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Sediments as Indicators of Petrochemical Industrial Effluents

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Abstract. Sediments of the Kama River in area of effluents of the petrochemical industries were investigated. Analysis of whole-sediment samples were included grain size, metals, polycyclic aromatic hydrocarbons and total petroleum hydrocarbons. The results of the study demonstrated that the content of Al, Fe, Mn, Ni, Cu, Zn, Pb was growing in sediments with different sorption capacity: sand<silty sand<silt. The trend of increase of Fe, Mn, Pb, Cu, Cr, Ni, Zn along the current of the Kama River was noted. The coefficient of enrichment showed that metals content in sediments is connected with natural processes of washing away of minerals. There were no standards exceeding neither sum PAH no separate components. Naphthalene (0.5-183.5 µg/kg) and acenaphthene (<0.5-33.3 µg/kg) made the main contribution to mass PAH content, content of chrysene in the area of petrochemical industries effluents was in range 8.4-44.7 µg/kg much more in comparison with other stations. Based on the ratio of marker PAH, most of samples are characterized by mixed type of PAH coming to the water course: from the oil production activity and fuel burning.

1. Introduction

The industry of fuel-energy complex, including oil-producing and petrochemical branches, are the largest source of environmental pollution in Russia. The policy of ecological safety at these industries has led to decrease of negative impact on the environment. However, there are environmental compartments, for example, sediments that are capable to accumulate pollutants and for a long time to keep "print" of activity of the industry by accumulation of the persistent pollutants [1-3].

Sediments can act as markers for identification of structure, intensity and scale of technogenic pollution in a water ecosystem. Their structure reflects not only biogeochemical features of catchment area, but also composition of the industrial industries effluents. Sediments represent complex multicomponent system and can deposit chemical compounds and be a source of secondary water pollution. Migration of pollutants in the "water-sediments" system makes considerable impact on water quality, can lead to depression or loss of the most sensitive species and to deterioration of the self-cleaning ability of a water ecosystem [4].

The objective of this study was to estimate pollution level of the persistent substances, accumulated in sediments of the Kama River in the area of effluents of the petrochemical industries.



2. Materials and methods

During this study, sediments were sampled in three areas (figure 1, table 1):

1. stations 10-14 – the area of effluents of petrochemical industries;
2. stations 7-9 – the area of confluence of the Vyatka and the Kama Rivers, below the area of effluents of petrochemical industries;
3. stations 4-6 – the Kama River near the Bersut settlement, below the area of effluents of petrochemical industries;
4. stations 1-3 – the Kama River near the Troitsk Uraj settlement, the area of effluents of petrochemical industries.

Sediments sampled from the surface layer Van Veen grab to obtain 2 L of sediment. Samples were transported to the lab in the plastic bags as soon as possible.

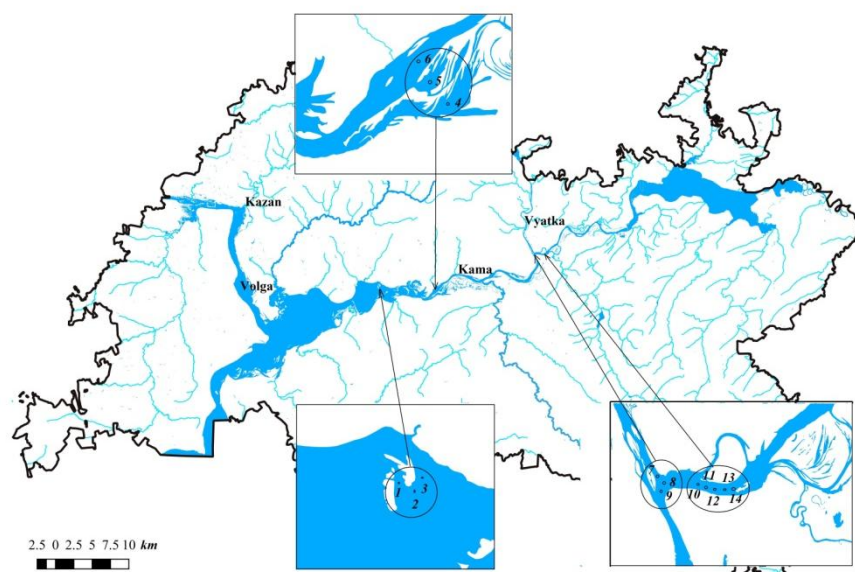


Figure 1. Location of sediment sampling stations.

Table 1. Stations of sediments sampling.

Location	Station	Coordinates		Depth, m
Troitsk Uraj	1	N 55 26 29.2	E 50 12 52.5	2.5
	2	N 55 26 04.7	E 50 13 25.8	13
	3	N 55 26 07.1	E 50 13 55.9	8.5
	4	N 55 29 27.6	E 50 51 47.8	3.5
Bersut	5	N 55 29 34.8	E 50 51 42.4	11
	6	N 55 29 51.3	E 50 51 55.2	3
	7	N 55 35 42.7	E 51 29 37.1	3.5
Grakhan (the estuary of the Vyatka River)	8	N 55 35 26.4	E 51 30 30.1	7.7
Above the effluent №1	9	N 55 35 17.0	E 51 30 40.0	3.5
	10	N 55 35 06.2	E 51 35 02.3	12
Low the effluent №1	11	N 55 35 07.5	E 51 34 37.7	14
	12	N 55 35 06.9	E 51 34 22.4	13.5
Effluent №2	13	N 55 35 08.7	E 51 34 01.4	13.5
Low the effluent №2	14	N 55 35 10.3	E 51 33 29.3	11

Analysis of whole-sediment samples included grain size, metals, polycyclic aromatic hydrocarbons (PAH) and total petroleum hydrocarbons (TPHs) [5-8].

3. Results

Fractional composition of sediments was presented mainly by silt (29%), fine sand (20%) and sand (23%) fractions. Based on the pelite fraction content, sediments were divided into groups: silt (pelite fraction content more than 20%), fine sand (pelite fraction content 10- 20%), and sand (pelite fraction content less than 10%).

The analysis of metals content (figure 2) has shown a light trend of increase of Fe and Mn concentrations in the Kama River along stream.

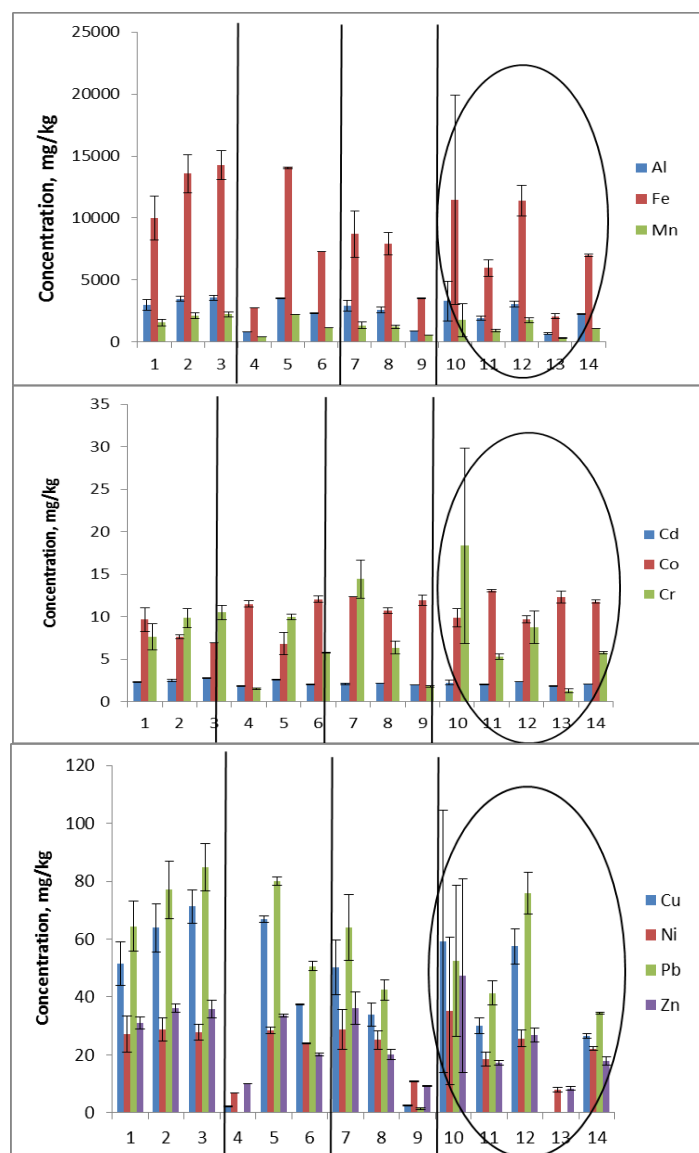


Figure 2. Content of metals in sediments (1-3 Troitsk Uraj; 4-6 Bersut; 7-9 Grakhan; 10-14 marked area of the effluents of the petrochemical industries).

The following trend was noticed in the spatial distribution of elements (figure 2):
 - increasing of the contents of Pb, Cu along the stream;

- weak trend of increase of Cr, Ni, Zn content or absence for Cd;
- decreasing of Co content, but it does not differ from in the estuary of the Vyatka River (no influence of the petrochemical industries).

Natural factors, such as content of the pelite fraction with large sorption ability, can influence on metals accumulation in sediments. Analysis of metals content in sediment depending on particle size distribution demonstrated that Al, Fe, Mn contents increased from sand type of sediments to silty sand and silt. The same trend was noticed for Ni, Cu, Zn, Pb: significant difference their content in sand in comparison with silty sediments.

Sediment enrichment factor (EF), calculated as ratio of metal to Fe content in sample to the same ratio in background (equation 1). The average value of an element was taken as a background.

$$EF = \left(\frac{Me_s}{Fe_s} \right) / \left(\frac{Me_b}{Fe_b} \right) \quad (1)$$

where Me_s , Fe_s and Me_b , Fe_b – content of metal, Fe in samples and background correspondingly.

Metal of natural origin (Fe) was used as a geochemical marker in calculating the enrichment factor for minimization the variability caused by particle size distribution and a geographical location. According to previous studies [9,10], accumulation of metals is caused by anthropogenic influence when $EF > 1.5$ and metals content in sediments is connected with natural processes such as washing away of mineral breeds when $EF = 0.5-1.5$. Metals content do not go beyond a limit 1.5 probably sediment multimetal structure was formed under the influence of natural factors.

The total petroleum hydrocarbons and polycycling aromatic hydrocarbons can act as markers of petrochemical industrial activity.

For assessment of TPHs in sediments criteria, adopted in the Tyumen region (20 mg/kg) and for Kuibyshev water reservoir (20 mg/kg for sandy sediments and 50 mg/kg for silt) were used [11]. Comparison of the actual content TPHs with above mentioned criteria has shown that, practically all types of sediments content increased concentrations of total petroleum hydrocarbons. Nevertheless, the contents in the zone of effluents of the petrochemical industries (s.11, s.13) were lowered (figure 3).

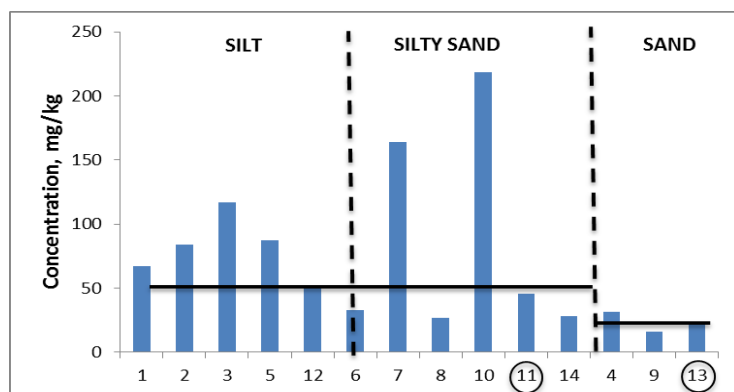


Figure 3. Total petroleum hydrocarbons content in different types of sediments (marked s.11 and s.13 – the area of the effluents №1 and №2).

Probably, the main factor of accumulation of TPHs in sediments is pelite fraction, which are capable to sorb pollutants on the surface. The exponential dependence between TPHs and pelite fraction content was found $y = 19.069^{0.0494x}$ ($R^2 = 0.81$).

PAH can be the markers of the petrochemical industries activity. Comparison PAH content in the area of petrochemical industries effluents and in the estuary of the Vyatka River with criteria, adopted in USA [12], showed that, there were no standards exceeding neither sum PAH no separate components. Conversely, the sum of PAH content in sediments of the estuary of the Vyatka river was higher in comparison with the area of petrochemical industries effluents (figure 4).

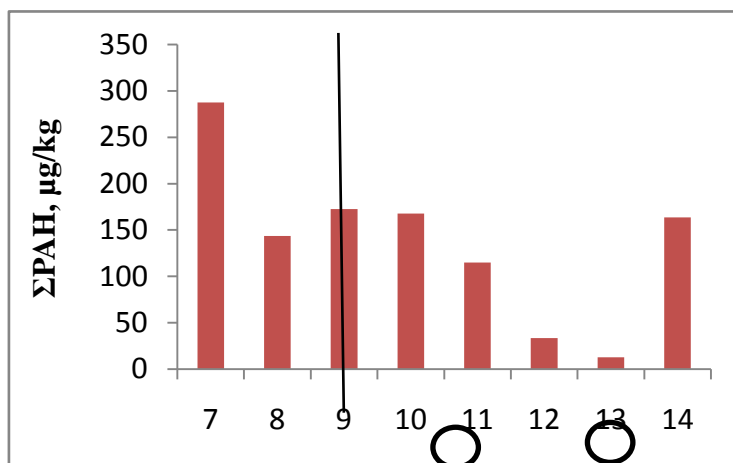


Figure 4. Sum of PAH content in sediments (marked s.11 and s.13 – the area of petrochemical industries effluents).

Naphthalene (0.5-183.5 μg/kg) and acenaphthene (<0.5-33.3 μg/kg) made the main contribution to mass PAH content, content of chrysene in the area of petrochemical industries effluents was in range 8.4-44.7 μg/kg much more in comparison with other stations. Benzo[a]pyrene varied in range 0.5-7.7 μg/kg.

PAH can come to the environment from diffusion sources (washouts from fields) and from air emission during combustion of hydrocarbons, including wildfire. For identification the origin of PAH contamination the ratio of phenanthrene/anthracene and fluoranthene/pyrene [13-16].

Based on the ratio of marker PAH, the most of samples was characterized $\text{Phe}/\text{Ant} < 10$ (phenanthrene/anthracene) и $\text{Flu}/\text{Pyr} < 1$ (fluoranthene/pyrene), points lie in the area which is characterized by mixed type of PAH coming to the water course (figure 5) from the oil production activity and fuel burning. The points corresponding to the area of petrochemical industries effluents, are in the pyrolytic zone and means that air emission during the fuel burning is the priority source of PAH contamination.

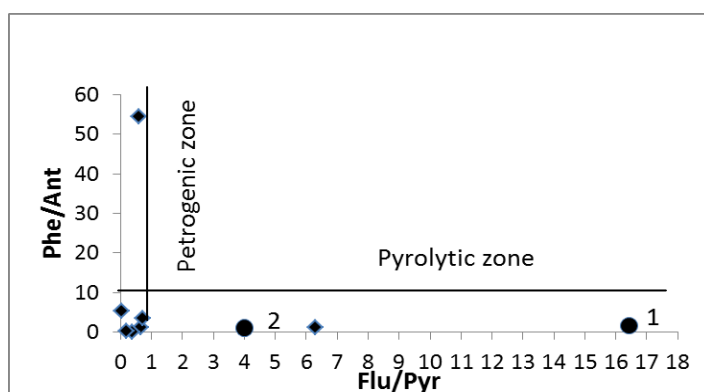


Figure 5. Ratio Phe/Ant and Flu/Pyr for identification of the PAH origin (1 – area of petrochemical industries effluents №1 and 2 - effluents №2).

4. Conclusions

1. The trend of increase of Fe, Mn, Pb, Cu, Cr, Ni, Zn along a current of the Kama River and reduction of Co content was revealed. This fact probably is not connected with the influence of the petrochemical industries because Co content significantly does not differ from contents in the estuary of the Vyatka River.
2. The content of Al, Fe, Mn, Ni, Cu, Zn, Pb is growing in sediments with different sorption capacity: sand < silty sand < silt. The calculated coefficient of enrichment showed that metals content in sediments is connected with natural processes of washing away of minerals.

3. It was noted that, the excesses of total petroleum content in all types of sediments in comparison with standards. However, its content in sediments in the zone of effluents of the petrochemical industries was below standards.

4. There were no standards exceeding neither sum PAH nor separate components. Naphthalene (0.5-183.5 µg/kg) and acenaphthene (<0.5-33.3 µg/kg) made the main contribution to mass PAH content, content of chrysene in the area of petrochemical industries effluents was in range 8.4-44.7 µg/kg much more in comparison with other stations. Based on the ratio of marker PAH, most of samples are characterized by mixed type of PAH coming to the water course: from the oil production activity and fuel burning.

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