U, and 232Th, respectively. 204Pb is the primordial isotope with a constant content in the Earth's crust over time [1]. The natural isotopic composition of Pb depends on the age of rocks and U/Pb and Th/Pb ratios, the geochemical behavior of U, Th and Pb during formation of the geological structures and the radioactive decay [2-4].

The ores in different world regions have their own stable Pb isotopic signatures [5, 6]. The Pb isotopic composition in different environmental objects depends only on the Pb isotopic composition in initial ores [3, 7, 8]. Physicochemical fractionation does not mainly affect Pb isotopic composition [2, 4, 9] and does not occur as result of mining, subsequent smelting and other industrial and environmental processes [2, 3]. The Pb isotopic signatures remain constant during the transportation of ore processing products over long distances [3, 6-8]. The Pb isotopic signature reflects chemical composition of the ore, natural and anthropogenic processes that affect the release, dispersion and
accumulation of Pb. The Pb isotopic signature is preserved during the formation of sedimentary materials and natural weathering processes [2, 3, 9].

The stable Pb isotopic ratios are used as tracers of pollution in environment [2-4, 9]: in determination of the transboundary transport of dust [6, 9], migration of pollutants in soil, sediment, and water systems [1], in the assessment of geochemical background concentrations of elements [6].

Isotope fingerprinting techniques allowed identifying the association between the metal pollution in the environmental compartments with the road traffic [9, 10]. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in road dust was used to estimate the contribution of automobile emission and discriminate anthropogenic sources [6]. Various types of the contemporary surface deposited sediments (USDS) represent a good indicator of the environmental processes and are often used in tracing pollution [6, 8, 10]. The aim of the study was to apply the Pb isotope fingerprinting technique for tracing pollution of urban surface deposited sediment.

2. Materials and methods
The main object of the study is one of the types of the contemporary USDS located on the urban surfaces in depressed zones of microrelief. This material represents a mixture of bedrock material with road abrasion products, vehicle wear products, weathering products of construction materials (brick and concrete), ground and soil particles, atmospheric dust and small garbage. The sediment is involved into processes of migration and accumulation of pollutants [11-12]. The examples of the USDS photos on the sampling sites are shown in Figure 1.

![Figure 1. The example of the urban surface deposited sediments in residential areas of surveyed cities: a) Magnitogorsk, b) Nizhny Tagil, c) Ufa, d) Chelyabinsk.](image)

The USDS samples were collected in the residential areas of Russian cities: Magnitogorsk – 38, Nizhny Tagil – 48, Tyumen – 39, Ufa – 43, Chelyabinsk – 60 samples. The surveyed cities are located in the zones of different natural geological and climatic conditions, and economic specialization. The
samples were taken from the surface geochemical traps (surface depressed areas of micro relief or puddles) in the residential areas. The residential areas represent the planning territorial structure typical for the soviet period. Each sampling site represents the area of the courtyard of the residential quarter with multistorey buildings. The USDS sample collection and preparation procedures were previously described in detail [11-13].

The total element concentrations in USDS samples were determined with inductively coupled plasma mass spectrometry (ICP MS ELAN 9000; Perkin Elmer Inc.). The sample preparation method was similar to the US EPA method EPA-821-R-01-01027. Pb isotope analysis was performed in The ‘Geoanalyst’ Center for collective Use of The Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences. The analysis was performed in the samples digested for ICP MS. Samples were passed through the chromatographic procedure. Pb isolation was carried out using certified measurement technique [14, 15]. Measurements of Pb isotopic ratios were conducted using a Thermo Fischer Neptune Plus MC-ICP-MS within the class 1000 clean room facility. Each sample was spiked with thallium prior to the analysis. Data processing was carried out online including 204Pb interference correction by the ratio 202Hg/204Hg = 4.350370 and normalization by the exponential law using 207Tl/205Tl ratio. Accuracy and long-term reproducibility of lead isotope ratio determination was assessed through the NIST SRM 981 analysis and yielded 204Pb/206Pb = 0.059060 ± 9, 208Pb/204Pb = 2.16799 ± 5, 207Pb/206Pb = 0.914530 ± 9 (±SD, n=87). Additionally, the analyses of USGS AGV-2 and geological certified reference material were carried out on a regular basis and resulted in 206Pb/204Pb = 18.863 ± 7, 208Pb/204Pb = 38.327 ± 16, 207Pb/204Pb = 15.614 ± 7 (±SD, n=15).

The initial geochemical baseline (IGB) between potentially harmful element (PHE) Pb and conservative lithogenic element (CE) Fe in the USDS was reconstructed based on the method suggested by Seleznev et al. (2018) [16]. A linear regression model was used for describing baseline association between PHE and CE in USDS sample population for the city. The IGB reconstruction allowed dividing the sample populations into the groups of “polluted” in which Pb concentration deviate from IGB and “unpolluted” samples.

3. Results and discussions
Table 1 shows the average values of Pb concentrations in groups of polluted and unpolluted samples in the surveyed cities where samples were taken, as well as the arithmetic mean 206Pb/204Pb isotope ratios.

Table 1. The average Pb concentrations in groups of “polluted” and “unpolluted” with Pb samples in the surveyed cities where samples were taken, as well as the arithmetic mean 206Pb/204Pb isotope ratios.

| City           | Average Pb concentration / Arithmetic mean 206Pb/204Pb | “Polluted”  | “Unpolluted” |
|----------------|------------------------------------------------------|-------------|--------------|
| Magnitogorsk   | 81/18.18                                             | 29/18.35    |              |
| Nizhny Tagil   | 162/18.02                                            | 52/18.51    |              |
| Tyumen         | 81/18.07                                             | 16/18.25    |              |
| Ufa            | 91/18.21                                             | 22/18.4     |              |
| Chelyabinsk    | 205/18.15                                            | 50/18.23    |              |

Maximum Pb concentrations were found in the group of 'polluted' samples corresponding to older residential areas (constructed in the middle of the 20th century). Younger residential areas (constructed in the 2nd half of the 20th century and in the beginning of the 20th century) were less polluted with lead and had statistically significant different isotope ratios 206Pb/204Pb in comparison
with the “polluted” groups. The difference between isotope ratios is obviously related to lead contamination of samples, which is characterized by $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ isotope ratios typical for ores of northern Kazakhstan and southern Siberia [17]. It can be assumed that greater lead contamination is associated with motor vehicle emissions in the period before the ban on leaded gasoline. In contemporary sediments and soils in cities, lead from leaded gasoline is still present.

Figure 2 shows the various patterns of the Pb isotope ratios $^{206}\text{Pb}/^{204}\text{Pb}/^{208}\text{Pb}$ distribution on the three-isotope diagram for cities Tyumen, Magnitogorsk, and Ufa and the cities of Chelyabinsk and Nizhny Tagil.

![Figure 2](image)

**Figure 2.** Patterns of the isotope ratios $^{206}\text{Pb}/^{204}\text{Pb}/^{208}\text{Pb}$ distribution on the three-isotope diagram for cities Tyumen, Magnitogorsk, and Ufa (a) and the cities of Chelyabinsk and Nizhny Tagil (b).

Patterns of the distribution of isotope ratios $^{206}\text{Pb}/^{204}\text{Pb}/^{208}\text{Pb}$ on the three-isotope diagram differ between the groups of cities: Tyumen, Magnitogorsk, and Ufa (first group) and Chelyabinsk and Nizhny Tagil (second group). A more homogeneous sample population in the cities of Tyumen, Magnitogorsk, and Ufa may indicate that there are no additional sources of lead other than motor vehicles in these three cities. The metallurgical industries in Chelyabinsk and Nizhny Tagil, including historical pollution since the 18th century in Nizhny Tagil, form the additional significant sources of lead in these cities. Aw well ore to these cities comes from different regions of Russia.

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References

[1] B. He, X. Zhao, P. Li, J. Liang, Q. Fan, X. Ma, G. Zheng, J. Qiu, “Lead isotopic fingerprinting as a tracer to identify the pollution sources of heavy metals in the southeastern zone of Baiyin, China,” *Science of The Total Environment*, vol. 660, pp. 348–357, 2019.

[2] G. Bird, “Provenancing anthropogenic Pb within the fluvial environment: Developments and challenges in the use of Pb isotopes,” *Environment International*, vol. 37 (4), pp. 802–819, 2011.

[3] H. Cheng, Y. Hu, “Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review.” *Environmental Pollution*, vol. 158, pp. 1134–1146, 2010.

[4] M. Komárek, V. Ettler, V. Chrastný, and M. Mihaljević, “Lead isotopes in environmental sciences: A review,” *Environment International*, vol. 34 (4), pp. 562–577, 2008.

[5] A. Bollhöfer, and K. J. R. Rosman, “Isotopic source signatures for atmospheric lead: the Northern Hemisphere,” *Geochimica et Cosmochimica Acta*, vol. 65 (11), pp. 1727–1740, 2001.

[6] N. S. Duzgoren-Aydin, X. D. Li, and S. C. Wong, “Lead contamination and isotope signatures in the urban environment of Hong Kong,” *Environment International*, vol. 30 (2), pp. 209–217, 2004.

[7] M. Chen, E. A. Boyle, A. D. Switzer, and C. Gouramanis, “A century long sedimentary record of anthropogenic lead (Pb), Pb isotopes and other trace metals in Singapore,” *Environmental Pollution*, vol. 213, pp. 446–459, 2016.

[8] P.-K. Lee, Y.-H. Yu, S.-T. Yun, and B. Mayer, “Metal contamination and solid phase partitioning of metals in urban roadside sediments,” *Chemosphere*, vol. 60 (5), pp. 672–689, 2005.

[9] R. Das, A. T. B. M. Mohtar, D. Rakshit, D. Shome, and X. Wang, “Sources of atmospheric lead (Pb) in and around an Indian megacity,” *Atmospheric Environment*, vol. 193, pp. 57–65, 2018.

[10] E. Liu, T. Yan, G. Birch, and Y. Zhu, “Pollution and health risk of potentially toxic metals in urban road dust in Nanjing, a mega-city of China,” *Science of The Total Environment*, vol. 476–477, pp. 522–531, 2014.

[11] A. Seleznev, and M. Rudakov, “Some geochemical characteristics of puddle sediments from cities located in various geological, geographic, climatic and industrial zones,” *Carpath. J. Earth Environ. Sci.*, vol. 14 (1), pp. 95–106, 2018.

[12] A. A. Seleznev, I. V. Yarmoshenko, and G. P. Malinovsky, “Urban geochemical changes and pollution with potentially harmful elements in seven Russian cities,” *Sci Rep*, vol. 10 (1), 2020.

[13] A. A. Seleznev, and I. V. Yarmoshenko, “Study of urban puddle sediments for understanding heavy metal pollution in an urban environment,” *Environmental Technology & Innovation*, vol. 1–2, pp. 1–7, 2014.

[14] J. Woodhead, “A simple method for obtaining highly accurate Pb isotope data by MC-ICP-MS,” *J. Anal. At. Spectrom*, vol. 17, pp. 1381–1385, 2002.

[15] B. S. Kamber, A. H. Gladu, “Comparison of Pb Purification by Anion-Exchange Resin Methods and Assessment of Long-Term Reproducibility of Th/U/Pb Ratio Measurements by Quadrupole ICP-MS,” *Geostandards and Geoanalytical Research*, vol. 33, pp. 169–181, 2009.

[16] A. A. Seleznev, I. V. Yarmoshenko, A. P. Sergeev, “Method for reconstructing the initial baseline relationship between potentially harmful element and conservative element concentrations in urban puddle sediment,” *Geoderma*, vol. 326, pp. 1–8, 2018.

[17] H. Mukai, T. Machida, A. Tanaka, Y. P. Vera, M. Uematsu, “Lead isotope ratios in the urban air of eastern and central Russia,” *Atmospheric Environment*, vol. 35, pp. 2783–2793, 2001.