Physical-chemical predictors of soil pollution in the megapolis

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Abstract. The problem of quantitative assessment of soil pollution of the capital metropolis by controlling physical-chemical factors of solid and liquid phases of soil is investigated. The metals were used as an integral indicator of pollution taking into account the mass fraction and the variation of soil bulk density. Multiple regression ($R^2=0.91$-$0.95$) of layered heavy metals, as well as accumulation of biophilic elements of the exchange fund from two main predictors – dispersion (effective specific surface area of solid phase, determined by the original thermal desorption method) and pH of salt extract was revealed.

1. Introduction
The emissions from industrial enterprises and transport get into soil of a megapolis and accumulate at that the dominant soil contamination (to 70\%) is due to motor transport \cite{1}. Pb, Cd, Al, Fe, Ni, Mn and other elements get into the soil near the roads. The heavy metals (HM) input into the environment as a result of transport activity may be added by abrasion of roadway surfacing. The main role of negative influence of transport plays Pb as a component of petrol additive - tetraethyl lead. During petrol combustion nearly 75\% of lead emit as aerosol and redistribute near the road ways. The accumulation of heavy metals and metalloid in soils is considered to be the most dangerous and steady pollution that takes place mainly due to aerosol impact \cite{1-4}. Technology-related dust and airborne aerosol change chemical composition of upper soil layers, increase pH and a content of fine soil fractions, and lead to a decrease of soil organic carbon. That in turn could create physical chemical factors for accumulation and stabilization of heavy metals. The negative influence of manufacturing industry on heavy metal soil pollution was shown in numerous research studies \cite{5-7}. The pollution of the topsoil level by Pb, Cu, Cr, Cd, Zn and their spatial distribution around a cement factory was estimated in \cite{6}. The metals were determined in 38 soil samples by FAAS after their nitric-perchloric digestion. Spatial mapping of the distribution of heavy metals was done through the use of IDW of ArcGIS 10 \cite{6}. The results showed that the contamination domain of Cd was in the extreme domain, while Pb and Cu levels in the soil were in the severe and moderate contamination domains. Zn and Cr posed no potential environmental hazard because of their low level in the soil. The data revealed that Pb and Cu soil contamination related with the cement factory and vehicular activity and Cd enrichment in the soil is related only with the cement production activity.
The distribution of heavy metals in the soil around Antang landfills (Indonesia) was estimated in [8]. The results obtained with the use of ICP-OES method showed that the soil around Antang landfill is contaminated with the heavy metals.

The aim of this investigation was the statistical estimation of soil pollution characteristics depending on their physical, chemical and physical-chemical properties for effective ecological control and rationing of technogenic impact in Eastern and North–Eastern administrative districts of Moscow.

2. Objects and methods

2.1. Site description and sampling

The study of urban soils was carried out in Eastern and North–Eastern Moscow Administrative okrugs in summer-autumn season of 2017-2018 years. The soils of such regions were polluted by manufacturing enterprises (asphalt, electromechanical and oil-processing plants, reinforced concrete plant “Rostokino” (points N 4 in Table 1, coordinates of one of the sampling points were latitude 55,84875\textdegree; longitude 37,6586\textdegree; altitude 145.3 м (GPS/GLONASS), and highways (points N 5 in Table 1, Verkhoyanskayaulitsa, ulitsa of a pilot Babushkin, Serebryakova prospect, Amudsonaulitsa) and Yaroslavskaya railway (coordinates of one of the sampling points were latitude 55,85616\textdegree; longitude 37,67328\textdegree; altitude 148.8 м (GPS/GLONASS) that are situated in a close proximity of sampling transects [9]. The soils were sampled layer by layer through 7 cm from a top layer to 21 cm below by the Kachinskiy drill for the synchronous estimation of soil density ($\rho_s$).

Soils are represented by urbanozems with average and strong concentrations of humus on the technogenic layer underlayed by covering silt and fluvioglacial accumulation. Relatively clean urban soil samples determined as derno-podzolic soils on the fluvioglacial accumulation from recreational area of the park (50 meters to the pond) embordered by Saltykovskaya ulitsa (Novokosino) in the west were used as background objects (points N 1.2.3 in Table 1, 55,44307\textdegree; 37,52593\textdegree; altitude 150 м (GPS/GLONASS). were studied [10, 11]. The results of 57 mixed samples including 8 background ones were studied as the mean value of three replications.

2.2. Laboratory methods

The concentration of heavy metals movable forms (Co, Mn, Cu, Zn, Ni, Pb, Cd, Cr, Mg, Fe) was determined with the use of an AAS-3 Analyzer in an ammonium acetate buffer solution at pH 4.8, according to common procedure used for the HM determination [12, 13]. The $\text{pH}_{\text{Hg}}$, $\text{pH}_{\text{is}}$, losses of ignition, the humus content determined on the basis of the carbon organic $C$ according to the Tyurin method, exchangeable cations, determined according the Shollenberg method: $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ were determined in the certified laboratory center of Dokuchaev Soil Science Institute [14]. Together with traditional characteristics of heavy metal pollution as a weight content, integral indicators of their accumulation in a layer with the use of ($\rho_s$) data according [15] were calculated [16, 17]. Effective surface area ($S$) as an integrated index of solid phase dispersion was determined by a new thermo gravimetric method [18]. The drying apparatus Binder (Germany) was used for the differential drying of samples at 30, 40, 50, 60, 70, 80\textdegree'C and a combine measuring instrument TESTO 410-2 (Germany) was used for the control of laboratory relative air humidity. Statistical data analysis was made according [19] using a program R 3.3.0 Windows with the export of data into spreadsheet table in Microsoft Office Excel 2007.

3. Results and discussion

The change in physical-chemical properties of urban soils together with considerable input of heavy metals leads to accumulation of HM in the top-layers of soils [1, 20, 21-24]. In the Table 1 the distribution of heavy metals in some regions of megapolis Moscow is presented. The comparison of urban soils near factory, road zones and park zone showed that the highest accumulation was of the slow-moving toxic Pb near manufacturing enterprises, while the lowest one was typical for the highly
We did not determine a high level of accumulation of Cu (0.43-44.03), Co (0.05-0.31), Cd (0.04-0.27 ppm), that was found in [4] in these areas.

Table 1. The content of metals in the soils of Moscow (concentrations of metals are given in ppm).

| Point | Depth, cm | Co  | Mn  | Cu   | Zn   | Ni  | Pb  | Cd  | Cr  | Mg  | Fe   |
|-------|-----------|-----|-----|------|------|-----|-----|-----|-----|-----|------|
| 1     | 0-7       | 0.08| 37.27| 1.28 | 21.58| 2.71| 4.24| 0.27| 0.19| 28.22| 77.76 |
| 1     | 7-14      | 0.31| 12.68| 0.87 | 8.06 | 2.31| 1.89| 0.10| 0.35| 2.36 | 28.73 |
| 1     | 14-21     | 0.12| 11.09| 1.15 | 8.66 | 0.66| 0.11| 0.02| 0.02| 1.48 | 15.68 |
| 2     | 0-7       | 0   | 39.05| 1.28 | 8.52 | 3.61| 4.02| 0.17| 0.26| 14.41| 51.02 |
| 2     | 7-14      | 0.16| 14.43| 0.66 | 4.10 | 2.12| 1.89| 0.04| 0.18| 3.54 | 8.79  |
| 2     | 14-21     | 0.05| 11.20| 0.56 | 2.14 | 2.06| 0.32| 0.07| 0.17| 0.95 | 0.95  |
| 3     | 0-7       | 0.09| 14.16| 0.95 | 8.12 | 2.71| 4.43| 0.18| 0.10| 20.66| 68.14 |
| 3     | 7-14      | 0   | 6.69 | 0.77 | 6.82 | 2.97| 1.48| 0.11| 0.35| 4.05 | 24.50 |
| 3     | 14-21     | 0   | 3.01 | 0.43 | 3.12 | 2.03| 0.48| 0.08| 0.31| 1.23 | 2.45  |
| 4     | 0-7       | 0.20| 13.62| 0.99 | 13.23| 1.27| 9.49| 0.19| 0.22| 96.27| 2.56  |
| 4     | 7-14      | 0.09| 13.64| 2.49 | 11.32| 2.55| 5.37| 0.18| 0.18| 114.78| 8.29 |
| 4     | 14-21     | 0   | 16.22| 2.33 | 15.05| 3.55| 5.60| 0.22| 0.19| 94.68| 2.22  |
| 5     | 0-7       | 0.28| 5.74 | 0.48 | 11.58| 1.34| 1.46| 0.22| 0.07| 169.99| 0    |
| 5     | 7-14      | 0.15| 9.08 | 44.03| 14.90| 9.27| 2.75| 0.25| 0.28| 120.11| 0.02 |
| 5     | 14-21     | 0.09| 14.54| 2.83 | 27.91| 3.34| 3.52| 0.22| 0.23| 104.29| 0.22 |

The attempts to find dependencies between traditional characteristics (weight content of chemical element with each other) and (pH, S, organic carbon content, porosity, field moisture) rarely gave good results and often the values of coefficients of determination were no more than 0.5 [3]. The use of volume concentrations and total reserve of elements along 7 cm soil layers instead of weight increase and revealed a good relationship according (R² 0.64-0.82) [19] of these characteristics with potential predictors such as pH, degree of dispersion, humidity, humus content and losses of ignition.

The combination of different characteristics in quality of predictors (ratios, multiplications and sums) did not lead to tightness of relationships whereas the use of multiple regression clearly defined the more significant predictors for the forecast of heavy metal pollution and modern fertility (sum of exchangeable bases) of studied urban soils. These revealed characteristics were dispersion (S) and pHs. The regression model (pedotransfer function) for layer-by-layer accumulation of heavy metals was as following: CHM=0.121*S+3,305*pH-12,578, R²=0.91 in the range of heavy metal accumulation in 7 cm layer from 0.4 g/m² (background, unpolluted lower layers) to 60 g/m² (roadways, industrial areas) at 3.7<pH<7.3 and dispersion 22m²/g<S<70m²/g. The relationship between studied and predicted values of accumulation normalized to their maximum values is shown in the Figure 1.
Figure 1. Multiple regression of heavy metals and exchangeable bases with two main predictors – dispersion and pHs (normalized reserves).

4. Conclusions

\(R^2=0.91-0.95\) of layered (7cm) accumulation of heavy metals and biophilic elements of exchangeable reserve fund with two main predictors – dispersion and pHs was obtained contrary to small and statistically insignificant values of pair correlation of each other’s properties. The method is economic, fast and useful to assessment of soil pollution by the simple physical-chemical factors instead of investigating the HMs concentration.

It is proposed that accumulation by solid phase is determined by dispersion, while pH characterizes mobility/precipitation in solution. The obtained result confirms the accepted in Russian Federation differentiation ОDК (ГН 2.1.7.2511-09) depending on dispersion and pH. “Effective specific surface of solid phase” as the strict characteristic of dispersion is proposed instead of “type of gravimetric composition”.

Acknowledgment

This work was supported by RFBR, project no.19-29-05006/19 (data processing and modeling) and by State Assignment theme no AAAA-A15-115122810146-4 (lab analysis).

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