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SOME GEOCHEMICAL CHARACTERISTICS OF PUDDLE SEDIMENTS FROM CITIES LOCATED IN VARIOUS GEOLOGICAL, GEOGRAPHIC, CLIMATIC AND INDUSTRIAL ZONES

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Abstract: Natural processes cause sedimentation in local depressed surface zones of urban landscapes with the formation of micro water bodies (puddles). Urban puddle sediments are a geochemical trap for contemporary anthropogenic sediments. These sediments accumulate pollutants over the surface and over time. Samples of urban puddle sediments were collected in residential areas of six Russian cities (the number of sites in parentheses): Tyumen (43), Chelyabinsk (60), Nizhniy Tagil (69), Magnitogorsk (41), and Ufa (43). The cities are located in different geological, geographical, climatic, and industrial zones. The particle size composition, pH, concentration of organic matter, and heavy metals in the puddle sediments were characterized for the surveyed cities which were then ranked by the degree of pollution. The main sources of heavy metal pollution were discussed.

Key words: puddle sediments, particle size composition, acidity, metals, pollution, urban environment, residential area.

1. INTRODUCTION

Contemporary surface sediments represent the upper part of the geological profile in urban areas and may be characterized as a product of the sedimentation processes occurring in the urban environment. The upper part of the geological layer in urban areas (the artificially created urban landscape and its compartments) is constantly being transformed. The sediments start accumulating in urban areas from the moment of building construction and development of the artificial landscape. The process of urban sediment formation occurs constantly and is caused by natural and anthropogenic factors determining the redistribution of the solid particle material. The natural mechanisms consist of the destruction of building materials (bricks and concrete), road surface, asphalt, and sidewalks under freezing and thawing; erosion of soils; atmospheric rainwater runoff; and surface deposition of atmospheric particulate matter. Anthropogenic factors include the destruction of soil and road surfaces by cars as well as excavation works. The disturbances resulting from urban management techniques influence the processes of surface sediment formation as well.

The study of these sediments allows us to obtain data on the contemporary processes of migration and accumulation of pollutants occurring in the artificial urban environment. Thus, methods based on the study of urban sediments provide further opportunities for the analysis of the urban environmental state (Selbig et al., 2013; Seleznev & Yarmoshenko, 2014; Seleznev et al., 2010, 2015, 2018; Wei et al., 2010). Various types of contemporary sediments are involved in environmental studies of urban territories, such as the bottom sediments of water bodies, road dust, sediments of the sewage system, puddle sediments (PS), etc. (Apeagyei et al., 2011; Duzgoren-Aydin et al., 2004; Hilliges et al., 2013; Jartun et al., 2008; Murakami et al., 2009) along with the urban soils (Sürücü et al, 2018; Świercz & Zajęcka, 2018).

Environmental assessment methods for urban areas based on the study of contemporary sediments are inexpensive and rapid. However, there is no complete understanding of how to apply and unify the same methods for multiple cities where the processes of contemporary sedimentation are different, for example, cities located in different geographical, climatic, and industrial zones and cities in regions with different geological structures. The processes of the formation and modification of the geochemical conditions will differ in such cities. Moreover, the geochemical conditions in these cities are determined by the transport load (the number of vehicles, fuel type used, density of the road network, characteristics of vehicles, and transport routes). Thus, the conditions of contemporary sedimentation are unique and differ significantly between the various cities.

In recent decades, there has been an increase in the volume of dust of various origins in urban areas (Apeagyei et al., 2011; Selbig et al., 2013). Dust continuously transferred and accumulated on surfaces in the form of loose sediments represents the main medium for the transport of pollution in cities (Wong et al., 2006). Dust and heavy metals are reported to be the main environmental risk factors for the urban population (Lim et al., 2012). The sources of heavy metals can include aerosols, solid particles, and dust entering the atmosphere with emissions from industrial enterprises and vehicles (Aerosol chemical processes, 2000; Amato et al., 2009; Chen et al., 2012). The heavy metals remain in environmental compartments within the cities long after the period of combustion of leaded gasoline and coal (Birke & Rauch, 2000).

The objectives of this study were (1) to characterize the geochemical properties (particle size composition, pH level, and content of organic matter) of surface sediments in cities located in different geographic, climatic, and industrial zones as well as in regions with different geological structures; and (2) to characterize the content of heavy metals in the sediments and to assess the degree of heavy metals pollution of the urban sediments in the surveyed cities. The typical pollutants for urban areas (heavy metals: Mn, V, Ni, Cu, Zn, and Pb) were chosen for analysis. The current study continues a series of investigations of contemporary surface sediments and their geochemical and environmental role in an urban environment.

2. MATERIALS AND METHODS

2.1. The object of the study

The object of the study is a geochemical trap in urban areas representing the contemporary sediments located in the depressed surface zones of the microrelief (in other words PS). The mechanism of formation of these sediments was described in detail in the previous studies (Seleznev & Yarmoshenko, 2014; Seleznev et al., 2010, 2015). The micro water bodies (puddles) in the local depressed surface areas in residential areas are filled with sedimentary material washed out and transported from the surrounding landscape zones. This sediment contains atmospheric dust, solid and suspended particles of soil, erosion material, and others. The puddle catchment area consists of the roofs of buildings, grounds, pavements, local roads within the district, green zones, and other water harvesting surfaces. The solid material of the sediments is intermixed within the puddle. The pollutants absorbed by the particles are transferred and accumulated in the PS as well. The PS are formed in the courtyard area inside blocks of houses. The average thickness of the sediments is 5 cm. The surface sediments may be removed from the area of the residential block as a result of cleaning activities. The fine sedimentary material is constantly transported over the area of the block, redistributed by surface rainwater runoff and vehicle wheels. The PS accumulate pollutants over space and time within the area of the residential yard reflecting its environmental state.

2.2. Sample collection and preparation

As shown in Table 1, the PS surveys were conducted in cities located in different geological, geographic, climatic, and industrial zones. Intensive urbanization with rapid population growth and the development of new residential districts has occurred in the studied cities over last 70 years.

Samples of PS were collected in the residential areas of the cities during the summer seasons in 2016 (in Tyumen, Chelyabinsk, and Nizhniy Tagil) and in 2017 (in Ufa and Magnitogorsk). The sampling site represents the courtyard area of a block of residential, multi-story apartment buildings in a microrayon. A microrayon is a primary structural element of residential area construction in the Soviet Union and in some post-Soviet countries. A typical microrayon covers an area of 10–60 hectares. The area of the surveyed blocks in the cities varied in the range 20,000–60,000m^2. Besides the residential dwellings, the microrayon comprises the local public infrastructure: hospitals, schools, kindergartens, malls, recreational areas, and parks. The residential blocks of the cities surveyed have the same construction features and the same set of landscape sites within the block: green zones, passages, and children's playgrounds. Most of the population of the surveyed cities live in microrayons.

The sampling sites were chosen on an irregular grid within the territory of each city. The method of collection for the PS samples was described previously

Table 1. Description of the surveyed cities

City (population, mln. ppl.), geographical coordinates (latitude, longitude)	Geographic and climate zone	Geological features	Industries
Tyumen (0.77), 57°09′N, 65°32′E	The Western Siberia, forest taiga zone with waterlogged areas, temperate continental climate	Sedimentary rocks of the West Siberian plain; sandy-loam, sandy and peat-bog soils	Metal processing, machinery, oil processing, gas-fired power plants
Chelyabinsk (1.2), 55°10′N, 61°24′E	The South Urals, forest-steppe zone, temperate climate	Western part of the city lays on the granitoid massif (South Ural mountains), eastern part at the sedimentary rocks (West Siberian Plain); dark chestnut, chernozem and gray mountain-forest type of soil	Ferrous and non-ferrous metallurgy, chemical industry, machinery, coal-fired power plants
Nizhniy Tagil (0.36), 57°55′N, 59°58′E	The Middle Urals, mountain-forest zone, temperate continental climate	Middle Ural mountains; Nizhny Tagil pyroxenite-dunite massif; chernozem and gray mountain-forest type of soil	Metallurgy, coking, machinery, chemical industry, production of building materials
Magnitogorsk (0.42), 53°23′N, 59°02′E	The South Urals, steppe zone, sharply continental climate	Eastern side of the South Ural mountains, Magnitogorsk Synclinorium (gabbroids, granitoids and sedimentary rocks); chernozem, dark and light chestnut soils	Metallurgy, metal processing, gas-fired power plant, gas-fired power plant
Ufa (1.1), 54°44′N, 55°58′	Forest-steppe zone, temperate continental climate	The bank of the Belaya River. Sedimentary rocks: sandstones, clays, marls, limestones, dolomites, gypsum; dark gray and loamy soils	Oil processing, oil chemical industry, machinery

by Seleznev et al., (2010, 2015) and Seleznev & Yarmoshenko (2014). Roads with heavy traffic and industrial plants are located at a considerable distance from the studied sites (500–3000 m), and roads with medium traffic intensity often across the microrayons and are located at a distance of approx. 100 m from the sampling cites. A member of the research team visited the residential yard and selected the depression sites where the puddles had been formed. The samples were taken from the upper 5-cm PS layer. There were usually 3–5 samples collected from the depression sites in the courtyard area, and the samples were then combined into one composite sediment sample. The total sample mass was approx. 1.5 kg (dry weight). Domestic waste, debris, large stones, and roots were removed during the sampling process. During the sample collection process, the sampling scoop was cleaned with disposable wet alcohol wipes to prevent pollution of the current sample by the previous one. Photo documentation of the sampling sites and samples was performed. Examples of the sampling areas in the residential blocks are shown in Figure 1 (Magnitogorsk, Nizhniy Tagil, and Chelyabinsk) and in Figure 2 (Tyumen and Ufa). Information on the location and site-specific descriptions of the sampling sites was documented.

The PS samples were air-dried at the ambient temperature in the laboratory. The dried sample was crushed with a rubber pestle, homogenized, and thoroughly mixed. The coarse particles (size > 3 mm) of debris, tree branches, roots, stones, and gravel were discarded. Then, three representative subsamples were collected from each homogenized PS sample: (1) subsample for measuring the total metal concentrations and organic matter content (20 g), (2) subsample for defining the pH value (50 g), and (3) subsample of 200–

250 g for the particle size fractionation.

The subsample for the measurement of the metal concentrations and organic matter content was abraded to powder in an agate pounder. The subsample for determining the pH was passed through a 1-mm sieve. During the sieving process, the material of the subsample with size >1 mm was crushed and returned to the subsample.

2.3. Chemical analyses

The chemical analyses of the samples were performed at the Chemical Analytical Centre of the Institute of Industrial Ecology. The total metals concentrations in the PS samples were determined with inductively coupled plasma mass spectrometry (ELAN 9000; Perkin Elmer Inc., USA). The sample preparation and analysis procedures were conducted according to the technique for measuring the metal content in solid objects by spectrometry with inductively coupled plasma certified by The State Bureau for Environmental Protection of the Russian Federation (PND F 16.1:2.3:3.11-98, 1998). Solid PS samples were prepared to determine the total element contents using extraction with three acids (HNO_3, $HClO_4$, and HF). The sample preparation method is similar to the United States Environmental Protection Agency (US EPA) method EPA-821-R-01-010 (2001).

a b c

Figure 1. Puddle sediments in local surface depressed zones of microlandscape at the passage in the courtyard area in residential blocks in Magnitogorsk (a), Nizhniy Tagil (b), and Chelyabinsk (c).

a b

Figure 2. Puddle sediments in local surface depressed zones of microlandscape at the passage in the courtyard area in residential blocks in Tyumen (a) and Ufa (b).

The acidity level (pH) was determined by the ionometric method in a water extract of the subsample according to the Russian National Standard Soils: „Methods for determination of specific electric conductivity, pH and solid residue of water extract" (GOST 26423-85c, 1985). The water extract was prepared by mixing part of the subsample (30 g) with distilled water. The method of measurement of the pH in the samples is analogous to the US EPA SW-846 Method 9040C (EPA SW-846, 2004).

The organic matter content was determined with a photoelectric colorimeter in a solution prepared from the subsample (5 g collected from the subsample) according to the Russian National Standard Soils: „Methods for determination of organic matter" (GOST 26213-91, 1991). The solution of the given subsample for the colorimetric measurements was obtained by mixing the subsample with a solution of potassium dichromate in sulphuric acid. Then, the mix was heated in a boiling water bath and cooled. After that, the colorimetric measurements were conducted for the solution.

The quality control procedure for the measurements was provided by the usage of certified methodologies and the accreditation of the Chemical Analytical Centre of the Institute of Industrial Ecology by The Russian System of the State Accreditation laboratories.

2.4. Granulometric analysis

To characterize the particle size composition of the sediments in each city, several PS samples were randomly selected from each city's sample population. These samples had to be taken from different geographic areas of the surveyed city. The prepared subsample of the PS was then divided into particle size fractions in the following sequence: 0.002–0.01 mm, 0.01–0.05 mm, 0.05–0.1 mm, 0.1–0.25 mm, 0.25–1 mm, and >1 mm. Distilled water was added to the subsample of 200–250 g mass to obtain a solution which was dispensed into ten beakers. Then, the solution with the particle size fraction 0.002–0.01 mm was separated by decantation. The decantation procedure was conducted multiple times until the solution became clear. Then, distilled water was added to the residual substance of the subsample in the beakers. After that, decantation was conducted to separate the solution with the particle size fraction 0.01–0.05 mm. The decantation procedure was again conducted multiple times until the solution became clear. The volume of the solution obtained containing the 0.002–0.01 mm fraction was up to 50 litres, and the volume for the 0.01–0.05 mm fraction was 40 litres. The solid material of the particle size fractions 0.002–0.01 mm and 0.01–0.05 mm was acquired by vacuum filtering of the solutions through filters with pore sizes of 0.002 mm and 0.008 mm, correspondently. Then, to obtain the 0.05–0.1 mm fraction, the remaining part of the subsample was sieved through a sieve with a cell diameter of 0.01 mm with the addition of distilled water (wet sieving). After that, the remaining part of the subsample was sieved through a sieve with a cell diameter of 0.25 mm with the addition of distilled water to separate the particle size fraction 0.1–0.25 mm. The remaining material of the subsample was then dried and sieved through a sieve with a cell diameter of 1 mm. Thus, the fractions 0.25–1 mm and > 1 mm were obtained. The solid material obtained for the particle size fractions was then dried and weighed. Then, the mass portion of each particle size fraction was calculated. The decantation procedure was analogous to that described in Test Method WA 115.1-2017 (WA 115.1-2017, 2017).

2.5. Pollution degree assessment of PS samples

The Pollution Index (PI) and Pollution Load Index (PLI) were assessed to characterize the degree of pollution of the PS samples from the five cities. The PI quantified the enrichment of heavy metals in each PS sample with respect to soil maximum permissible concentration (MPC) level (HS 2.1.7.2041-06, 2006; HS 2.1.7.2042-06, 2006; Guidelines 2.1.7.730-99, 1999) and was calculated as below (Hakanson, 1980; Kowalska et al, 2018; Liu et al., 2013):

$$PI_i = C_i / C_{i\ MPC},$$

where C_i represents the content of heavy metal i in the i^{th} PS sampling site and $C_{i\ MPC}$ is the MPC of heavy metal i. The values of the PI are interpreted as follows: PI < 1 corresponds to low contamination of the PS sample; 1 ≤ PI < 3, moderate contamination; 3 ≤ PI < 6, considerable contamination; and PI ≥ 6, high contamination (Loska et al., 1997).

For each PS sampling site, the PLI was calculated to indicate the degree of integrated heavy metal pollution (Kowalska et al, 2018):

$$\mathrm{PLI} = \sqrt[n]{(\mathrm{PI}_1 \times \mathrm{PI}_2 \times \mathrm{PI}_3 \times \cdots \times \mathrm{PI}_n)},$$

where n is a number of elements taken into account.

Based on the PLI, the degree of pollution was categorized as follows: no pollution (PLI < 1), moderate pollution (1 ≤ PLI < 2), high pollution (2 ≤ PLI < 3), and very high pollution (PLI ≥ 3) (Wang et al., 2012).

3. RESULTS AND DISCUSSION

The sampling of PS was conducted in five cities (the number of samples collected in each city is shown in parentheses): Nizhniy Tagil (69 samples), Chelyabinsk (60), Tyumen (43), Ufa (43), and Magnitogorsk (41).

According to the site-specific description of the sampling sites, the landscape at all of the surveyed residential territories is artificially created as a result of construction activities. The sedimentary material at the studied sites was formed due to soil erosion processes and the surface destruction of pavements, asphalt, and building construction materials (surfaces of roofs and walls). In the studied cities, the base surface of the landscape zone is represented by a variety of materials such as urban sealed soil and ground, anthropogenic landfill, turf, asphalt, and different pavement surfaces. In the studied cities the surface sediments have a loose homogeneous structure, thus they are easily visually identified and distinguished from the base surface substrate. Based on the visual inspection of the sampling sites, the majority of the samples collected in Nizhniy Tagil, Chelyabinsk, and Magnitogorsk contain particles of metallurgical slag. The granulated slag is used as backfill to create drainage instead of gravel in the landscaping and planning of urban territories. The yards surveyed in this study are mostly in good condition; the courtyards are regularly cleaned. The thickness of the PS varies within a range less than 5 cm. During the survey, traces of ground excavation as well as landscape planning activities (greening, soil replacement) were sometimes found. Cars were parked in all of the studied courtyards; there were both organized and unorganized (when the car is parked on the lawn) parking lots and intra-yard passages. Approximately half of the vehicles were parked in the unorganized parking lots of the yards surveyed. By visual inspection, the unorganized parking lots were estimated to take up to one third of the courtyard area.

The geological conditions, climate, industries, and types of soils in the cities surveyed varied. As the surveyed residential areas have the same construction features, the mechanisms of PS formation are similar in all of the cities. Thus, the PS samples containing particle material from the different landscape sites reflect the geochemical conditions of the given block area.

3.1. Particle size composition of PS samples

The results of the granulometric analysis of the PS collected in the surveyed cities are shown in Figure 3 along with the amount of fractionated samples. The particle size composition of PS differs by the surveyed cities. The highest content of the 0.002–0.1 mm fraction (fine, medium, and coarse silt, fine sand, and dust) in the PS is 60% and is observed in the PS from Magnitogorsk, located in the steppe climatic zone.

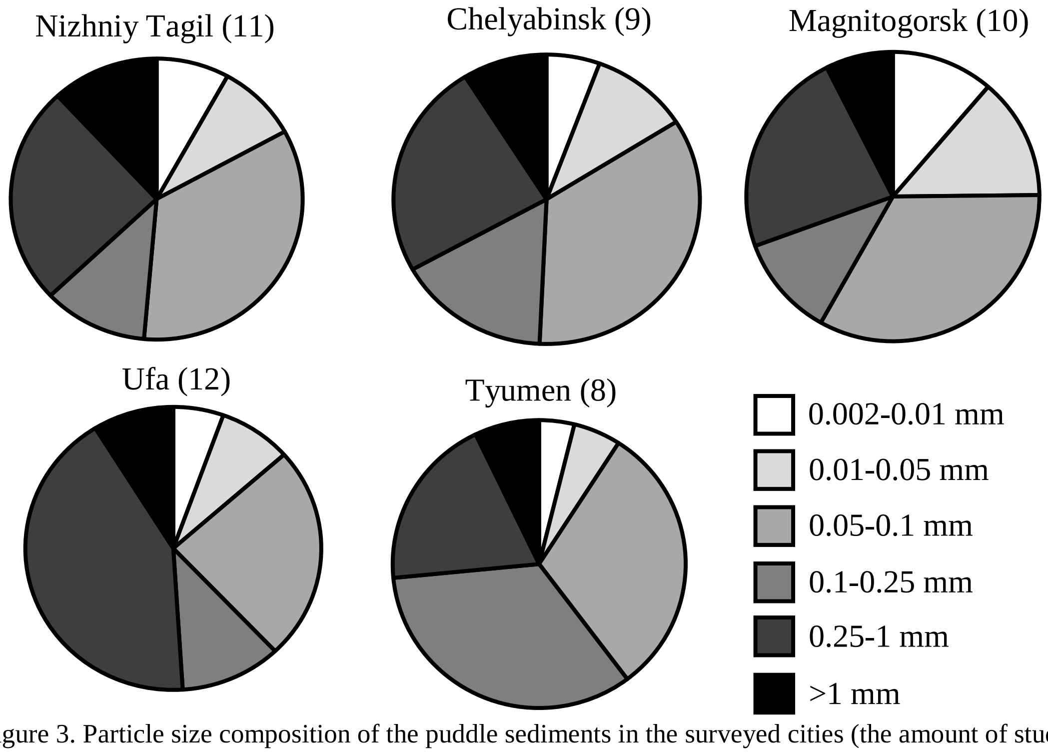

Figure 3. Particle size composition of the puddle sediments in the surveyed cities (the amount of studied samples is represented in parentheses).

The type of grain size distribution of the PS material is the same in Nizhniy Tagil and Chelyabinsk. An equal content of particle size fraction 0.002–0.1 mm (approx. 40%) is observed in the PS samples from Tyumen and Ufa, and the content of the sand fraction, 0.1–1 mm, in the PS is the same as well (53%). The surveyed cities can be ranked by the content of the dust fraction (0.002–0.050 mm) in the PS from the residential areas in the order: Magnitogorsk (25% of the total mass of PS) > Nizhniy Tagil (17%) > Chelyabinsk (16%) > Ufa (13%) > Tyumen (9%). The 0.002–0.050 mm particle size fraction of the PS includes suspended particulate matter, thoracic and respirable particles, inhalable coarse particles, fine and ultrafine particles, and soot. This particle size fraction of the PS represents the greatest environmental hazard for the urban population because it participates in the transfer of heavy metals, organic contaminants, and pathogens (Brown et al., 2013; Lim et al., 2012). The grain size content of the randomly collected PS samples from the sample population reflects the grain size composition of the contemporary surface sediments from the whole residential area of the surveyed cities.

The similarity of the granulometric content of PS in Nizhniy Tagil and Chelyabinsk is caused by the geological conditions at these cities. These two cities are situated on the eastern side of the Ural Mountains in zones of the same predominant soil type. Small differences in the granulometric composition of PS in these cities may be due to the presence of sedimentary rocks of the West Siberian lowland in the eastern residential areas of Chelyabinsk. The intensive industrial growth and residential construction occurred in these two cities in the same period (second part of the 20th century). Both of these cities have similar sources of pollution – ferrous metallurgical enterprises.

Tyumen and Ufa lie on sedimentary rocks, which determine the particle size composition of the urban surface sediments. The PS in Tyumen contain the least amount of the silt fractions, 0.002–0.01 mm and 0.01–0.05 mm fractions, (4% and 5%, respectively) among the surveyed cities.

The PS cocktail may contain particles of natural soils formed on the parent rocks of the city. However, the soils in the residential areas are constantly transformed, and the grain size composition of the PS may reflect the variability of the particle size composition of the anthropogenic soil.

3.2. Acidity level and organic matter content in PS

The total metal concentrations, pH, and organic matter content were measured in all of the collected samples. The pH values and organic matter contents of the PS samples are shown in Figure 4. The pH values of the PS in the studied cities correspond to alkalescent and alkaline conditions.

According to the analysis of variances (ANOVA), the pH of the PS significantly differs for the territories of the surveyed cities ($p < 0.05$). The lowest pH values of PS are observed in Nizhny Tagil

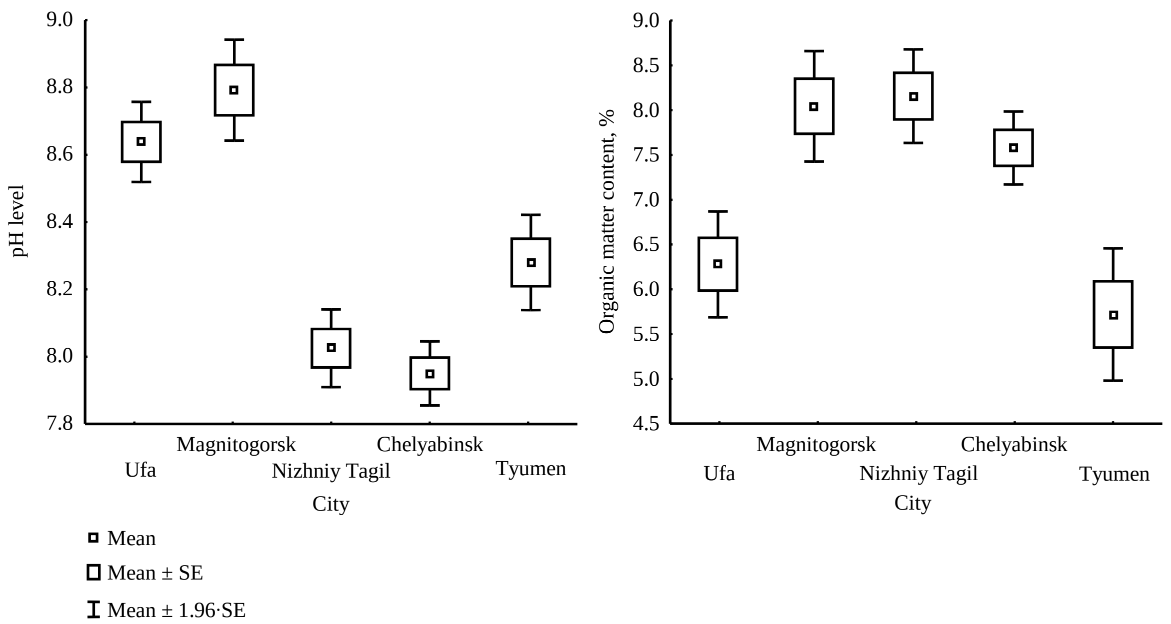

Figure 4. The acidity level (pH) (a) and organic matter content (b) in the puddle sediments samples in the surveyed cities (ordered from west to east).

and Chelyabinsk (mean pH values of 7.9 and 8.0, correspondently). Apparently, the alkalescent media of the PS is specified by the regional geological features of these cities, which are located in the Ural Mountains area where the parent rocks are basic and represented mainly by granitoids and pyroxenites; the natural soils at these sites were thus formed by the weathering of basic rocks.

The highest pH values were obtained for PS collected in Ufa and Magnitogorsk (mean pH values of 8.7 and 8.8, respectively), and the pH values for the PS do not significantly differ in these cities (ANOVA, $p < 0.05$). The alkalization of the surface PS increases in the cities located in areas with a predominance of carbonate parent rocks (dolomites and limestones) and loam.

The pH values of PS in Tyumen are significantly lower than in Ufa and Magnitogorsk and significantly higher than in Nizhny Tagil and Chelyabinsk. We hypothesize that such pH values are related to the sandy-loam, sandy, and peat-bog soils.

At the same time, a significant part of the PS cocktail consists of particles of brick and concrete produced from the parent rock material taken from the areas surrounding the studied cities. For example, the Magnitogorsk cement-refractory plant is located in Magnitogorsk and produces construction materials for Magnitogorsk. Thus, the acidity level (pH) is a characteristic of the predominant soil type and regional geological features of the area where the city is located.

According to the ANOVA, the average organic matter content in the PS significantly differs between the cities located in the Ural Mountains area and in the areas of sedimentary rocks ($p < 0.05$). A low organic matter content (5–7%) was found in the PS samples collected in Ufa and Tyumen where the lithogenic substrate was represented by sedimentary rocks. The highest organic matter content was obtained for the samples collected in Nizhniy Tagil (average content of 8.1%), Chelyabinsk (7.6%) and Magnitogorsk (8.0%). The low organic matter content in the PS characterizes the existence of sandy and loamy soils within the city, whereas the high organic matter content may be associated with a dark chestnut, chernozem and/or gray mountain–forest type of soil as the predominant natural soil type for the studied cities.

3.3. Heavy metal pollution of PS

The statistical distribution parameters for the concentrations of metals in the PS collected in the surveyed cities are summarized in Table 2. The distribution of Cu, Pb, and Zn concentrations shows a normal distribution for the PS samples from all of the surveyed cities. Apparently, the origin of Pb, Cu, and Zn in PS does not depend on the regional industries of the studied cities. Furthermore, the sources of these metals may be mostly related to the emissions from automobile traffic and automobile by-products. Pb was an additive to gasoline in Russia until 1997 and was therefore a component of automobile emissions. Cu and Zn occur from brake and tyre abrasions. Other sources of Pb, Cu, and Zn in an urban environment can include incinerators, pipes, cables, and paints (Biasioli et al., 2006; Hooker & Nathanail, 2006; Wang et al., 2012). Zn and other heavy metals remained in environmental compartments in the cities after the period of coal combustion (Birke & Rauch, 2000). The distribution type of the other elements in PS has, apparently, specific features typical for each particular city which are separately related to the pollution sources in each city.

According to Table 2, the concentration of Mn in PS in the cities of Nizhniy Tagil, Chelyabinsk, and Magnitogorsk is higher than in Ufa and Tyumen. High Mn concentrations may be related to the emissions of ferrous metallurgical plants and the use of manganese ores common in the Urals.

The assessed coefficients of variation show a high variability of the concentrations of all metals in the surveyed cities. Such variability may reflect the processes by which the pollution of the PS with heavy metals is formed which are difficult to take into account in the urban environment.

The content of V in PS collected in Nizhniy Tagil is several times higher than in the other surveyed cities. The average content of V in PS samples is lower than the soil MPC level in Chelyabinsk, Magnitogorsk, Ufa, and Tyumen. The source of V in PS in Nizhniy Tagil is polymetallic and iron ores enriched with V and metallurgical waste.

It should be noted that in three of the surveyed cities, Nizhny Tagil, Chelyabinsk, and Magnitogorsk, there are powerful sources of heavy metals: metallurgical industries with a complete processing cycle having blast furnaces and coke production. Along with steel production, these plants produce non-ferrous metal (copper, vanadium, titanium) from polymetallic ores typical of the Ural region. There is also a zinc plant in Chelyabinsk.

According to Table 3, the average PI values for metals in PS show low and medium degrees of pollution for the studied residential districts in the five cities. More than 75% of the PS samples collected in Nizhniy Tagil correspond to moderate contamination with heavy metals. In the other cities, the PS samples are polluted to a lower degree.

Table 2. Concentrations of metals in urban puddle sediments in the surveyed cities and MPC level for Urban soil.

City	Parameter	Element's concentration, $mg.kg^{-1}$					
		V	Mn	Ni	Cu	Zn	Pb
Magnitogorsk	Arithmetic mean	149	1211	59	51	289	37
	Geometric mean	146	1191	57	50	226	33
	Standard deviation	30	226	18	12	325	25
	Range	100-221	838-1767	35-139	30-97	100-1780	18-164
Ufa	Arithmetic mean	59	553	72	56	158	42
	Geometric mean	57	532	67	43	141	29
	Standard deviation	14	162	45	69	86	57
	Range	35-93	321-1083	36-348	22-416	59-445	9-361
Chelyabinsk	Arithmetic mean	83	763	61	50	338	66
	Geometric mean	82	748	59	48	293	53
	Standard deviation	10	185	17	18	202	70
	Range	60-112	564-1907	39-136	28-113	109-1368	22-537
Nizhniy Tagil	Arithmetic mean	264	2373	92	264	463	73
	Geometric mean	255	2284	81	237	420	59
	Standard deviation	77	665	53	121	218	71
	Range	142-719	925-4287	32-338	63-619	94-1337	18-536
Tyumen	Arithmetic mean	43	452	106	30	122	46
	Geometric mean	40	431	81	26	94	30
	Standard deviation	14	134	99	21	133	51
	Range	17-81	171-769	27-572	9-132	28-901	9-235
MPC level for Urban soil		150	1500	80	132	20	32

Table 3. The values of Pollution Index for heavy metals in the samples of urban puddle sediments in surveyed cities.

City	Metal	Value of Pollution Index					
		Arithmetic mean	Standard Deviation	25 percentile	Median	75 percentile	Range
Magnitogorsk	V	0.99	0.20	0.88	0.95	1.09	0.9-1.5
	Mn	0.81	0.15	0.70	0.79	0.85	0.6-1.2
	Ni	0.74	0.22	0.62	0.69	0.81	0.4-1.7
	Cu	0.39	0.09	0.32	0.37	0.43	0.2-0.7
	Zn	1.31	1.48	0.73	0.91	1.13	0.5-8.1
	Pb	1.17	0.78	0.82	0.98	1.19	0.6-5.1
Ufa	V	0.39	0.10	0.32	0.36	0.45	0.2-0.6
	Mn	0.37	0.11	0.29	0.36	0.42	0.2-0.7
	Ni	0.90	0.56	0.67	0.84	0.95	0.5-4.4
	Cu	0.42	0.52	0.24	0.27	0.36	0.2-3.2
	Zn	0.72	0.39	0.45	0.64	0.81	0.3-2.0
	Pb	1.30	1.78	0.60	0.82	1.18	0.3-11.3
Chelyabinsk	V	0.55	0.07	0.51	0.55	0.58	0.4-0.8
	Mn	0.51	0.12	0.45	0.49	0.53	0.4-1.3
	Ni	0.77	0.21	0.64	0.73	0.82	0.5-1.7
	Cu	0.38	0.14	0.29	0.35	0.44	0.2-0.9
	Zn	1.54	0.92	0.93	1.32	1.96	0.5-6.2
	Pb	2.06	2.19	1.22	1.60	2.11	0.7-16.8
Nizhniy Tagil	V	1.76	0.51	1.50	1.67	1.88	0.9-4.8
	Mn	1.58	0.44	1.24	1.55	1.82	0.6-2.9
	Ni	1.14	0.66	0.72	0.91	1.41	0.4-4.2
	Cu	2.00	0.92	1.41	1.78	2.52	0.5-4.7
	Zn	2.10	0.99	1.51	1.91	2.45	0.4-6.1
	Pb	2.30	2.20	1.25	1.77	2.46	0.6-16.7
Tyumen	V	0.28	0.09	0.22	0.27	0.34	0.1-0.5
	Mn	0.30	0.09	0.23	0.30	0.37	0.1-0.5
	Ni	1.33	1.24	0.56	1.03	1.40	0.3-7.2
	Cu	0.23	0.16	0.14	0.19	0.26	0.1-0.9
	Zn	0.55	0.61	0.23	0.43	0.69	0.1-4.1
	Pb	1.40	1.59	0.44	0.73	1.67	0-7.3

Table 4. Values of Pollution Load Index for heavy metals in the samples of urban puddle sediments in surveyed cities.

City	Mean	Standard Deviation	25 percentile	Median	75 percentile	Range
Magnitogorsk	0.80	0.18	0.70	0.76	0.86	0.5-1.5
Ufa	0.55	0.17	0.45	0.53	0.61	0.3-1.1
Chelyabinsk	0.76	0.19	0.64	0.75	0.86	0.5-1.5
Nizhniy Tagil	1.66	0.42	1.40	1.62	1.97	0.6-2.6
Tyumen	0.47	0.23	0.30	0.39	0.63	0-1.2

The use of MPC as a reference value for the pollution degree assessment is quite appropriate from the hygienic point of view. The results obtained are suitable for environmental management of the urban areas. However, from the geochemical point of view, the use of MPC as a reference concentration does not relate to the specific geochemical conditions of the regions surrounding the studied cities.

The following associations for the ratios between the average heavy metal concentrations in PS and MPC for the cities were obtained (in the order of decreasing PI):

Tyumen: Pb-Ni-Zn-Mn-V-Cu,
Ufa: Pb-Ni-Zn-Cu-V-Mn,
Chelyabinsk: Pb-Zn-Ni-V-Mn-Cu,
Nizhniy Tagil: Pb-Zn-Cu-V-Mn-Ni,
Magnitogorsk: Zn-Pb-V-Mn-Ni-Cu.

Thus, despite the fact that leaded gasoline has not been used for a long time, Pb remains the main pollutant in the residential areas of the surveyed cities.

PLI values for the selected set of metals show no metal contamination of PS in the residential areas of the surveyed cities, with the exception of Nizhny Tagil. More than 70% of the PS samples have metals concentrations almost two times higher than the MPC level in Nizhny Tagil. According to the PLI values, the cities can be ranked from the most polluted to the least: Nizhny Tagil – Magnitogorsk – Chelyabinsk – Ufa – Tyumen.

It should be noted that half of the residential area of Tyumen is represented by low-rise buildings with stove heating. Residential districts with stove heating do not have a significant effect on the pollution of the contemporary surface sediments in multi-story residential areas. At the same time, Tyumen does not have such powerful sources of pollution as Nizhny Tagil, Chelyabinsk, and Magnitogorsk, and pollution of the city is determined by the emissions of vehicles. Oil refineries in Ufa (located in the northern part of the city) also do not have a significant effect on the heavy metal pollution of PS.

4. CONCLUSION

The sediments studied are characteristic of the artificially created landscape in urban territories and represent the upper part of the constantly modified urban geological layer. The sediment contains particles of various origins; however, all of the artificially created components of the urban environment are formed from natural substrates (minerals, rocks, and soils) typical for the city and its surroundings. Thus, the material of PS can be defined as a quasi-natural component of an artificial landscape.

The geographic location, geological features, and industrial and vehicle emissions determine the geochemical properties of the urban surface sediments. The granulometric composition of the sediments varies depending on the geological conditions of the city's location. The important characteristic feature of the PS in an urban area is the accumulation of the transportable dust fraction of 0.002–0.05 mm (up to 25%), which represents the main environmental hazard for the city's population.

Based on the sampling of PS, an assessment of the heavy metal pollution of the urban areas was conducted, and the cities were ranked by the degree of pollution. The study of contemporary sediments in urban areas provides further opportunities for the assessment of the geochemical transformation of the urban landscape and its compartments.

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REFERENCES

Aerosol chemical processes in the environment, 2000. Ed. by K.R. Spurny. Boca Raton: CRC Press.

Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N. & Hopke, P.K., 2009. *Quantifying road dust resuspension in urban environment by multilinear engine: a comparison with PMF2.* Atmospheric Environment, 43, 2770-2780.

Apeagyei, E., Bank, M.S. & Spengler, J.D., 2011. *Distribution of heavy metals in road dust along an urban-rural gradient in Massachusetts.* Atmospheric Environment, 45, 2310-23.

Biasioli, M., Barberis, R. & Ajmone-Marsan, F., 2006. *The influence of a large city on some soil properties* *and metals content.* Science of the Total Environment, 356, 154-164.

Birke, M. & Rauch, U., 2000. *Urban geochemistry: investigations in the Berlin metropolitan area.* Environmental Geochemistry and Health, 22, 233-248.

Brown, J. S, Gordon, T., Price, O. & Asgharian, B., 2013. *Thoracic and respirable particle definitions for human health risk assessment.* Particle and Fibre Toxicology. 10: 12.

Chen, J., Wang, W., Liu, H. & Ren L., 2012. *Determination of road dust loadings and chemical characteristics using resuspension.* Environmental Monitoring and Assessment, 184, 1693-1709.

Duzgoren-Aydin, N.S., Li, X.D. & Wong, S.C., 2004. *Lead contamination and isotope signatures in the urban environment of Hong Kong.* Environment International, 30, 209-17.

EPA SW-846, 2004. *Method 9040C: pH Electrometric Measurement, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.* U.S. Environmental Protection Agency, Washington, DC.

EPA-821-R-01-010, 2001. *Method 200.7, trace elements in water, solids, and biosolids by inductively coupled plasma-atomic emission spectrometry. In: Revision 5.0.* U.S. Environmental Protection Agency. Office of Science and Technology, Washington, DC.

GOST 26213-91, 1991. *Russian National standard. Soils. Methods for determination of organic matter.* (in Russian)

GOST 26423-85c, 1985. *Russian National standard. Soils. Methods for determination of specific electric conductivity, pH and solid residue of water extract.* (in Russian)

Guidelines 2.1.7.730-99. 1999. *Hygienic Evaluation of Soil in Residential Areas.* The Head State Health Officer of Russian Federation.

Hakanson, L., 1980. *An ecological risk index for aquatic pollution control. A sedimentological approach.* Water Research, 975-1001.

Hilliges, R., Schriewer, A. & Helmreich, B., 2013. *A three-stage treatment system for highly polluted urban road runoff.* Journal of Environmental Management, 128, 306-12.

Hooker, P. J. & Nathanail, C. P., 2006. *Risk-based characterisation of lead in urban soils.* Chemical Geology, 226, 340-351.

HS 2.1.7.2041-06. 2006. *Hygienic Standard. Maximum Permissible Concentrations of Chemical Substances in Soil.* The Federal Service for Supervision of Protection Consumer Rights and Welfare Rights of Russian Federation.

HS 2.1.7.2042-06. 2006. *Hygienic Standard. Approximate Permissible Concentrations of Chemical Substances in Soil.* The Federal Service for Supervision of Protection Consumer Rights and Welfare Rights of Russian Federation.

Jartun, M., Ottesen, R.T., Steinnes, E. & Volden, T., 2008. *Runoff of particle bound pollutants from urban impervious surfaces studied by analysis of sediments from stormwater traps.* Science of the Total Environment, 396, 147-63.

Kabata-Pendias A. 2010. *Trace Elements in Soils and Plants. 4th Edition.* Boca Raton, FL: Crc Press.

Kowalska, J. B., Mazurek, R., Gasiorek, M. & Zaleski, T., 2018. *Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination–A review.* Environmental Geochemistry and Health, 1-26.

Lim, S. S. Vos T., Flaxman A. D. , Danaei G., Shibuya K., Adair-Rohani H., AlMazroa M. A., Amann M., Anderson H. R., Andrews K. G., Aryee M., Atkinson C., Bacchus L. J., Bahalim A. N., Balakrishnan K., Balmes J., Barker-Collo S., Baxter A., Bell M. L., Blore J. D., Blyth F., Bonner C., Borges G., Bourne R., Boussinesq M., Brauer M., Brooks P., Bruce N. G., Brunekreef B., Bryan-Hancock C., Bucello C., Buchbinder R., Bull F., Burnett R. T., Byers T. E., Calabria B., Carapetis J., Carnahan E., Chafe Z., Charlson F., Chen H., Chen J. S., Cheng A. T.-A., Child J. C., Cohen A., Colson K. E., Cowie B. C., Darby S., Darling S., Davis A., Degenhardt L., Dentener F., Des Jarlais D, C., Devries K., Dherani M., Ding E. L., Dorsey E. R., Driscoll T., Edmond K., Ali S. E., Engell R. E., Erwin P. J., Fahimi S., Falder G., Farzadfar F., Ferrari A., Finucane M. M., Flaxman S., Fowkes F. G. R., Freedman G., Freeman M. K., Gakidou E., Ghosh S., Giovannucci E., Gmel G., Graham K., Grainger R., Grant B., Gunnell D., Gutierrez H. R., Hall W., Hoek H. W., Hogan A., III H. D. H., Hoy D., Hu H., Hubbell B. J., Hutchings S. J., Ibeanusi S. E., Jacklyn G. L., Jasrasaria R., Jonas J. B., Kan H., Kanis J. A., Kassebaum N., Kawakami N., Khang Y.-H., Khatibzadeh S., Khoo J.-P., Kok C., Laden F., Lalloo R., Lan Q., Lathlean T., Leasher J. L., Leigh J., Li Y., Lin J. K., Lipshultz S. E., London S., Lozano R., Lu Y., Mak J., Malekzadeh R., Mallinger L., Marcenes W., March L., Marks R., Martin R., McGale P., McGrath J., Mehta S., Memish Z. A., Mensah G. A., Merriman T. R., Micha R., Michaud C., Mishra V., Hanafi ah K. M., Mokdad A. A., Morawska L., Mozaff arian D., Murphy T., Naghavi M., Neal B., Nelson P. K., Nolla J. M., Norman R., Olives C., Omer S. B., Orchard J., Osborne R., Ostro B., Page A., Pandey K. D., Parry C. D. H., Passmore E., Patra J., Pearce N., Pelizzari P. M., Petzold M., Phillips M. R., Pope D., Pope C. A., Powles J., Rao M., Razavi H., Rehfuess E. A., Rehm J. T., Ritz B., Rivara F. P., Roberts T., Robinson C., Rodriguez-Portales J. A., Romieu I., Room R., Rosenfeld L. C., Roy A., Rushton L., Salomon J. A., Sampson U., Sanchez-Riera L., Sanman E., Sapkota A., Seedat S., Shi P., Shield K., Shivakoti R., Singh G. M.,. Sleet D. A, Smith E., Smith K. R.,

Stapelberg N. J. C., Steenland K., Stöckl H., Stovner L. J., Straif K., Straney L., Thurston G. D., Tran J. H., Van Dingenen R., Van Donkelaar A., Veerman J. L., Vijayakumar L., Weintraub R., Weissman M. M., White R. A., Whiteford H., Wiersma S. T., Wilkinson J. D., Williams H. C., Williams W., Wilson N., Woolf A. D., Yip P., Zielinski J. M., Lopez A. D., Murray C. J. L., & Ezzati M.,** 2012. *A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and risk factor clusters in 21 regions, 1990–2010: a systematic analysis for the Global Burden of Disease Study 2010.* Lancet, 380, 2224-60.

Liu, C., Cui, J., Jiang, G., Chen, X., Wang, L. & Fang, C., 2013. *Soil heavy metal pollution assessment near the largest landfill of China*. Soil and Sediment Contamination: An International Journal. 22:4, 390-403.

Loska, K., Cebula, J., Pelczar, J., Wiechula, D. & Kwapulinski, J., 1997. *Use of enrichment, and contamination factors together with geoaccumulation indexes to evaluate the content of Cd, Cu, and Ni in the Rybnik water reservoir in Poland.* Water, Air, and Soil Pollution, 93, 347-365.

Murakami, M., Fujita, M., Furumai, H., Kasuga, I. & Kurisu, F., 2009. *Sorption behaviour of heavy metal species by soakaway sediment receiving urban road runoff from residential and heavily traficked areas.* Journal of Hazardous Materials, 164, 707-12.

PND F 16.1:2.3:3.11-98, 1998. *The Method of Measurement of Metal Content in Solid Objects by Spectrometry with Inductively Coupled Plasma.* The State Bureau for Environmental Protection of Russian Federation, Moscow (in Russian).

Selbig, W.R., Bannerman, R. & Corsi, S.R., 2013. *From streets to streams: Assessing the toxicity potential of urban sediment by particle size.* Science of the Total Environment, 444, 381-391.

Seleznev, A.A., Yarmoshenko, I.V. & Ekidin, A.A., 2010. *Accumulation of 137Cs in puddle sediments within urban ecosystem.* Journal of Environmental Radioactivity, 101 (8), 643-656.

Seleznev, A.A. & Yarmoshenko, I.V., 2014. Study *of urban puddle sediments for understanding heavy metal pollution in an urban environment.* Environmental Technology & Innovation, 1-2, 1-7.

Seleznev, A.A., Yarmoshenko, I.V. & Sergeev, A.P., 2015. *^{137}Cs in puddle sediments as timescale tracer in urban environment.* Journal of Environmental Radioactivity, 142, 9-13.

Seleznev, A.A., Yarmoshenko, I.V. & Sergeev, A.P., 2018. *Method for reconstructing the initial baseline relationship between potentially harmful element and conservative element concentrations in urban puddle sediment.* Geoderma, 326, 1-8.

Sürücü, A., Mohammad, D. M., Günal, E. & Budak, M., 2018. *Concentration of heavy metals in soils along three major roads of Sulaimani, Northeast Iraq.* Carpathian Journal of Earth and Environmental Sciences, 13(2), 523-538.

Świercz, A. & Zajęcka, E., 2018. *Accumulation of heavy metals in the urban soils of the city of Skarżysko-Kamienna (Poland) with regard to land use*. Carpathian Journal of Earth and Environmental Sciences, 13 (1), 249-266.

WA 115.1-2017, 2017. *Pavements and Structures Engineering. Document Number 115.1. 04/10437 Particle Size Distribution: Sieving and Decantation Method.* Main roads. Western Australia. Australia.

Wang, M., Bai, Y., Chen, W., Markert, B., Peng, C. & Ouyang, Z., 2012. *A GIS technology based potential eco-risk assessment of metals in urban soils in Beijing, China.* Environmental Pollution, 161, 235-242.

Wei, B., Jiang, F., Li, X. & Mu, S., 2010. *Contamination level assessment of potential toxic metals in road dust deposited in different types of urban environment.* Environmental Earth Sciences, 61, 1187-1196.

Wong, C.S.C., Li X. & Thornton, I., 2006. *Urban environmental geochemistry of trace metals.* Environmental Pollution, 142. 1-16.

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