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USE OF PYROPHOSPHATE EXTRACT TO DETERMINE ORGANIC-BOUND FORMS OF COPPER AND IRON IN BOTTOM SEDIMENTS: THE CASE STUDY OF THE VYSHNEVOLOTSKY RESERVOIR, RUSSIA

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ABSTRACT

Speciation of heavy metals in bottom sediments defines their ecotoxicity and mobility and therefore needs to be studied thoroughly. Usually single and sequential extraction techniques are used to determine water-soluble, exchangeable, specifically sorbed and carbonates, bound to organic matter, bound to Fe and Mn hydroxides and residual forms.

Bottom sediments of the Vyshnevolotsky reservoir (the Upper Volga, the Central region of Russia) were chosen for the research. Lithological and mineral composition of samples was characterized. Extraction of organic-bound forms of copper and iron was conducted with use of sodium pyrophosphate. Since sodium pyrophosphate also partially attacks Fe and Mn hydroxides, modificated Tessier sequential extraction scheme was applied to control extracted forms of metals. Copper and iron contents in extracts were determined by means of atomic absorption spectroscopy.

The results of the study indicate that sodium pyrophosphate mainly extracts organically bound copper and amorphous hydroxide and oxide forms of iron which comply with prevailing forms of these elements.

Keywords: copper, iron, bottom sediments, organic-bound forms, sodium pyrophosphate extract, sequential extraction scheme.

INTRODUCTION

Bottom sediments of reservoirs are a complex of mineral and organic particles secondarily deposited and accumulated over time on bottom and slopes of reservoirs and reach more or less significant thickness. Since heavy metals in bottom sediments can act as environmental toxicants this paper focuses on heavy metals speciation defining elemental mobility and therefore ecotoxicity.

Commonly single and sequential extraction techniques are used to determine water-soluble, exchangeable, specifically sorbed and carbonates, bound to organic matter, bound to Fe and Mn hydroxides and residual forms [1]. Nowadays, one of the most widely used reagent for extraction of organic-bound forms is 0,1M sodium pyrophosphate. Pyrophosphate at pH 10 peptizes very fine amorphous particles, to some extent irrespective of their composition, and extracts organic-bound forms of trace elements (fulvatic and humic complexes) with no significant attack on silicates (table 1).

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Table 1. Ranges of compounds removable by pyrophosphate at various pH [2].

Inorganic iron compounds				Organic complexes	
Silicates	Well crystallized oxides	Amorphous 'aged' hydrous oxides	Amorhpous 'gel' hydrous oxides	Acid soluble 'Fulvate'	Acid insoluble 'Humate'
			(pH 7) *pyrophosphate*		
				(pH 10) *pyrophosphate*	

---- extraction poor — extraction good

In this paper we analysed the effects of sodium pyrophosphate on organic-bound forms of copper and iron in bottom sediments of the Vyshnevolotsky water reservoir, Russia.

MATERIALS AND METHODS

Bottom sediments. The Vyshnevolotsky water reservoir belongs to the Upper Volga cascade reservoirs in the Central region of Russia. The average morphometric characteristics of the reservoir are as follows: length – 12 km, width – 9 km, depth – 3 m, area – 109 km^2, water volume – 0,32 km^3. The reservoir is used for water supply, water transport, energy, fisheries and recreation (mainly for unorganized recreation) [3]. Total of 9 bottom sediments samples were collected for geochemical studies (fig. 1).

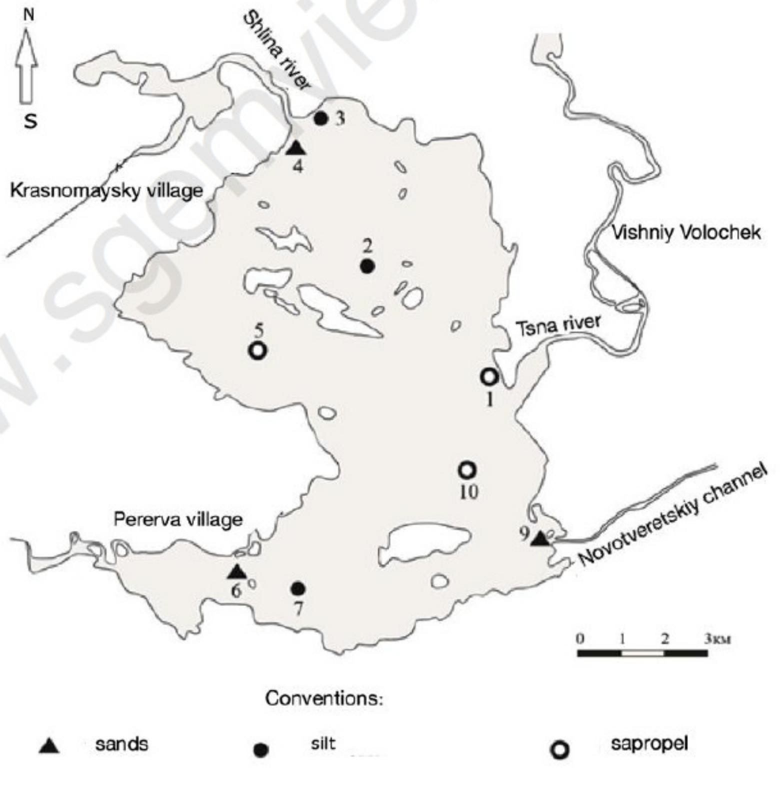

Figure 1. Sampling map

Samples were taken from different depths and were represented by sand (samples 4, 6, 9), silt (samples 2, 3, 7) and sapropel (samples 1, 5, 10).

Analytical research. Scheme of analytical research is given in fig. 2.

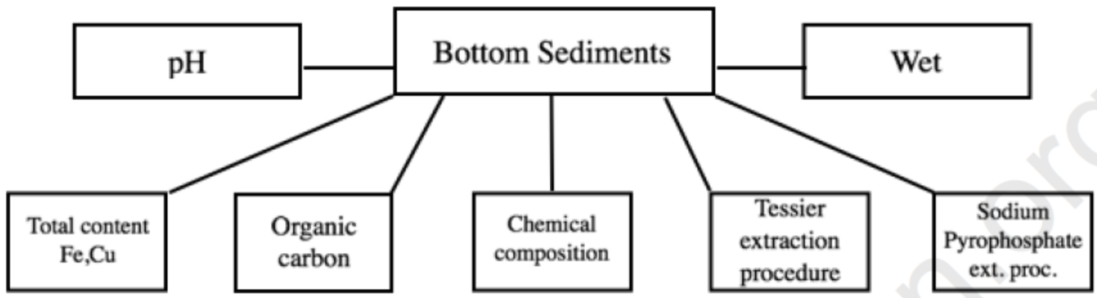

Figure 2. The scheme of analytical studies

Organic-bound forms of copper and iron were extracted with use of sodium pyrophosphate. To 2 g of the sediment was added 40 ml of sodium pyrophosphate and a day later the suspension centrifuged and filtered. The content of copper, iron and organic matter was determined in the extract. Since sodium pyrophosphate also partially attacks Fe and Mn hydroxides [2], modificated Tessier sequential extraction scheme [4] was applied to control extracted forms of metals (table 2).

Table 2. Stages of modificated Tessier sequential extraction scheme (for 1 g).

Stage	*Fractions*	*Extraction agent*	*Simulated conditions*
1	Exchangeable and bound to carbonates	8 mL of NH_4OAc (pH 4,8)	5 h, 25°C
2	Bound to Fe-Mn oxides	20 mL of 0,04 M $NH_2OH{\cdot}HCl$ in 25% HOAc (pH~2)	6 h, 96°C
3	Bound to organic matter	3 mL of 0,02 M HNO_3 + 5 mL 30% H_2O_2 +3 mL 30% H_2O_2 +5 mL 3,2 M NH_4OAc	2 h, 85°C 3 h, 85°C 0,5 h, 25°C
4	Residual	Acid digestion with HF-$HClO_4$ mixture	

Concentration of metals in solutions was determined with atomic absorption spectrometer ContrAA®700.

RESULTS

The detailed characteristics of the bottom sediments is given in the table 3.

The chemical composition of bottom sediments is following: SiO_2 varies from 37,63% to 81,75%; Al_2O_3 from 5,15% to 9,23%; FeO from 0,72% to 3,95%; Fe_2O_3 from 1,62% to 4,58%; TiO_2 from 0,36% to 0,58%; P_2O_5 from 0,2% to 0,56%; CaO from 0,67% to 2,02%; MgO from 0,36% to 1,58%; MnO from 0,04% to 0,16%; Na_2O from 0,37% to

0,64%; K_2O from 1,05% to 1,63%; H_2O from 0,13% to 6,58%; loss on ignition (LOI) from 5,92% to 39,47%.

Clay minerals in bottom sediments are represented mainly by magnesian chlorite (27-44%), hydromica (18-35%), kaolinite (14-28%) and mixed mica-smectite (14-30%).

Table 3. The characteristics of bottom sediments.

Sample	*Location*	*Description*	*pH*	*Wet, %*	*C_{org}, %*	*LOI, %*	*C_{org} $Na_4P_2O_7$, %*
1	Novodvinskaya jetty	Black sapropel, biogas emanation	6,8	800	14,3	27,8	1,65
2	Reach near Tobolka river	Dark, uliginous, claggy silt, with ferrugination	7,1	160	3,3	5,9	0,31
3	Shlina river mouth, dam	Dark, uliginous, claggy silt, with ferrugination	7,1	390	8,9	18,2	1,05
4	Shlina river mouth	Finely-granular ginger sand	7,5	32	0,5	0,9	<0,01
5	Reach near Gradolublya village	Black, claggy sapropel, with ferrugination	6,8	950	18,1	32,9	1,37
6	Pererva village	Finely-granular, light ginger sand	7,3	23	0,6	0,1	<0,01
7	Tsna river mouth	Grey silt, no ferrugination	6,9	325	8,0	15,6	0,79
9	Novotveretskiy channel headstream	Finely-granular, light brown sand, with plants and gruss	7,6	28	0,6	0,9	0,02
10	Kasharovo reach	Black, watery sapropel, with ferrugination	6,8	960	21,8	39,5	2,02

Sodium pyrophosphate extracts 8-12% of the total organic matter in the samples.

Cu and Fe contents in the samples and extracts are given in the tables 4 and 5.

Table 4. Copper content in the samples and extracts.

Sample	*Copper extracted with*				*Total content, mg/kg*
	$Na_4P_2O_7$, mg/kg	*NH_4OAc, mg/kg*	*$NH_2OH{\cdot}HCl$, mg/kg*	*H_2O_2, mg/kg*	
1	2,4	1,3	2,6	7,4	22,3
2	1,8	1,5	2,4	2,3	13,5
3	2,9	0,8	2,7	4,8	20,6
4	<0,5	0,3	0,9	1,5	3,8
5	4,0	0,8	3,8	11	29,7
6	<0,5	0,3	0,7	0,7	3,7
7	1,6	0,7	3,2	3,2	17,8
9	<0,5	0,1	0,4	0,8	2,5
10	4,8	2,4	3,0	11	27,7

Table 5. Iron content in the samples and extracts.

Sample	Iron extracted with				Total content, mg/kg
	$Na_4P_2O_7$, mg/kg	NH_4OAc, mg/kg	$NH_2OH{\cdot}HCl$, mg/kg	H_2O_2, mg/kg	
1	4900	3780	11120	6575	51640
2	1850	1630	5250	1250	15940
3	7100	4370	13690	4580	54970
4	< 200	300	2100	100	5730
5	5550	4410	13500	14960	78910
6	< 200	100	400	100	2190
7	5200	2450	7800	4520	36295
9	< 200	200	500	100	3360
10	4350	3060	9975	15100	54385

Organic matter contents obtained in extracts were compared to contents in solid phases and with loss on ignition. Absolute values differ but correlate significantly (correlation coefficients are from 0,959 to 0,997).

The total contents of copper and iron don't exceed background values for the bottom sediments of the Upper Volga. Figure 3 shows the distribution of mobile forms, depending on the types of bottom sediments. Content of organic-bound forms increases both for Cu and Fe in sediments that are rich in organic matter (sapropel).

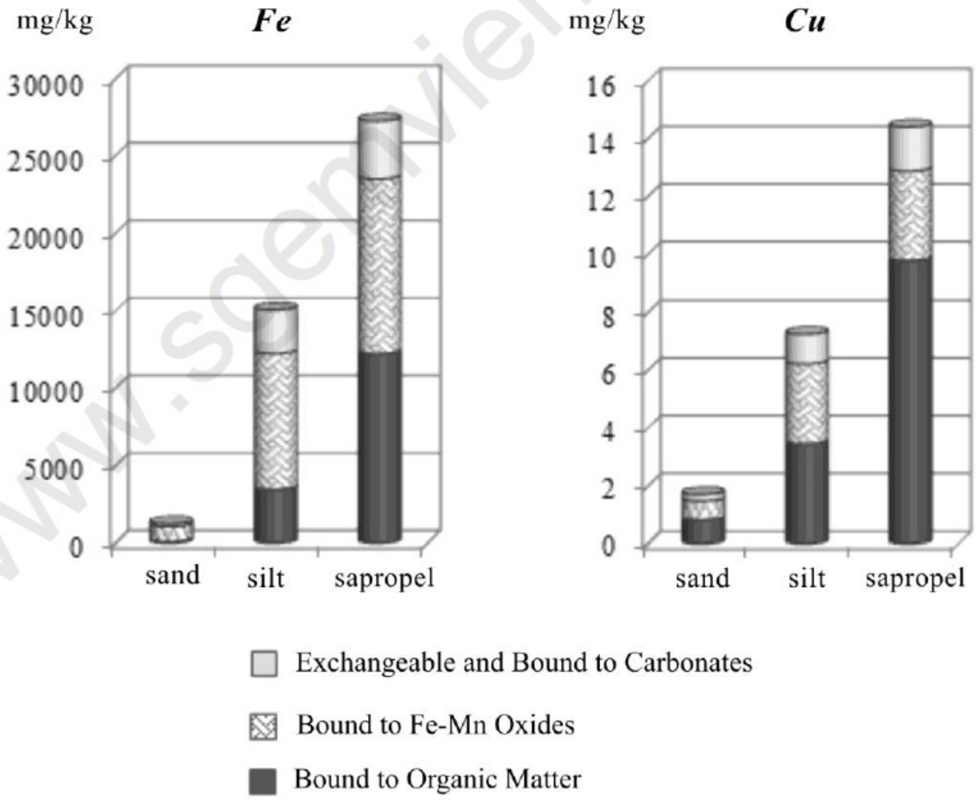

Figure 3. Distribution of mobile heavy metal speciation in bottom sediments.

Up to 76% of Fe mobile forms of iron in sand are associated with amorphous iron and manganese hydroxides, in silt and sapropels this quantity decreases to 60 and 42%, respectively. About 50% of Cu mobile forms bound to organic matter in sands and silts and increases to 70% in sapropels. These regularities are also characteristic for other objects located in the same climatic zone [5].

Contents of microelements and organic matter in extracts from sand samples were excluded from further consideration because values in pyrophosphate extracts are below detection limit. We suppose that pyrophosphate extraction method is insufficient for determination of organic-bound forms in sand sediments in natural objects with low anthropogenic load.

For total Cu concentration, Cu contents in extracts, organic matter content and content of Fe and Mn hydroxides in solid phase pairwise correlation coefficients R_{XY} were calculated and dendrogram was constructed (fig. 4).

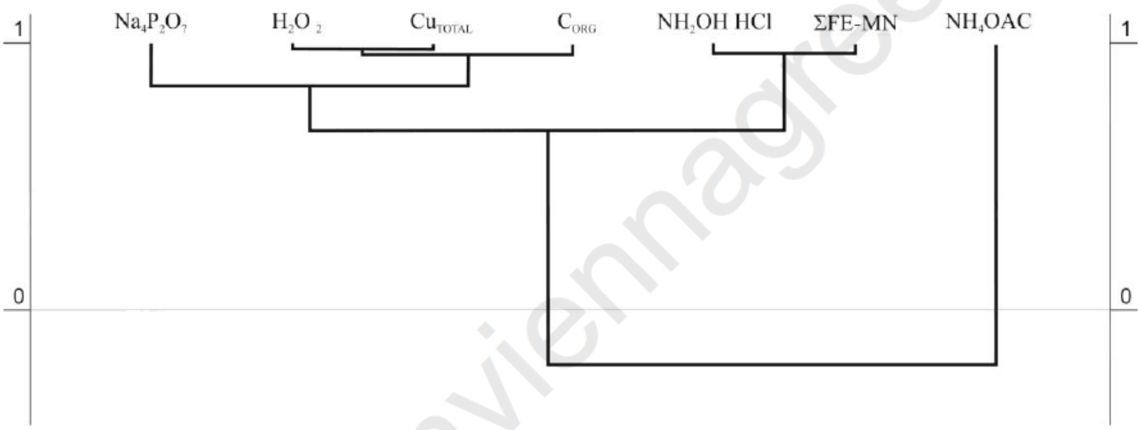

Figure 4. Correlation dendrogram for Cu content data and other characteristics of bottom sediments. Critical value of correlation coefficient R_{XY} for 6 samples (4 degrees of freedom) at the 5% level of significance is 0,811.

The following conclusions were drawn based on the observed correlation:

- Significant correlation between organic matter and total Cu contents (R_{XY} = 0,921) indicates that this microelement is present in the sediments in organic-bound form.
- Significant correlation between organic matter content in solid phase with hydrogen peroxide extract (R_{XY} = 0,937) and pyrophosphate extract (R_{XY} = 0,883) shows that these reagents dissolve organic-bound forms of Cu.
- Pyrophosphate and hydrogen peroxide extract the same forms which is confirmed by correlation coefficient (R_{XY} = 0,911) between Cu contents in these extracts.

In the same manner correlation was assessed for Fe content data. Correlation dendrogram is presented in figure 5.

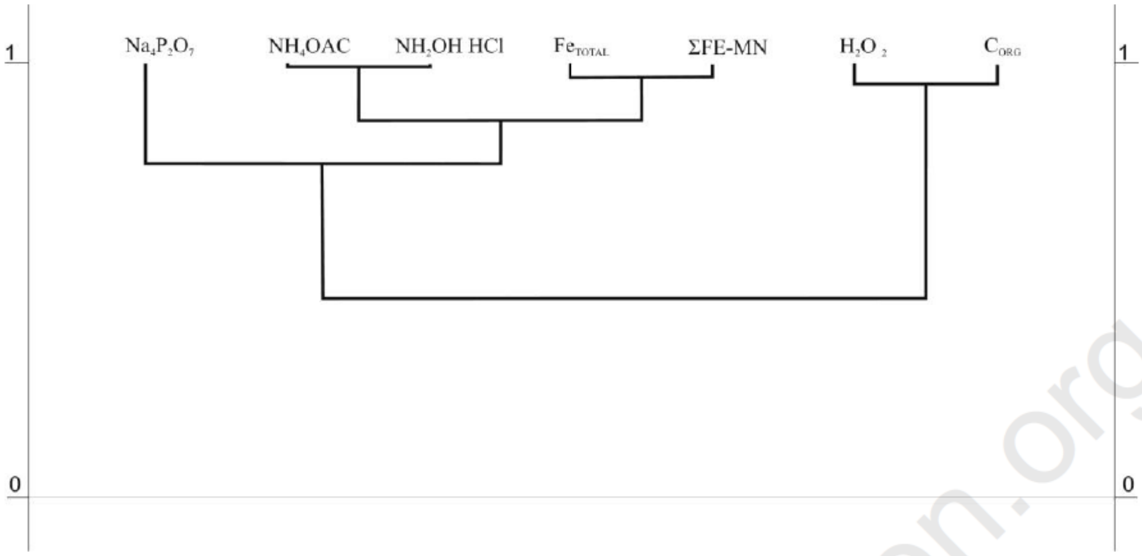

Figure 5. Correlation dendrogram for Fe content data and other characteristics of bottom sediments. Critical value of correlation coefficient R_{XY} for 6 samples (4 degrees of freedom) at the 5% level of significance is 0,811.

From dendrogram it can be noted that:

- There is significant correlation between sum of FeO, Fe_2O_3, MnO contents and total Fe content (R_{XY} = 0,981) that indicates curence of Fe in sediments in the form of (hydro-)oxides.
- Significant correlation coefficient between FeO, Fe_2O_3, MnO content in solid phase and Fe in pyrophosphate extract (R_{XY} = 0,811), NH_4OAc extract (R_{XY} = 0,914) and $NH_2OH{\cdot}HCl$ extract (R_{XY} = 0,929) shows that these reagents extracted Fe bound to Fe-Mn (hydro-)oxides.
- Fe content in pyrophosphate extract significantly correlate with its content in extracts made with NH_4OAc (R_{XY} = 0,837) and with $NH_2OH{\cdot}HCl$ (R_{XY} = 0,855) whereas no correlation observed between Fe contents in pyrophosphate extract and in H_2O_2 extract (R_{XY} = 0,249). Therefore, sodium pyrophosphate have more aggressive effect on Fe and Mn (hydro-)oxides than on organically bound Fe.

CONCLUSION

In this work a thorough study of the organic-bound forms of Cu and Fe in bottom sediments of the Vyshnevolotsky reservoir with use of sodium pyrophosphate was made. Modificated Tessier sequential extraction was involved for control of the results because pyrophosphate also partially attacks Fe and Mn hydroxides.

The total contents of copper and iron don't exceed background values for the bottom sediments of the Upper Volga.

The form bound to organic matter is basic for copper. Inorganic form (carbonate and oxide-hydroxide) is basic for iron.

Content of organic-bound forms increases for both Cu and Fe in sediments that are rich in organic matter (sapropel).

It is shown that pyrophosphate extraction method has a softer effect on bottom sediments in contrast to Tessier extragents. It is not recommended to assess content of organic-bound forms using pyrophosphate extraction in sand sediments in natural objects with low anthropogenic load.

Based on correlation coefficients between Cu and Fe contents data in extracts, organic matter content and Fe and Mn hydroxides content in solid phase it is demonstrated that sodium pyrophosphate mainly extracts organically bound copper and iron from amorphous hydroxide and oxide. Referred results of extraction with pyrophosphate comply with prevailing forms of copper and iron.

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