ESTIMATION OF WATER AND BOTTOM SEDIMENTS COMPOSITION IN SMALL RIVERS OF THE NOVOSIBIRSK CITY

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ABSTRACT

Nine rivers flowing in the Novosibirsk city were studied. Samples of water and bottom sediments were collected from upper- and downstream in each of them. Standard methods of geochemical research were used. Atomic emission spectroscopy (ICP-AES) was applied to study the liquid components (river water and pore solutions from bottom sediments). X-ray fluorescence analysis with synchrotron radiation (SR-XRF) has been used to analyze solid components (bottom sediments and suspension particles from water).

Obtained results show high level of water and bottom sediments contamination in Novosibirsk rivers. Anomalies in Fe, Mn, As, Ni, Ti, Pb concentrations are identified. Elevated concentrations of Fe and Mn in all rivers are caused by natural conditions. But wide spectrum of elements gets into the rivers from different industrial sources: metallurgical plants and coal heat plants (CHPs). Comparative mobility of the elements in the water-bottom sediment system is conditioned by their geochemical features. Orders of mobility are for major elements Ca>Sr>Mn>Fe>K>Ti and for trace elements As>Cd>Br>Ga>Zn>Pb>Cu>Th>Y>Cr>Ni>Rb>Zr. Investigation of the mineral composition of the heavy fraction in the sediment allows to identify mineral mode of occurrence of heavy metals in bottom sediments. Natural minerals from host rocks are magnetite, titaniferous magnetite, olivine, ilmenite. Minerals related to urban activites are chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), barite ($BaSO_4$), monacite ($CePO_4$). Obtained results allow to determine the most polluted areas, which demand treatment and remediation.

Keywords: Environment, Water, Elements mobility, ICP-AES, SR-XRF

1. INTRODUCTION

Cities in the modern world are a complex structure in which both large and relatively small plants locate directly in residential neighborhoods. The growth of urban structures and building different types of industry, which was originally made outside the city limits, are in close proximity to places of residence and rest of citizens. Small rivers flowing in the limit of industrial cities are very important components of the environment. The rivers decorate a landscape, and are recreational areas and sources of fresh water for city population. At the same time city rivers reflect a multicomponent pollution from different industrial sources. Small rivers receive urban and industrial waste and are sites of pollutant accumulation and recycling [1].

Novosibirsk town is a big industrial center in South Siberia (Russia). Some industrial plants (Sn-Metallurgical Plant, Chemical Plant and others), and five CHPs (Coal Heat Plants*)* are located within the city limits. The industrial and domestic wastewaters are often discharged into surface water and flow into small rivers in the city.

Investigations of the geochemical composition of small rivers determine rivers management and protection measures. The aim of the research was the assessment of Novosibirsk small rivers geochemical composition and detection of anomalous zones, both for water and bottom sediments, to elaborate protection measures.

2. STUDY AREA

Six small rivers flowing within the Novosibirsk city limits are right tributaries of the Ob River (South Siberia, Russia, Fig. 1). The source area of the rivers originates in wetlands at the eastern part of the Novosibirsk region. The bedrocks are granites of Middle Devonian age [2]. The most important soil type within Novosibirsk region is subacid and acid podzols [3]. Rivers length varies from 6 up to 15 km, and not more than 10–15 m wide. The climate of the South Siberia is characterized as sharply continental climate with monthly average temperatures ranging from -19ºC in January to + 19ºC in July. The average annual precipitation is 425 mm, of which 25 % falls as snow. The dominant winds within the study area are from the S and SW during winter. That wind direction has a great importance for the atmospheric dispersion of pollutants from the Novosibirsk metallurgical plant and CHP. In the summer more northwesterly to northerly winds are dominant. Granite massif is dissected by a series of geological faults. Predominant direction is the orientation SW-NE. Tributaries of the Ob river are laid out along the direction of geological faults: Zyrianka, Eltsovka, Inya, Plyushchikha, Eltsovka 1 and 2, and others [2].

Novosibirsk is a large industrial center in Siberia. The Sn-Metallurgical Plant at SW urban district, five CHPs at SW, NE and central urban districts release different pollutants to the atmosphere, which precipitate on the city area with rains and snow. Moreover wastewaters from the plant at NE district discharge into the Elzovka-2.

3. METHODS

Sampling of the rivers was carried out in the summer period (June-July). Samples of water were collected mainly downstream each river. Waters were collected in plastic containers (bottles) of 1.5 liter, pre-washed carefully. During sampling bottles were rinsed three times with water from the sampling point. Values of pH and Eh were measured in situ by portable device «HANNA» HI 9025C. Bottom sediments were collected at each sampling point (in places with a steady flow, or backwaters) in plastic bags, and then dried at room temperature.

The samples were analyzed in cooperation with the Analytical Center of the Institute of Geology, SB RAS.
The analyses of major and trace elements were performed with Thermo Jarell Ash Corporation IRIS ICP-AES. The error of measurements – 10-25 % SO_4-- concentrations were measured by a standard photometric technique [4]. Cl- concentration measurements were made by titrimetric method with silver salt [5]. HCO_3- concentrations in water samples were analyzed by titrimetric method [6].

Since fine-grained sediments usually dominate water-mineral interaction, only the -0.25 cm portion of the collected samples was subjected to various analyses. These include element analysis, mineral identification by powder X-ray diffractometry, examination of mineral grain composition by scanning electron microscopy.
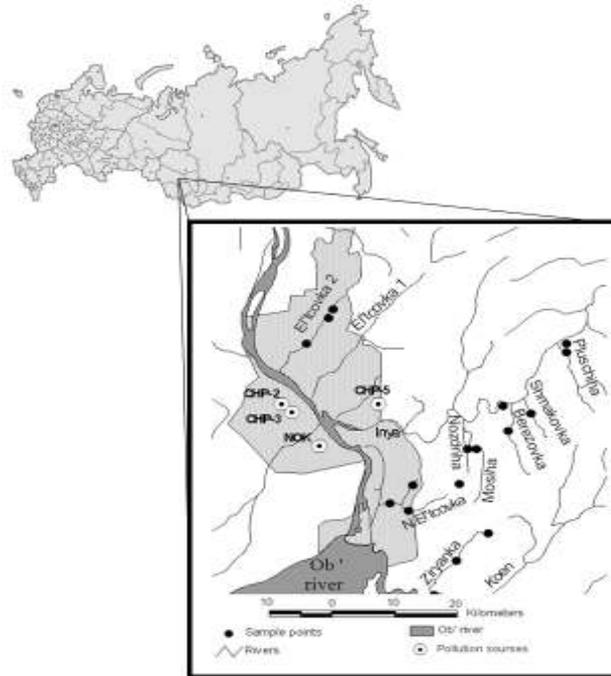
Figure 1. Points of sampling for water and bottom sediments

Trace element content in bottom sediments were defined using X-ray fluorescent method with synchrotron radiation [7] at the station VEPP-3 at Institute of Nuclear Physics SB RAS, Novosibirsk, Russia. Measurements were made at activation energy of 30 keV. The method of internal standards was applied. Processing of issue spectra was spent using AXIL program. The definition error is 15-20 %.

We used the following calculations for estimation of pollution level of water and bottom sediments. Ratios "studied river water/average river water" for major components [8] and for trace elements [9] show a degree of water pollution. Maximum permissible concentrations [10] were used for risk assessment. Element content in bottom sediments was normalized to "average clays" [11]. To determine the anthropogenic influence on bottom sediments the average element concentrations in granitic rocks [11] were used as natural sources of elements in sediments (because of Novosibirsk city is situated on granitic massif).

4. RESULTS

4.1 WATER OF THE RIVERS

Studied rivers, generally similar in composition, refer to bicarbonate calcium-magnesium type (Fig. 1). The main anion is HCO_3-. Average HCO_3- concentration (319 mg/L) are on the level for the background rivers, located in Novosibirsk region (311 mg/L, [8]) Level of HCO_3- is rather stable in waters of all rivers; variations do not exceed 2 times. Classification diagram shows the relative importance of carbonate weathering in the catchment of the rivers. But some rivers are influenced by other sources. Two rivers (Eltsovka-1 and Eltsovka-2) and the city pond are more influenced by Cl- originating probably from precipitation. This assumption is confirmed by uneven distribution of Cl- concentrations: variations are more than 90 times (from 2.8 up to 260 mg/L). Cl- in Eltsovka-1,

Eltsovka-2 and city pond 4-8 times higher than in background rivers (34 mg/L, [8]). SO_4^{--} concentrations are elevated at the same rivers and pond and exceed the background level by 5-8 times (38 mg/L, [8]). Rather high SO_4^{--} is recorded at the Tula river which is replenished by sinks from Sn-Metallurgical Plant.

Rivers have very high N concentrations. Average NH_4^+ content is 0.7 mg/L, and (NO_2^-+NO_3^-) is 11 mg/L, where very toxic NO_2^- accounts the most share - up to 6.7 mg/L, that 2 times exceed MPC. Obviously the main part of N enters the rivers via urbanic waste waters. This is relatively high NO3-concentration (4.2 mg/L) in relation to regional background level (0.9 mg/L, [8]) and NO2- presence, which is not found in natural background rivers. Ratio NO_2^- : NO_3^- : NH_4^+ varies within wide range (Fig. 2). Clear increases in N concentration were observed in rivers Eltsovka-1, Plushiha, and city pond. So, anion composition and ratios between major anions are sensitive indicators of ingress contamination from different sources.

TDS in rivers varies from 250 up to 770 mg/L. It is very high level compared with average river water (100 mg/L, [12]) and up to 1.5 times exceed the regional background level (451 mg/L, [8]). Maximal TDS (more than 700 mg/L) is characteristic for rivers Eltsovka – 1, Tula and city pond, depending on concentration of anions mainly: SO_4^{--}, Cl-, and N species. Waters of the rivers is alkaline with average pH of about 8.3. From sources toward downstream in rivers Zyryanka, N. Eltsovka, Eltsovka-1 values of pH decrease (the difference between the pH of the source and the mouth of some rivers may reach 0.58 pH in the river Zyrianka), but dependence between TDS level and pH values isn't observed.
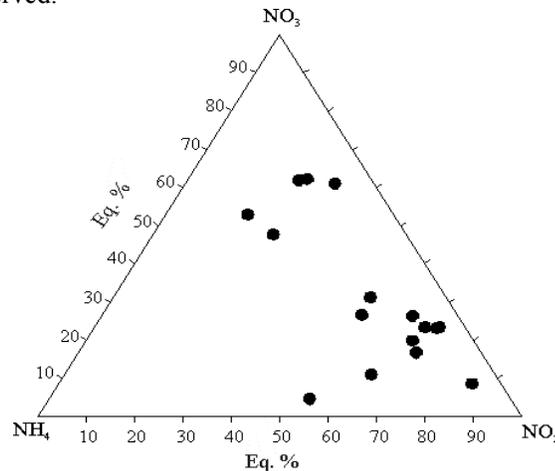

Figure 2. Ratio NO_2^- : NO_3^- : NH_4^+ in river waters

The concentrations of dissolved alkaline metals (K, Na) are close to "Average River Water" [9] and regional background level, but Ca and Mg contents are 6 times higher. So, we can conclude that urbanic influence on rivers is expressed in elevation of specific anions (Cl-, SO_4^{--}, N species) contents and water hardness (Ca+Mg).

It should be emphasized an elevated iron content in all rivers, but especially in Plyuschiha and Inya rivers where iron content reaches up to 5.8 – 5.4 mg/L (about 4.5 equ.% among major cations). The second element being in quite high concentration in water of all rivers is manganese (up to 0.68 mg/L). Iron and manganese connect by close positive correlation (r = 0.815). We refer these two elements to the pollutants of natural origin, reflecting the features of the regional geochemical background. As far as sources of studied rivers originate in wetlands obviously elevated level of Fe and Mn is caused by high concentrations of these elements in swamp waters.

Anthropogenic pollution of water (in some parts of rivers) is manifested in the high content of a wide spectrum of elements. Considerably elevated levels were recorded for some elements in water of city pond, Eltsovka-2, Plyushiha and Tula rivers compared with Ziryanka river, which flows beyond the city range.

Comparison of trace element concentrations with "average river water" shows that level of all detected elements (with exception of Si) is greatly elevated. Most anomalous elements are: Sb, U, Sr, Ge, B, which concentrations are hundreds of times higher than the "average river water" in the city pond and in the rivers Plyushiha and Tula. These elements are not found in the natural background levels in rivers [8]. Metals Cu, Ni, Cd, Ti, Sn show an anomalous contrast (10 times higher than "average river water") also.

At the same time, the contents of many elements have high contrast: the difference between maximum and minimum concentrations of: Mn, Ge, Br > 20 times; Rb, I, Te, Cu > 10 times; Sr, Mo, Sb, As, Th > 5 times. A wide range in element concentrations indicates active water - solid interaction, consequently the possibility of element to release into water at alterations of physico-chemical conditions.

Based on average values and percentage in sum of trace element concentrations the following order of abundance has been observed. In general, this division is valid for water of all studied rivers and maintained with minor variations (Tab. 1):

Table 1 Groups of elements in river waters

Group	Elements	Percentage
I	Fe, Mn, Sr	> 10 %
II	B, Ba, Ti	1 – 9.9 %
III	Li, Cu, Zn, V, Br	0.9 – 0.5 %
IV	Ga, As, Cr, Ni, I, U	0.49 – 0.1 %
V	Zr, Pb, Ni	0.099 – 0.05 %
VI	Rb, Mo, Th	0.049 – 0.01 %
VII	Sb, Te, Ag, Cd, Sn	< 0.01 %

High positive correlations between some elements indicate a common sink in the river waters with the following associations: 1) Sb–Se–Cd–Sn-Ni and 2) U-Cs, 3) Ga-Ge-Y. The first association corresponds to the main pollutants coming from Sn-Metallurgical Plant. The greatest excess over the "average river water" were recorded for antimony (accompanying element in Sn-ore). The second element association can be expected to have a natural origin, since Novosibirsk is located on a granite base with high content of radioactive elements, but it is possible to flow from the Chemical Plant. Origin of the third association is not clear; perhaps the source of these elements is granitic host rocks too.

4.2 BOTTOM SEDIMENTS

Concentrations of majority elements in bottom sediments are close to or even below the "Average element content in clay rocks" [11]. The maximum Ag, Cd, Sb, and Hg levels were detected at Eltsovka-2, whereas the maximum Cu, Zn, Sn, and I levels were detected at Tula river. Associations of polluted elements reflect the peculiarity of the industry. Tula river is influenced by Sn-Metallurgical Plant, and Eltsovka-2 is replenished by waste water from the Chemical Plant.

Metal ratios for the river sediments ("studied sediments"/"average clay") show various degrees of enrichment. The values are greater than one except for rock-forming elements K, V, Ni, Ga, Rb, Sr, Nb. High ratios of Ag, Cd, Sb, As, I in some sediment samples have been recorded. We assume that a high Cu, Zn, Sn ratios at the Tula river was attributed to the atmospheric deposition of aerosols containing these elements from the nearby Sn-Metallurgical Plant. These high metal ratios exactly indicate the anthropogenic source of heavy metals in the river sediments.

The studied river have two sources of heavy metals: natural sources from weathering of granitic host rocks and industrial sources from urban plants. For the estimation of industrial influences on the river sediments, the average granite concentration is used as the source of the natural fraction. It is estimated that 73% Ag, 80% Cd, 11% Sb, 39% as, 90% Cd concentrations in Novosibirsk rivers are derived from industrial input in the total metal concentrations. It means occurrence zones in some rivers which suffer constant pollution stress. These anthropogenic fractions are easily available to the river's ecobiological cycle and possibly enter into the food chain under suitable physicochemical conditions, exposing millions of people to unnaturally high metal concentrations in one or other way. Comparison of element ratios in water and bottom sediments shows a much greater excess of values "studied river water/average river water" than in "bottom sediments/average clay" (Fig. 3). Such a relationships show the predominantly aerosolic input of elements number in the river water, because there is not the apparent connection between the elements enrichment in water and sediment.
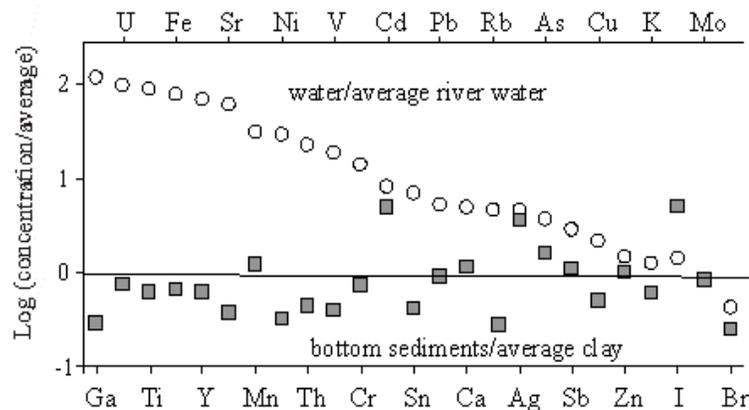

Figure 3. Element ratios in rivers water and bottom sediments

The established pattern of the small rivers geochemical state shows a serious contamination level by a range of metals for both water and sediment. In connection with the results obtained, the mobility of all analyzed elements based on patterns of their distribution between the solid phase (bottom sediments) and coexisting solution (river water) was analyzed. The very mobile elements (K = lg (Mesolid / Mewater) <3.0) in this system include: Mg, Ca, Sr (the macro components), I, Br, U, As, (from the trace element composition). Mobile elements (K = 3.0-4.0) are Zn, Cu, Pb, Ga and close-to - Sb, Te, V, Mo, Ag. Inert elements - Y, Zr, Rb, Th, Cr, Ni, Ti (K> 4).

The last 3 metals can become mobile and highly mobile, obviously, depending on their fixation form in the sediments. Comparison of water and sediment enrichment factors (Fig. 3) and the relative mobility of elements (Fig. 4) confirms the assumption made about the elements source in the water. In the list of elements with the maximum excess concentration in relation to clark values along with the highly enriched uranium are moving relatively inert Th, Fe, Ti, Y, and for moving I and Br enrichment factor is below 1. The results obtained can serve as an indirect indicator of a sufficiently

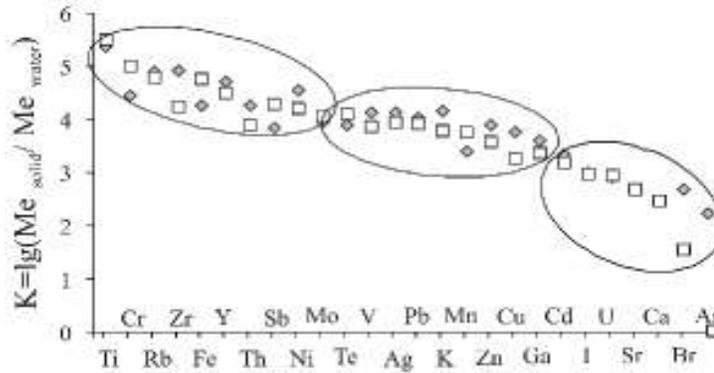reliable binding elements in bottom sediments, probably due to adsorption on clay minerals and iron hydroxide.

Figure 4. Relative mobility of elements in the system "river water – bottom sediments"

4.3 PORE WATER

The most informative indicator of river pollution is a porewater composition. A low ratio of water/rock in the "pore solution - bottom sediments" allows to capture dissolved forms of metals, as their content is much higher in the pore solutions, than in surface waters. Besides the solution composition is kept in a porewater for a long time. But remobilisation of contaminant metals from sediments can occur by chemical, biological or physical changes. This in turn can lead to contaminant fluxes to the porewaters and ultimately the water column. Accumulation of contaminants within sediments poses problems because the sediments may act as a source of pollution long after a pollution event has abated [13].

So, concentrations of elements in sediment porewaters were 0.5-2 orders of magnitude greater than in the surface waters (Fig. 5). It should be particularly emphasized very high level of dissolved Al (up to 2.7 mg/L), Cu (up to 4 mg/L), Zn (up to 15 mg/L), Cr (up to 0.02 mg/L), Ni (up to 0.19 mg/L), and Cd (up to 0.014 mg/L). The most difference between concentrations in porewater and surface water was detected for natural pollutants Fe, Mn, and heavy metals Cu, Zn, Cd, Cr, Ni. High level of dissolved metals in porewaters indicates a potential danger of river contamination by sediment detachment during spring flood or cloudburst.
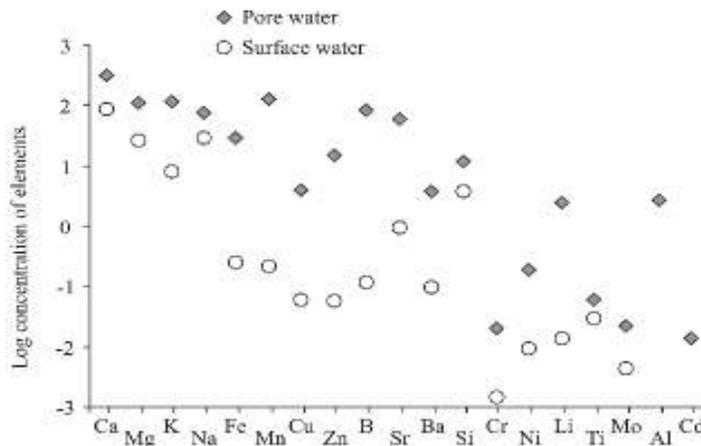

Figure 5. Comparison of elements concentrations in surface river waters and porewater

Investigation of the heavy fraction in the mineral composition of sediments allows to identify mineral mode of heavy metals occurrence in bottom sediments. Natural minerals from host rocks are magnetite, titaniferous magnetite, olivine, ilmenite. Minerals of urban acticities are chalcopyrite ($CuFeS_2$, Fig. 6), bornite (Cu_5FeS_4, Fig. 6), barite ($BaSO_4$, Fig. 7), monacite ($CePO_4$, Fig. 8).
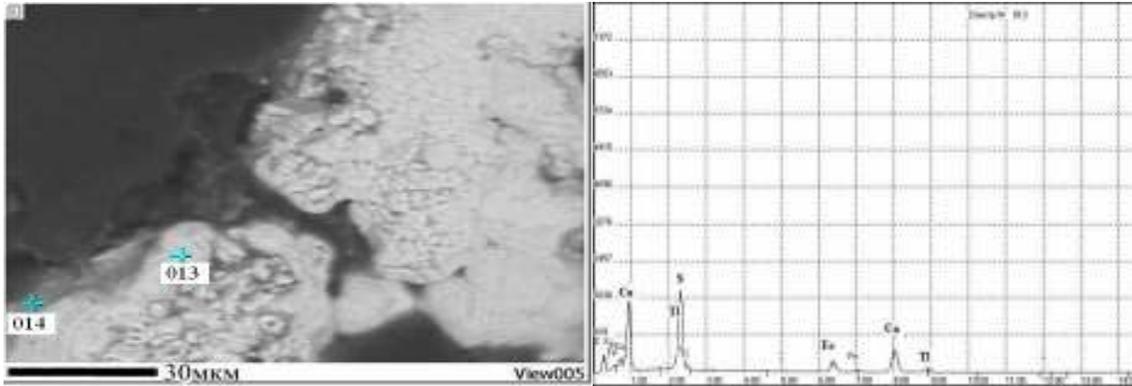

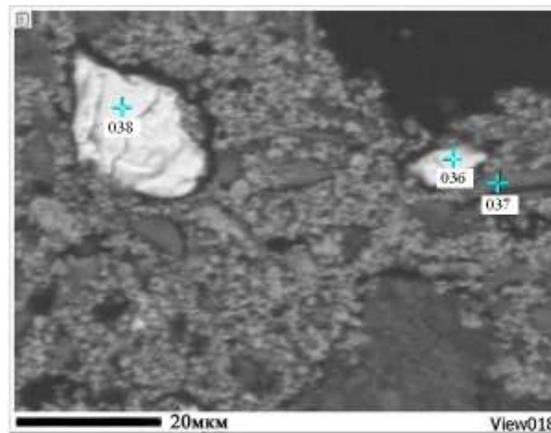**Figure 6. Chalcopyrite doped with Tl (013), bornite (014), 013 point spectrum**

Figure 7. Orthoclase (037), barite (036, 038) with an impurity.
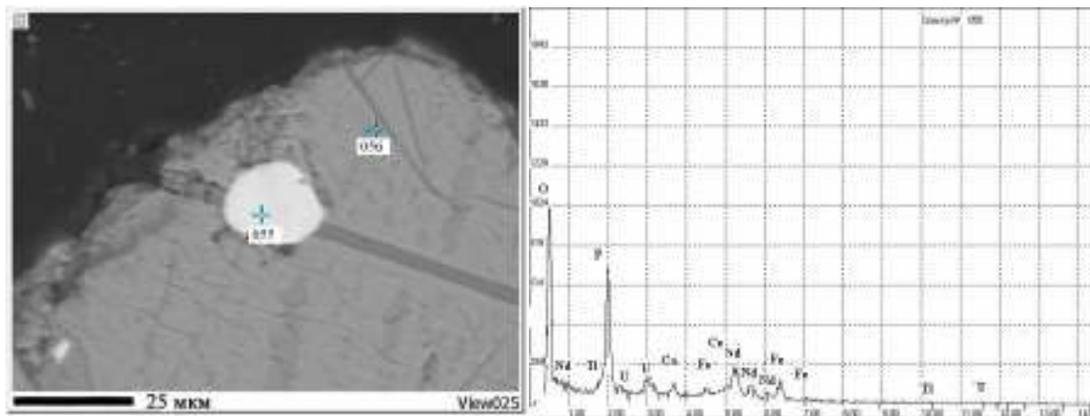

Figure 8. Magnetite (056), monazite (055), 055 point spectrum.

5. CONCLUSIONS

The present geochemical study of Novosibirsk small rivers supports the concept that urban effluents have a great influence on the concentration and distribution of toxic heavy metals in river water and sediments. Urban activities are associated with the high concentration of heavy metals such as Cr, Ni, Cu, Pb, Zn, and Cd both in water and sediments. Natural pollutants such as Fe and Mn originate from wetlands, but a wide spectrum of toxicants is replenished in rivers from city plants and CHP. Comparison of water and sediments pollution indicates that aerosols supply a lot of trace elements into river and consequently – onto urban area.

ACKNOWLEDGMENTS

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