New approaches to the estimation of the geosystem properties transformation in technogenesis

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Abstract. A new approach to the estimation of environmental situation of the urbanized territories of a large city is offered. The approach is based on a complex of physical and chemical parameters adequately describing transformation of soil properties, with the use of landscape-geochemical method and GIS technologies. The pollution of soil horizons by heavy metals (HM) and mineral oil (MO) in a zone of influence of dangerous industrial objects exceeds orders the maximum permissible concentration (MPC). Sharp deterioration of a nitric and carbon mode, increase of the alkalinity and the decrease in buffer activity of ground were revealed. The dynamics of technogenic streams and aureole of the contaminants migration in soils can result not only in the further transformation of their properties, but in closing the migration cycles of MO and HM. As a rule this is accompanied by the formation of secondary local sites of toxic substances accumulation and abnormal geochemical fields - laterally technogenic module. The revision of approaches to the analysis of soils under technogenesis and the development of new system of ecological monitoring represent a challenging goal.

1. Introduction
Industrially overloaded regions of Siberia and boundary territories cause the problems of nature protection, the decision of which is complicated by the absence of the state program of environmental safety [1]. In the Baikal Natural territory, which is being under UNESCO protection, multiple technogenic influence on the environment characterized by synergistic effect is observed. The scale of soils and the water-currents degradation, the out-of-date schemes of sampling, the simplified techniques of contaminants determination (dated back to the beginning of the last century), and the absence of modern system of monitoring do not promote to the development of new approaches to correct estimation of environmental situation of the territories.

The urgency of the investigations conducted is due to the necessity of obtaining the reliable criteria of transformation of natural geosystems under the influence of technogenesis. New approaches are based on revealing the correct characteristic describing modern and predicted situation of technogenic-changed soil and water geosystems involving a complex of physical and chemical parameters and models [2].

In the urbanized territories, technogenic streams of contaminants can essentially differ from those of in natural environment. However, the migration of pollutants in geosystems and their transformations under the action of various environmental factors in the course of technogenesis and the formation of new geochemical fields are not practically studied.
2. The purposes
The investigation is aimed at the revealing of regularities of pollutants migration and accumulation in soil water to understand the mechanism of their transformations during technogenesis. This is connected with necessity of the revision of out-of-date notions on the dynamics and normalization of contaminants in geosystems, especially in the urbanized territories and in a zone of influence of large industrial complexes. The new approach to ecological diagnostics of technogenically modified soils and water-currents are necessary. This will allow the modern quality monitoring under changing conditions of the environment to be developed. The necessity of the development of new system of ecological monitoring was underlined at session of the State Advice of the Russian Federation on May 27th, 2010.

We carry out systematic geoecological research according to the complex program:

- Studying the transformation of properties of soil and water ecosystems to reveal migration streams of the contaminants in the urbanized territories of large cities;
- Studying the transformation of soil and water-currents properties in a zone of technogenic influence during the extraction and processing of mineral raw material under mountain conditions.

3. Methods and objects of research
Soil is the main buffer, which takes the whole complex of long-term influence from industrial production and anthropogenic sources. Therefore, objects of the research are soils and grounds ecologically vulnerable areas of Siberia and the urbanized territories of cities in a zone of influence of dangerous objects, which according to the forecast of mineral resources development will be intensively developed up to 2030 [3].

The present work deals with the results of the investigation of technogenically changed soils (urbicosoils) in a zone of dangerous industrial objects of a large city with the population of 1.5 million. The objects of research are gasoline stations (GS), petroleum depots, dams of hydraulic ash-disposal areas of thermal power stations located on territory of a city. The pollution was estimated under the content of mineral oil (MO) and heavy metals (HM) - Cu, Cd, Ni, Pb, Zn, Hg, as well as As.

Methodological methods of investigations:

- landscape and geochemical in combination with cartographical are most appropriate for ecological estimation of territories;
- determination of physical and chemical and geochemical parameters of soils, which adequately reflect the content and forms of contaminants and their properties;
- establishing the spatial and time dynamics of the contaminants distribution in soil horizons;
- compiling the monoelement maps using GIS-technologies to forecast the conditions of geosystems;
- modelling of the pollutants migration in soil ecosystem under the influence of environmental factors.

The following methods were used to study the soil samples: physical and chemical, including atomic absorption spectroscopy with the inductive connected plasma, gel-penetrating chromatography, electronic absorption spectra, microelement analysis, wet and dry combustion, DTA, and also the correlation analysis, computer modeling and GIS-technologies and so on.

4. Discussion of results
The fertile layer of northern territories does not exceed 5-10 cm. Therefore, long-term intensive accumulation of diverse pollutants inevitably leads to the significant changes of morphology and structure of soils, transforming them into lands, technical soils and urbicosoils.

The urban territory is a specific geoecological system having original structure and composition of components [1, 3]. Under conditions of urbanization, ecosystems, as a rule, are transformed: the relief and lithogenous basis, hydro-geological and climatic conditions are changed, geochemical processes in soils being broken. As a result, new natural-technogenic soil complexes with new properties are
formed. There are various geochemical anomalies and geopathogenic zones, which features are not practically investigated. The analysis of microelement structure of soils on background and technogenically transformed sites allows to estimate a level of landscapes pollution. Therefore, the characteristic of territorial and intraprofile distribution of microelements and substances in soils, definition of features of their migration and accumulation constitute a basis for an estimation of geosystems stability under the conditions of technogenesis [4-6].

To analyze the soils, the most widespread contaminants, MO and HM, included in the priority list of contaminants according to Russian specification SanPiN 2.1.7.1287-03, have been chosen. These are the most widespread toxicants in a zone of negative influence of gasoline stations, petroleum depots, the mining enterprises, etc. They belong to 1st and 2nd danger classes since they possess high affinity to physiologically important organic compounds and are capable to inactivate them in the living processes. In the state ecological control, the number of samples for one controllable object does not exceed 1-2. It does not allow to reveal fairly a real picture of the soil pollution and to estimate the ecological safety of territory.

On the basis of the developed and tested model of sampling, the number of soil samples was increased up to 30 for every studied object. The coverage of the territory with asphalt and its landscape inclination has been taken into account. The soils were investigated in the depth of 30-40 cm i.e. up to a zone of roots of grass and bushes.

In the result of investigations, the contents of HM in soil horizons of territories, exceeding by orders maximum permissible concentration (MPC) (table 1), have been found. This has caused a specific accumulative type of distribution of both HM and MO into depth of 40 cm. Calculated coefficients of concentration of chemical elements $K_c$ and the obtained associative series, for example, $Cu_{4.5}Ni_{2.7}Zn_{4.1}As_{5.2}$ are indicative of the emergence of geochemical anomaly in the city centre due to technogenic pollution ($K_c$ should not exceed 1).

However, the organization of soil-chemical monitoring should account for not only the composition of soil, its property, presence of the contaminants, but also the factors influencing the mobility of chemical elements. The following parameters exert the most significant action on the migratory streams of substances and elements: acidity and alkalinity of soils, an oxidation-reductive mode, the content of humus, the presence of readily soluble salts. Acid properties of soil, pH values and the content of carbon and nitrogen, were chosen by us as one of key parameters of its resistance to technogenic influence.

### Table 1. The content of heavy metals* and As (mg/kg) in soils of gas station site.

| № point of sample splitting | Cu  | Cd  | Ni  | Pb  | Zn  | Hg  | As  |
|-----------------------------|-----|-----|-----|-----|-----|-----|-----|
| 1                           | 15.04 | 0.071 | 11.54 | 20.36 | 58.61 | 1.53 | 5.13 |
| 2                           | 16.42 | 0.090 | 10.36 | 18.23 | 58.30 | 1.38 | 4.92 |
| 3                           | 15.10 | 0.061 | 10.36 | 16.78 | 62.30 | 1.42 | 4.95 |
| 4                           | 18.86 | 0.070 | 6.55  | 16.66 | 64.30 | 1.29 | 5.26 |
| 5                           | 18.52 | 0.050 | 8.66  | 19.36 | 61.54 | 1.81 | 4.95 |
| 6                           | 18.00 | 0.050 | 8.78  | 18.77 | 54.35 | 1.83 | 4.65 |
| 7                           | 17.68 | 0.050 | 9.23  | 18.69 | 64.87 | 1.79 | 5.62 |
| MPC                         | 5    | 0.5  | 10  | 32  | 55  | 2.1  | 2 |

*Total forms

The experiment has shown a weak alkaline character of soil in a zone of the studied industrial objects. So, for soil samples around of the gas station and petroleum depots, the pH values equal 7.50-7.64. For natural pure soils, the pH values range 4.5-6.5. This acidity provides self-clearing properties of soil and decreases the negative effect of toxic metals in the case of soil pollution. The registered
The value of pH is attributable to the precipitation of urban alkaline dust containing Ca and Mg carbonates. The alkaline dust comes from a highway and building objects using solutions with lime carbonate and cement. Such substrates are easily blown away, realizing to atmosphere Ca and Mg, the latter precipitate on soil. Therefore the value of pH for urbicosols can reach 8-9.

The dynamics of distribution of metals and As in the analyzed soils in dependence on the pH value, determined by correlation analysis (software package Statistica in Excel), does not obey to the normal law (see, for example figures 1 and 2). This testifies to the breaking of exchange geochemical and migratory processes in the urbanized ground.

**Figure 1.** Dynamics of As and Cu content depending on pH value.

**Figure 2.** Dynamics of Cd and Hg content depending on pH value.
Buffer properties of soils are caused by the content of humus substances, which basic components are carbon and nitrogen. The method of wet combustion (Tyurin’s method) was employed to determine the N content (%) in soil samples (table 2), content of HM was found by atomic absorption spectroscopy on a Perkin Elmer-500 instrument, and urbicsoils mineral oil content was defined by spectrophotometric analysis [5].

From the table 2 follows that the soil is extremely impoverished by nitrogen, and MO content exceeds maximum concentration limit by 2-3 times (maximum concentration limit ranges 100 to 300 mg/kg according to different techniques). The deterioration of a nitric content of soil along with essential increase of pH values (9 to 7.6) was observed. Strong decrease of organic carbon content in soils was registered. Together with a drop in the content of nitrogen, it leads to drastic deterioration of buffer properties of urbicsoils and increases environmental danger of urban territory. The key ratio of C/N is 20-25, while this value for pure soils is 10.

Monoelement maps of MO and HM distribution (for example, figures 3 and 4) have been compiled using the GIS-technologies (Surfer 8, MapInfo). It has been found, that HM are not accumulated in humus-deficient soils of the polluted territory and migrate to landscapes.

**Table 2.** The content of the N\textsubscript{total}, mineral oil in soil and value of pH.

| Sample | Depth (cm) | N\textsubscript{total} (%) | pH\textsubscript{salt} | Mineral oil (mg/kg) |
|--------|------------|-----------------------------|------------------------|---------------------|
| 1      | 0-5        | 0.065                       | 7.57                   | 668                 |
| 4      | 0-5        | 0.098                       | 7.53                   | 490                 |
| 7      | 0-5        | 0.090                       | 7.61                   | 570                 |
| 8      | 10         | 0.074                       | 8.09                   | 600                 |
| 9      | 20         | 0.115                       | 8.09                   | 400                 |
| 10     | 0-5        | 0.063                       | 6.98                   | 820                 |
| 11     | 10         | 0.098                       | 7.35                   | 610                 |
| 12     | 20         | 0.061                       | 7.86                   | 590                 |

**Figure 3.** Zn distribution map in a zone of influence of the enterprise: 1, 2 - sources of pollution, 3 - office, 4 - a motorway.
Figure 4. Mineral oil distribution map in a zone of influence of the enterprise: 1, 2-sources of pollution, 3 - office, 4 - a motorway.

Aureoles of their distribution and content confirm the formation of abnormal geochemical zones and accumulation of chemical compounds and elements both in radial and lateral directions. Figure 5 show the particular character of dependence of MO content on concentration of nitrogen in soils of the area.

Figure 5. Dependence of mineral oil content on concentration of nitrogen in soils.

In technogenically-changed soils with the broken natural morphological attributes, the HM and MO are not detected on territory of pollution object. Migratory streams and accumulation of contaminants are found far outside the contamination source in a radius of 100-200 m and more [6].
Thus new zones of the enhanced ecological danger, technogenic geochemical modules, (laterally technogenic module) are formed. This fact convincingly proves the necessity of change of approaches to the analysis of soils during monitoring of ecological conditions in urbanized territories. Ecological geochemical and the cartographical analysis of urbanized soils has found their substantial pollution with HM and MO, sharp deterioration of nitric and carbon content, increase of alkalinity, decrease in buffer activity of soil. It is explained by signs of transformation of soil properties and makes it important to develop new approaches to the estimation of its ecological conditions [7, 8].

Conclusions
Physical and chemical parameters and the geochemical characteristics which adequately reflect the change of soil ecological systems have been determined.

Dynamics of technogenic streams in urbicsoils which can result not only in transformation of its properties, but in closing the cycles of MO and HM migration has been found. As a rule, it is accompanied by the formation of secondary local sites of contaminants accumulation, laterally technogenic module.

Monoelement maps of the distribution of heavy metals and mineral oil in a zone of influence of dangerous objects have been compiled. The data obtained prove the necessity of change of the approaches to monitoring of soils. The results of research constitute the basis for the development of modern system of ecological monitoring under technogenesis. Integration of methods of modern ecological diagnostics will promote to the acceptance of optimal decisions in nature management and to operative revealing the zones of ecological danger.

The investigations are of significance not only for ecological diagnostics of geosystems. The developed approach will allow to discover new geochemical regularities as well as to find the associations of elements in technogenic landscapes for practical purposes in the course of the development of technogenic deposits of minerals.

For optimization of an estimation of technogenically modified soils it is possible to recommend:
• development of the state program of soils monitoring in a zone of influence of industrial objects;
• development of the reasonable schemes, methods and choice of places of approbation of the polluted territory;
• revision of contaminants normalization taking into account their transformations and migration;
• creation of banks of the geochemical and cartographical data for aureoles of pollutants distribution in a zone of dangerous objects and in the urbanized territories.

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