Particle-size distribution and heavy metals accumulation in soils of Rostov-on-Don

O S Bezuglova¹, S N Gorbov¹, A A Okolelova², N V Salnik¹, S S Tagiverdiev¹ and G A Plachov¹

¹ Southern Federal University, 344090, Rostov-on-Don, Stachky prospect, 194, Russian Federation
² Volgograd State Technical University, 400005, Volgograd, Lenin prospect, 28, Russian Federation

E-mail: osbesuglova@sfedu.ru

Abstract. The surface horizons of the soils of traffic areas of Rostov-on-Don are characterized almost twice higher content of soil particles from 1 mm to 0.01 mm than native chernozems. The higher anthropogenic load provides the higher the content of sand fractions in the particle-size distribution. The accumulation of heavy metals (HM) in urban soils of roadside areas is relatively small, which is also due to a decrease of the soil sorption capacity. Significant excess of the estimated permissible concentrations was detected only for zinc and lead, and the higher the pollution level, the weaker the correlation between the particle size distribution and the HM content. This is justified by the influence of external factors on the accumulation rate of chemical elements.

1. Introduction

Rostov-on-Don is one of the two cities in the Southern Federal District with the population of over a million citizen. The city has a well-developed infrastructure, heavy automobile traffic and serves as a base for various industrial companies. All of this contributes to a high accumulation probability of pollutants, such as heavy metals in the soil. The specific of soil contamination with heavy metals in the cities is in their proximity to the industrial sources of aerogenic metal produced by the industrial plants. This creates high levels of soil contamination in limited areas. The entry of metals into the soil near emission sources predominantly occurs in the form of insoluble compounds. However, the mobility in the soil profile of zinc compounds is determined by their intake in the form of soluble salts. The gross quantity of certain metals in such zones may exceed the maximum permissible concentration (MAC) by multiple times. Depending on the pollution level and the dispersed composition of emissions in the local zone about 10 to 15% of metals released into the atmosphere falls on the ground. The configuration of the isolines of the metal content in the soil around the emission source mainly corresponds to the climatic wind rose.

For example, on the territory adjacent to Novocherkask TPP (thermal power plant), as the distance from the source of pollution increases, the concentration of metals gradually decreases and approaches the baseline values only at the distance of 20 km [1]. Moreover, this pattern is valid not only for the soil, but also for plants: as the distance from the source of pollution increases, the concentration of heavy metals in plants becomes lower [2].
The content of metals in the soils of the Rostov region varies widely and is determined by two main factors. The first of them is a natural environment based on geochemical aspects. The second is anthropogenic pollution of soils with heavy metals from various sources.

In Rostov-on-Don local soil anomalies of lead, copper, chromium and vanadium take place [3]. According to the data collected in the late 1980s zinc anomalies captured the entire old city center (up to 4 or more MACs). A special place in the pollution of the city with zinc belongs to the paint-and-lacquer factory “Empils”.

Road traffic also makes a significant effect on soil pollution with heavy metals. In cities the main source of soil contamination with lead are major highways, the congestion of which exceeds 200 cars per hour. The accumulation of this metal along the highways in Rostov-on-Don in some places exceeds 4 MACs.

Accumulation patterns depend on the soil location relative to the polluting objects as well as on the soil sorption capacity. Within the urban ecosystems, the anthropogenic impact affects even the most stable soil characteristics, such as particle-size distribution (PSD). This in turn transforms other soil properties including the chemical ones. Therefore, PSD largely determines the quantitative characteristics of the accumulation of toxicants in the soil. The combined research of PSD and the pollution rate of the soil poses theoretical and practical value.

2. Object of Study and Methods
The object of study was the sinitogenic horizon Urbic (UR) of Urbic Technosols. Urbic consists of loose layers with significant inclusion of anthropogenic material formed on the soils of natural origin, often transformed by the previous functional stages in the urban conditions. The 45 surface samples of Urbic from the variety of functional city zones were collected for analysis. The selected samples were located within 10-15 cm from the surface (figure 1, table 1).

Figure 1. Locations of soil pits (yellow markers) and top soil selection (red markers) in Rostov-on-Don.

The mixed sample was formed out of several point samples at the selected location using an agrochemical drill. The statistical analysis of the obtained results was accomplished with the samples, grouped into clusters arranged by the functional city zones. For clarification of the established patterns,
soil cuts were made with sampling from the genetic horizons. The position of the cuts and the names of the soil types in accordance with the WRB [4] are given in table 1.

The PSD analysis in all samples was made pipetting method after the soil preparation with sodium pyrophosphate. Quantity of heavy metals (gross content) was determined using the X-ray fluorescence spectrometer Spectroscan MAX-GV.

**Table 1.** Soil types used in the study with coordinates of them locations.

| Soil pits and surface samples, ## | Position                     | Soil types                              |
|----------------------------------|------------------------------|-----------------------------------------|
| 1401                             | N 47.2410 E 39.8185          | Haplic Chernozem (Technic)              |
| 1404                             | N 47.2738 E 39.8588          | Technosol Urbic (Linic)                 |
| 1405                             | N 47.2527 E 39.7696          | Technosol Urbic (Linic)                 |
| 1501                             | N 47.2332 E 39.6988          | Urbic Technosol                         |
| 1504                             | N 47.2333 E 39.6482          | Haplic Chernozem                        |
| 1604                             | N 47.224409 E 39.63012       | Urbic Technosol                         |
| 1701                             | N 47.234234 E 39.657186      | Haplic Chernozem                        |
| 1703                             | N 47.236620 E 39.656863      | Haplic Chernozem                        |
| 1704                             | N 47.237541 E 39.656966      | Haplic Chernozem                        |
| 1—45                             | N from 47.285571 to 47.182643 | Urbic Technosols (Linic)                |
|                                  | E from 39.853067 to 39.620723 |                                         |

3. Results and Discussion

The average PSD values of the Urbic horizon taken in the roadside areas are presented in the table 2.

**Table 2.** Particle-size distribution in the top layer of the Urbic horizon in the roadside soils of various functional zones in the city of Rostov-on-Don.

| Fraction size in (mm) and its contents in (%), M±m | Recreation Zone | Residential Zone | Industrial Zone | Left Bank of the Don River (floodplain) |
|--------------------------------------------------|-----------------|------------------|-----------------|----------------------------------------|
| 1-0.25                                           | 6.8±1.8         | 25.3±1.0         | 28.6±4.0        | 11.6±6.7                               |
| 0.25-0.05                                        | 24.5±5.2        | 24.4±0.4         | 21.0±0.9        | 33.6±20.5                              |
| 0.05-0.01                                        | 27.0±0.7        | 6.0±0.6          | 5.8±0.3         | 30.1-33.7                              |
| 0.01-0.005                                       | 6.0±1.8         | 6.0±0.1          | 5.2±1.6         | 20.4±1.5                               |
| 0.005-0.001                                      | 9.4±1.8         | 9.7±0.4          | 8.2±4.8         | 5.2±1.6                                |
| <0.001                                          | 26.3±4.0        | 23.8±1.7         | 22.2±1.0        | 21.0±5.8                               |
| <0.01                                           | 41.7±6.4        | 39.5±2.3         | 33.9±2.7        | 62.1-66.8                              |
| >0.01                                           | 58.3±6.4        | 60.5±2.3         | 66.1±2.7        | 33.2-37.9                              |

High concentrations of the heavy metals are confined to the industrial zone, with the highest content of Mn, Co, Zn, Sr, Pb (table 3).
However only Zn exceeds the estimated permissible concentrations not only in the industrial zone, but also in the floodplain on the Left Bank of the Don River. For some metals the permissible concentrations in Russia were established while considering the particle size distribution. Therefore, when the average PSD tends to the characteristics of light soils, it is advisable to focus on more strict recommendations. With this in mind, the assessment of soil contamination by metals such as zinc, lead and copper is changing. Particularly the 3-5 times increase of permissible concentrations of zinc was noted on average within the city limits. The concentration of lead was higher permissible values throughout the city with the two-fold increase in the industrial zone.

The comparison of the obtained results with the baseline concentrations of elements described by VV Akimtsev and co-authors in the 1962 publication showed that all metals except chrome and nickel exceeded the baseline values. This provides evidence to toxic accumulation (table 4). While accumulation rate of cobalt and copper is relatively low, concentration ratio for lead even in the clean residential zone reached 1.69. In the most polluted industrial zone, the concentration coefficient of lead increases to 2.12, which is due to the impact of vehicle exhaust on roadsides. Significant deviation from the baseline values also noted for zinc. Its accumulation rate in the residential zone measured at 3.22 and in industrial zone at 4.37, which reflects negative impact of the functioning paint-and-lacquer factory JSC «Empils» located in the city. Nevertheless, generally, the accumulation of metals in the roadside zone for a industrial city such as Rostov-on-Don is relatively small.

**Table 3.** Average gross content of the HM in the surface layer of Urbic horizon in the roadside soils of the functional zones in the city of Rostov-on-Don.

| Elements, M ±m, ppm | Recreation Zone | Residential Zone | Industrial Zone | Left Bank of the Don River (floodplain) | Estimated Permissible Concentrations (Hygiene Standards 2.1.7.2511-09) for Clay and Sandy soils | Baseline concentration [6] |
|---------------------|-----------------|------------------|-----------------|------------------------------------------|-------------------------------------------------|--------------------------|
| V                   | 89.3 ±7.9       | 562.6 ±50.8      | 11.8 ±1.4       | 12 ±12.3                                 | 8                                               | 67                       |
| Cr                  | 100.1 ±6.7      | 32.3 ±4.2        | 37.4 ±2.9       | 32.2 ±4.1                                | 45                                              | 100                      |
| Mn                  | 92.8 ±4.1       | 661.7 ±26.8      | 11 ±0.8         | 38.2 ±1.9                                | 30                                              | 50                       |
| Co                  | 94.9 ±4.3       | 38.2 ±1.9        | 38.2 ±1.6       | 38.5 ±2.2                                | 65                                              | 80/20                    |
| Ni                  | 83 ±8.2         | 161.1 ±17.9      | 161.1 ±17.9     | 132/33                                   | 220/55                                          | 130/32                   |
| Cu                  | 93 ±7.3         | 682 ±59.8        | 12 ±12.3        | 38.4 ±2.2                                | 130                                              | 130/32                   |
| Zn                  | 102.6 ±8.9      | 274.2 ±77.7      | 274.2 ±77.7     | 284.1 ±76.3                              | 55.6 ±21.4                                      | 150                      |
| Pb                  | 79.66 ±5.3      | 2586.3 ±246.5    | 33.4 ±2.6       | 222/55                                   | 30                                              | 80/20                    |

On the other hand, nickel accumulation rate is lower than 1, which indicates of lower content of this metal than in the baseline characteristics for chernozem. Perhaps this can be explained by the lighter particle-size distribution of the urban soils. In absence of contamination of a given territory with this metal, such a phenomenon is possible. This assumption is supported by the fact that the lowest accumulation rate was discovered in the Left Bank of the Don River, in the coastal floodplain, where the soils have the lightest PSD.

In order to assess the link between such important parameters of soil condition as particle-size distribution and gross content of heavy metals, the correlation rates were calculated as well. The content of physical clay (i.e., sum of particles with < 0.01 mm [7]) was chosen as a particle size distribution indicator, since it has a high sorption capacity and the probability of heavy metals accumulation in it is higher than in the physical sand (i.e., sum of particles with > 0.01 mm [7]). The research showed that
the relationship between these indicators for the surface soil horizon in the roadside areas is often the opposite, as indicated by the minus sign of the correlation ratio. Considering the significant increase of the sand fractions in the roadside soils due to the anthropogenic impact on the soil, and therefore regarding the sand as a contaminating element, it can be concluded that HM are transported with these fractions of physical sand rather than with the physical clay (i.e., sum of particles with < 0.01 mm). A high to very high correlation strength was found between the studied components in the soils of the recreational zone. For V, Co, Ni, Mn the link is estimated as reliable (t> 3) with a correlation rate in the range from -0.76 to -0.86. Zinc and lead being the main polluting elements of our city revealed a positive relationship in the recreational zone, which indicates the accumulation of these elements in thin fractions.

Table 4. Heavy Metals concentration ratio in the Urbic horizon of the roadside soils in the Rostov-on-Don (the comparison with the baseline concentrations [6]).

|       | V  | Cr | Co  | Ni  | Cu  | Zn  | Pb  |
|-------|----|----|-----|-----|-----|-----|-----|
| Recreation Zone | 1.33 | 1.0 | 1.48 | 0.72 | 1.25 | 3.22 | 2.06 |
| Residential Zone | 1.38 | 0.95 | 1.38 | 0.85 | 1.27 | 2.48 | 1.69 |
| Industrial Zone | 1.24 | 0.93 | 1.5 | 0.72 | 1.28 | 4.37 | 2.12 |
| Left Bank of the Don River | 1.19 | 1.03 | 1.21 | 0.62 | 1.11 | 4.22 | 2.78 |

However, the correlation strength is small: weak in zinc and average in lead, which is probably due to their predominant presence in the soil affected by anthropogenic factors. In all other zones, the relationship between the studied indicators is weak to very weak, and there are no regularities in the nature of the connection; it can be either direct or inverse. Generally, it was established that the greater the degree of contamination, the weaker the correlation strength, since it is determined by the external factors listed above, including random factors. Therefore, the lowest correlation rates are found for the soils of the industrial zone.

Figures 2 and 3 show zinc and lead distribution patterns in the Urbic Technosol (Linic) and Haplic Chernozem soil profiles. In figure 2 the max accumulation of zinc is clearly marked in surface horizons. Only absolute values differ, they are higher for Urbic horizon. The fixation of zinc in the soil occurs due to the formation of easily exchangeable forms associated with organic matter [8, 9]. Further down the profile, there is a fairly clear graphical correlation in the character of the distribution lines of physical clay and zinc, which indicates the significant role of fine fractions in fixation of this metal. Lead shows an entirely different distribution pattern along the profile of the studied soil. Two max values can be observed in the surface layer and in the horizon with the most carbonates accumulation (CаС), thus the graphic link to the physical clay is absent. It is known that in soils containing carbonates, the binding of an element occurs mainly due to the deposition of cerbite PbCO₃. Soil organic matter can form complexes with Pb²⁺ [10, 11]. The curves of the lead distribution along the profile of Urbic Technosol Linic and Chernozem presented in figure 3 clearly illustrate these patterns.

The contamination by other heavy metals have not been observed. Nevertheless, it is possible to note some change in regularities of their content in chernozems profile. Copper is a relatively little-mobile element in soils. Because of this, the variation of the copper content in the soil profile is insignificant. A relative increase of copper content is noted in the middle part of the profile, where processes of weak accumulation of clay particles take place in the chernozem. This may contribute to the copper sorption
on the newly formed clay material. Nickel and cobalt exhibit a tendency to accumulate in the middle of the soil profile as well. Most likely, the soluble forms of these metals, moving along the profile, in its middle part are encountering with highly dispersed forms of calcium carbonate and clay minerals, and, are fixed via sorption on them [3].

**Figure 2.** Distribution of zinc and physical clay along the soil profile in soil pit #1405 (Urbic Technosol (Linic) – A) and soil pit #1701 (Haplic Chernozem – B).

**Figure 3.** Distribution of lead and physical clay in soil pit #1405 (Urbic Technosol (Linic)– A) and soil pit #1701 (Haplic Chernozem – B).
4. Conclusion

In the surface soil layers of Urbic horizon located at the roadside areas of the Rostov-on-Don, the physical sand content is almost twice as high compared to the baseline characteristics of chernozem. Greater anthropogenic load results in the higher content of sand fractions in the particle-size distribution. Basically, the degree of anthropogenic load correlates with the sand content in the surface horizons of the soil. A twofold increase of the physical sand in the PSD of the city roadside soils causes a decrease in the sorption capacity of the soil and the ability to bind toxic substances into sedentary forms. Incoming sand reduces the relative content of fine fractions and this gives the impression of confinement of TM to sand fractions. This in turn reduces the protective role of these zones relating to the environment of the city.

The accumulation of heavy metals in the roadside soils is relatively small, which is also explained by the decreased sorption capacity of the soil. Significant excess of the estimated permissible concentrations was detected only for zinc and lead, and the higher the pollution level, the weaker the correlation between the particle size distribution and the HM content. This is justified by the influence of external factors on the accumulation rate of chemical elements. Such external factors primarily include confinement to a particular functional area.

Acknowledgments

This research was supported by the project of Ministry Education and Science of Russia, no. 6.6222.2017/8.9 and with the governmental support of the Russian Federation Leading Scientific School (NSH-3464.2018.11). Analytical work was carried out in the Centers for Collective Use of SFU "Biotechnology, Biomedical and Environmental Monitoring", "High Technology".

References

[1] Minkina T, Motuzova G, Mandzhieva S, Nazarenko O, Burachevskaya M and Antonenko E 2013 Fractional and Group Composition of the Mn, Cr, Ni, and Cd compounds in the soils of technogenic landscapes in the impact zone of the Novocherkassk Power Station Eurasian Soil Sci. 46 375–85
[2] Minkina T, Mandzhieva S, Chaplygin V, Bauer T, Burachevskaya M, Nevidomskaya D, Sushkova S, Sherstnev A and Zamulina I 2017 Content and distribution of heavy metals in herbaceous plants under the effect of industrial aerosol emissions J. Geochem. Explor. 174 113–20
[3] Bezuglova O, Gorbov S, Tischenko S, Aleksikova A, Tagiverdiev S, Sherstnev A and Dubinina M 2016 Accumulation and migration of heavy metals in soils of the Rostov region, South of Russia J. Soils Sediments 16 1203–13
[4] World References Base for Soil Resources 2006 First update 2007 World Soil Resources Reports (Rome: FAO) 103
[5] Bezuglova O and Khirkhyrova M 2008 Soils of the Rostov Region (Rostov n / D: SFU Publishing House) 352 p (In Russian)
[6] Akimtsev V, Boldyreva A and Golubev S 1962 The content of trace elements in the soils of the Rostov region Microelements and Natural Radioactivity (Rostov n / D: Publishing House of the RSU) pp 38–41 (In Russian)
[7] Kachinsky N A 1965 Soil Physics (M.: Vysshaya shkola) p 324 (in Russian)
[8] Degryse F, Voegelin A, Jacqua O, Kretzschmar R and Smolders E 2011 Characterization of zinc in contaminated soils: complementary insights from isotopic exchange, batch extractions and XAFS spectroscopy Eur. J. Soil Sci. 62 318–30
[9] Ren Z, Sivry Y, Tharaud M, Cordier L, Li Y, Dai J and Benedetti M 2017 Speciation and reactivity of lead and zinc in heavily and poorly contaminated soils: Stable isotope dilution, chemical extraction and model views Environ. Pollut. 225 654–62
[10] Cui Y and Weng L 2015. Interpretation of heavy metal speciation in sequential extraction using geochemical modelling Environ. Chem. 12 163–73
[11] Schneider A, Cances B, Ponthieu M, Sobanska S, Benedetti M, Pourret O, Conreux A, Calandra I, Martinet B, Morvan X, Gommeaux M and Marin B 2016 Lead distribution in soils impacted by a secondary lead smelter: experimental and modelling approaches Sci. Total Environ. 568 155–63