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S.V.Morzhukhina[1], V.V.Uspenskaya[1], L.P.Chermnykh[1], I.L.Khodakovsky[1], M.V.Frontasyeva, S.F.Gundorina

NUCLEAR AND RELATED ANALYTICAL TECHNIQUES USED TO STUDY THE ANTHROPOGENIC IMPACT ON THE SISTER RIVER IN THE VICINITY OF THE TOWN OF KLIN (MOSCOW REGION, RUSSIA)

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[1]Department of Chemistry, International University of Nature, Society and Man, Dubna, Russia

Introduction

The Sister is a small river in the upper basin of the Volga. It has a small water volume and is therefore, very sensitive to the anthropogenic impact. The Sister experiences a strong technogenic impact in and around the town of Klin, a big regional and industrial center, which is a source of a large amount of industrial and household wastes of an organic and inorganic nature. Among the largest representatives of industry in the territory is KLINVOLOKNO, a joint-stock enterprise producing viscose and caprone fiber, whose contribution to environmental pollution is essential.

Today, the wastes treatment plants of the town and KLINVOLOKNO are overloaded and their efficiency is low. Frequent are break-downs and malfunctioning of separate elements in the technological chain. This leads to skipping of or poor performance in some stages of processing and as a result, discharge into the Sister of not completely treated water.

Experimental

To do research in the field, experiments were carried out to assess the contamination level of the Sister and the Dubna, the small rivers of Moscow Region, and decide whether or not the quality of their water and sediments, including the multielement composition of water and suprobiological factor, meet the existing standard of water use [1].

Sampling of water and sediment was carried out at permanent sites indicated in Figure 1.

The presented results of chemical analysis of surface water in the Sister show that it is strongly contaminated by organic substances, heavy metals, and NO_2^-, NH_4^+ over almost its entire length (Table 1).

Table 1: Concentration of contaminants in the water of the Sister river

Ingredient	Background area	Contaminated area	MPC
Oxygen concentration mg O_2/L	9.2 – 9.8	0 – 8.7	No lower than 6
COM, mgO/L	12 – 36	32 – 342	30
BOD_5, mgO_2/L	1.5 – 2.9	3.0 –48	3.0
Phenols, mg/L	0	0.002 – 0.026	0.002
CSAS, mg/L	0	0.16 – 0.98	0.10
NO_2^-	0.01 – 0.03	0.05 – 0.78	0.02
NH_4^+	0.2-0.3	0.5-9.25	0.4
SO_4^{2-}	22-52	48-154	100

Heavy metals (copper, zinc, cadmium, and lead) were identified by the method of inversion voltamperometry employing the polarograph ABC-1 and the electromagnetic sensor "Module EM-04" and following a certified procedure. The samples were prepared by photochemical decomposition of dissolved organic substances and their complexes with metals in the photolysis chamber FK-12M.

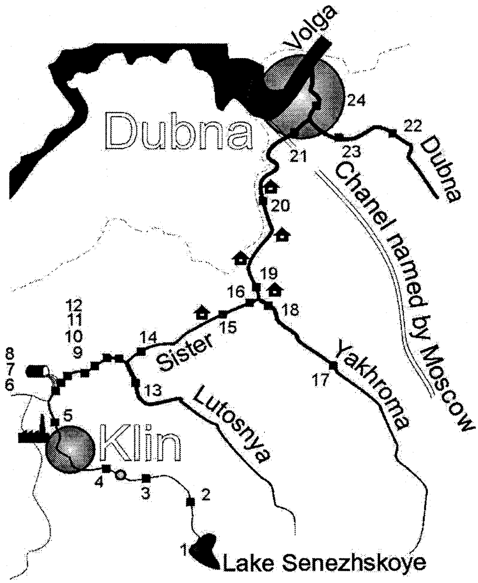

Figure 1. Scheme of flowing river Sister.

The calculation of forms of Cu- and Zn occurrence in surface water was conducted by the Mironenko M.V. program which realizes an algorithm of search for a free energy minimum in the Gibbs system. The calculated system included inorganic macrocomponents (H, O, Na, K, Mg, Ca, C, S, Cl, N) and microelements (Zn, Cu, Cd, Pb) as independent components. All the calculations were performed for 25 ^{o}C and a total pressure of 1 atm. The spectrum of dissolved particles involved 36 ions, including primary ions and their formed ionic pairs as well as ions of heavy metals and some of their organic complexes. The conducted calculations of the forms of chemical occurrence in the studied water and the activity coefficients of dissolved ions make it possible to calculate the products of activity coefficients of low dissolved compounds in water and assess their saturation levels with respect to their solid phases.

As for Zn, Cu, Pb, Cd, the river water is undersaturated relative to their solid phases. This means that heavy metals do not deposit from water as low dissolved compounds but migrate as constituents of complex compounds or suspended particles [2].

To determine heavy metal contents in **sediments,** we used neutron activation analysis and identified 42 elements (Table 2), including Pb, Cu, Cd, and Zn, whose contents were earlier determined by the polarography method (inversion voltamperometry) (Figure 2).

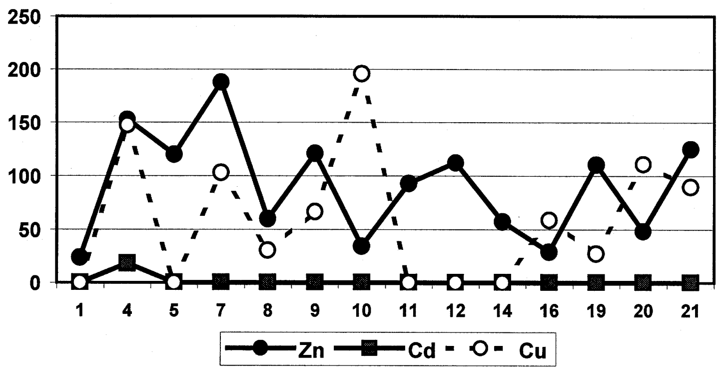

Figure 2. Zinc, copper and cadmium in the Sister water (1999), μg/L

The results of epithermal neutron activation analysis show that sediments in the Sister sorb petroleum products (strong V-Ni correlation, R=0.9). Besides, a specific feature of the sediments is the anthropogentic contamination characteristic of galvanic production in the town of Klin and a small aviation town situated up the Sister river from Klin (strong correlation of Zn – Pb (R=0.92), As – Ga (R = 0.94), Fe – Cr (R=0.9)) (Table 3).

Heavy metals form a descending row in sediment enrichment coefficient, the Metal/Al ratio [3]: Fe> >>Zr>Mn>Zn >Cr>V>Ni=As>Co. The data from neutron activation analysis and polarographic analysis were used to compose a correlation matrix which confirmed specific contamination by heavy metals in the Sister river.

For Cd, Zn, Cu, and Pb, their migratory forms were determined. To know heavy metals forms of occurrence in the sediments, a number of sequential extracts were done: 1 M $MgCl_2$, acetate ammonium extract (pH 4.75), 0,1 M HCl, 0.1 M NaOH [4].

At changing reduction-oxidation conditions and seasonal changes in the hydrochemical and hydrodynamic regime, the major part of heavy metals obtained by extracts may transfer to porous solution and water mass.

Investigations of HM migratory forms show that HM complexes in the sediments make up a descending row: Acid-soluble fraction- 43% > carbonate fraction –16.7 % > exchange fraction 15.3% > organic matter-related fraction 10.5 %.

For biological characterization of water in the Sister river there were mainly used indicator species in the zooplankton since the main characteristic of the zooplankton is a constant diversity index and dynamic stability [5].

An analysis of the biotic component of the Sister ecotope revealed a saltation reconstruction of biocenosis in agreement with the chemical analysis data. On the whole, the amount of plankton was not very large, which may possibly be explained by too high summer temperatures in 1999.

Table 2. Neutron activation analysis and polarographic analysis data on the elemental composition of sediments in the Sister river, ppm

	Minimum	Maximum	Mean	Median	Stat.dev.
Na	4353	7189	6189	6181	854
Mg	6781	28310	13493	11650	6361
Al	9150	31630	16148	16450	6356
K	6185	16260	10370	10120	2705
Ca	1963	16230	6894	4566	4700
Ti	80	763	312	337	19.2
Cr	11.2	127	38.83	34.7	28.4
Mn	144.3	2672	668.5	533.3	685.7
Fe	4948	31820	14004	14070	8124
Rb	25.05	65,88	42.09	42.6	12.6
Cs	0.31	2.48	1.08	0.91	0.68
Sr	59.2	140.2	94.5	85.2	23.1
Ba	202	486	341	348	85
Ga	6.9	31.1	14.6	13.9	7.7
Pb*	2.1	45.1	18.16	18.3	12.2
As	3.8	22.3	10.93	8.7	5.9
Sb	0.06	0.70	0.28	0.19	0.20
Br	0.6	7.8	2.7	2.1	2.2
Cu*	0.3	256.0	5.7	1.8	7.1
Zn	22.0	605.9	185.7	137.8	169.0
Cd*	0.2	60.1	9.1	1.3	19.0
Hg	0.01	2.29	0.27	0.02	0.70
Sc	1.5	8.9	4.2	3.9	2.1
Zr	292	1891	1161	1160	466
Hf	1.8	12.7	7.5	7.7	3.1
V	8.0	61.7	25.9	23.0	17.1
W	0.15	0.91	0.46	0.39	0.28
Co	2.22	11.23	4.99	4.68	2.69
Ni	2.8	125.0	26.2	9.8	39.6
La	4.74	26.98	14.36	13.36	6.9
Ce	13.5	56.8	33.5	32.2	15.1
Nd	5.5	29.0	17.9	17.0	7.6
Gd	11.1	71.7	36.7	35.5	19.4
Yb	0.46	2.07	1.17	1.06	0.57
Th	1.13	7.19	3.95	3.78	2.02
U	0.52	1.78	0.98	0.8	0.45

Table 3. Correlation matrix of contaminants concentrations in the Sister sediments

	Na	Mg	Al	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Zn	Ga	As	Sr	Zr	Sb	W	Pb*	Cu*	Cd*
Na	1.00																					
Mg	0.67	1.00																				
Al	0.69	**0.97**	1.00																			
K	0.74	**0.89**	0.84	1.00																		
Ca	0.52	0.84	0.77	0.72	1.00																	
Ti	0.72	**0.97**	**0.99**	0.84	0.75	1.00																
V	0.62	**0.97**	**0.98**	0.80	0.80	**0.97**	1.00															
Cr	0.42	0.75	0.78	0.49	0.59	0.76	0.83	1.00														
Mn	0.52	0.83	0.85	0.58	0.72	0.84	0.89	**0.96**	1.00													
Fe	0.61	0.89	**0.91**	0.69	0.66	0.91	**0.94**	0.90	0.92	1.00												
Co	0.62	0.87	0.90	0.67	0.67	0.90	**0.94**	0.89	0.93	**0.99**	1.00											
Ni	0.48	0.88	0.90	0.65	0.79	0.87	**0.89**	0.84	0.89	0.83	0.81	1.00										
Zn	0.48	0.87	0.89	0.69	0.82	0.85	0.87	0.80	0.83	0.79	0.76	0.93	1.00									
Ga	0.62	**0.98**	**0.97**	0.86	0.83	**0.96**	**0.99**	0.79	0.86	**0.93**	**0.92**	0.88	0.87	1.00								
As	0.60	**0.95**	0.88	0.86	0.82	0.89	**0.91**	0.67	0.75	0.85	0.84	0.78	0.77	**0.94**	1.00							
Sr	0.64	0.86	0.82	0.83	0.82	0.80	0.82	0.62	0.69	0.80	0.78	0.75	0.76	0.87	0.89	1.00						
Zr	0.43	0.61	0.57	0.59	0.38	0.58	0.59	0.55	0.49	0.70	0.67	0.46	0.41	0.62	0.72	0.76	1.00					
Sb	0.57	**0.94**	**0.92**	0.80	0.87	0.90	**0.95**	0.86	**0.91**	**0.90**	**0.90**	**0.90**	**0.90**	**0.96**	**0.90**	0.88	0.60	1.00				
W	0.65	0.90	0.85	0.78	0.70	0.86	0.87	0.79	0.82	**0.92**	0.90	0.75	0.74	0.88	**0.92**	0.88	0.83	0.88	1.00			
Pb*	0.56	0.71	0.77	0.55	0.72	0.75	0.73	0.63	0.68	0.66	0.64	0.77	**0.90**	**0.71**	0.59	0.65	0.24	**0.74**	0.56	1.00		
Cu*	-0.01	0.31	0.26	0.12	0.29	0.24	0.28	0.39	0.29	0.18	0.16	0.43	0.37	0.24	0.26	0.06	0.17	0.29	0.19	0.22	1.00	
Cd*	0.19	0.47	0.52	0.17	0.41	0.49	0.60	0.93	0.87	0.69	0.70	0.67	0.62	0.55	0.35	0.36	0.29	0.68	0.54	0.46	0.34	1.00

Water samples from the Sister that carries on wastes of the plant and the town sewage demonstrate ecological and metabolic regress of biocenosis along over 20 km down the river. Industrial runoff has caused a decrease in the abundance and biomass of the plankton as well as in species diversity due to disappearance of oligosaprobic forms. The displacement of crustacean species by saprobiontic amebas is taking place. The abundance and biomass of bacteria are increasing and the portion of saprophyte bacteria is growing.

Conclusions

1. By many parameters, the contamination of the river water and the sediment extends up to 50 km from the sewage discharge site.
2. The contaminated river water and sediment do not reach inhabited places thanks to natural purification processes (deposition, sorption, decay of organic substances, etc.).
3. According to the obtained data, the Sister sediment up the river from Klin is essentially enriched with cadmium whose source is obviously the runoff from the aviation town.
4. The conducted calculation of heavy metal forms shows that the river water is undersaturated relative to the solid phase, which means that adsorption on suspended matter dominates in the natural purification process.
5. Considerably higher concentrations of heavy metals in the sediment were detected. This constitutes a risk of secondary contamination in water bodies.
6. Bacterial processes are intensifying. The number of saprophyte and pathogenic micro-organisms is growing and contamination response-specific forms are appearing.
7. The number, biomass, and diversity of fresh water invertebrates are falling because of dying out of oligosaprobic forms.

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Моржухина С.В. и др. E14-2001-54

Использование ядерных и других методов анализа для изучения антропогенного влияния на реку Сестру очистных сооружений г. Клина (Московская область)

Дана комплексная гидрохимическая и сапробиологическая характеристика вод и изучен состав донных отложений малой р. Сестры Московской области. Показано, что в окрестностях г. Клина р. Сестра сильно загрязнена, во-первых, в связи со сбросом сточных вод городскими очистными сооружениями и АО «Клинволокно». По многим показателям загрязнение речной воды и донных отложений распространяется от места сброса сточных вод на расстояние до 50 км ниже по течению реки. Второй источник загрязнения расположен выше г. Клина по течению р. Сестры. Донные отложения здесь сильно обогащены кадмием, цинком, свинцом, медью. По-видимому, происхождение геохимической аномалии на этом участке связано с деятельностью гальванических производств и сливом отработанного электролита цинк-кадмиевых аккумуляторов, используемых в авиации. Для изучения состава донных отложений впервые был применен метод инверсионной вольт-амперометрии, а также нейтронно-активационный анализ. Донные отложения р. Сестры аккумулируют тяжелые металлы (Zn, Cd, Hg, Cu, Pb, Ni), As, нефтепродукты, что грозит опасностью вторичного загрязнения водотока. Показано, что сочетание этих двух методов дает более полную картину об уровне загрязнения донных отложений. В связи со сбросом сточных вод в р. Сестру бактериальные процессы интенсифицируются, увеличивается количество сапрофитных и патогенных микроорганизмов, появляются специфические по реакции на загрязнения формы. Снижается численность и биомасса, сокращается видовое разнообразие пресноводных беспозвоночных за счет выпадения олигосапробных форм.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ и в Международном университете природы, общества и человека «Дубна».

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Nuclear and Related Analytical Techniques Used to Study the Anthropogenic Impact on the Sister River in the Vicinity of the Town of Klin (Moscow Region, Russia)

The ecological fate of small rivers, tributaries of the Volga River, is of great concern in the national program of the Russian Federation «Restoration of the Volga River». The results on the elaborated hydrochemical and saprobiological water examination of the Sister River are reported along with the results on the multielement chemical analysis of surface sediments in the catchment of the town of Klin (Moscow Region) known for its numerous industrial and chemical enterprises with heavy contaminant inputs. Epithermal neutron activation analysis was used to study heavy metals and other toxic elements in bottom sediments. A total of 42 elements including Pb, Cu, Cd and Hg were determined by polarography (method of inverse voltamperometry). Metal/Al rations which express the relative mobility of the elements follow the sequence: Fe > Mg > K > Na > Ca >> Zr > Mn > Zn = Sr > Cr > V > Ni = As > Co. Elevated concentrations of Cd, Pb, Zn and Cu in the bottom sediments of the Sister River reinforced us to determine their chemical forms using fractionation scheme. Cadmium is mostly associated with carbonate content and thus has a possibility of becoming readily bioavailable. Its toxicity and bioavailability poses a serious problem to ecosystem. Copper and zinc besides having less environmental risk are present in forms in which they cannot be easily leached out. Accumulation of toxic metals, arsenic and oil products are of potential hazard for the secondary pollution of the surface waters. It is shown that the main sources of pollution in the vicinity of the town of Klin are the domestic sewage waters and sewage waters from the chemical complex «Klin-Fiber» producing synthetic materials. The extremes of the distribution patterns of pollutants in the bottom sediments and water are to be found approximately 50 km down the stream from the discharge sources. The second source of geochemical anomaly is located upstream of the Sister River, before the town of Klin.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR and at the Department of Chemistry, International University of Nature, Society and Man «Dubna».

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