BIOACCUMULATION OF Tc-99, Pu-239 AND Np-237 BY BOTTOM SEDIMENTS OF FRESH WATER LAKES OF MOSCOW REGION

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Investigation of radionuclides' accumulation by natural associations of microorganisms is important for comprehension of their behavior in ecosystems. In some works transfer factors for Tc from water to sediments were analysed (see for example [1, 2, 3] and ref. therein). Although many works are devoted to humic acids effects, the influence of general water content is not thoroughly studied. Then, temperature influence, season variation and the reversibility of radionuclide sorption are important subjects of radionuclide behavior in these ecosystems.

We present the results of model laboratory study of the absorption of the long-lived radionuclides. The isotopes were introduced as ^{99}Tc (VII), ^{237}Np (V), ^{239}Pu (VI) into batch samples containing lake water and sediments taken from the eutrophic lake Beloye Kosino (Moscow reg.) and dystrophic peat lake (Shatura reg.) at initial concentrations of Tc, Pu and Np 10^{-5}-10^{-6} M.

Eutrophic lake sediment was mainly formless organic detritus, gray colored, H_2S odoriferous. Dystrophic lake sediment was 98% organic peat and humics, 2% sand.

Table.1. Main eutrophic lake sediment and water phase content

Microorganism	Cells' number N/ml	Comments
		Ratio in batch: $V_{sediment} : V_{liquid}$ = 1:3; $M_{solid} : M_{liquid}$ = 1:30
Microalgae	10^6	Total = 2*10^9 bacteria/g, pH = 7.0 (stable); Eh = -0.20V NHE (inner sediment part); water phase: [HCO_3^-] = 1 – 4 mg-C/l; [HSO_4^-] = 0 – 50 mg/l, [Cl^-] = 35 mg/l. summer - autumn: sediment rich in organic easy for assimilation by microorganisms winter-spring : sediment rich in fermentated organic
<u>Bacteria:</u>		
Sulphate reducing	10^4	
Methanogenic	$10^4 – 10^5$	
Nitrifying	10^3 - 10^4	
Denitrifying	10^5	

<u>Sample treatment:</u> 1) Centrifuge MPW-210 (15000 rpm), 2) Microfilterfuge: tubes 30,000 NMVL Polysulphone (RAININ Instr.Co., Inc.), 3) Filters Millipore Type VM 0.05 µm. No more than 5 % of water phase was sampled during the experiments in total. More than 95% of Tc-99 were truly dissolved species of TcO_4^- in water phase all time through the experiment.

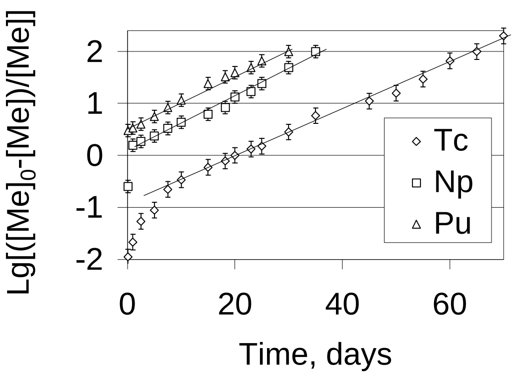

Fig.1. Radionuclide uptake by eutrophic lake bottom sediment, $[Tc]_0 = [Np]_0 = [Pu]_0 = 10^{-5}$M

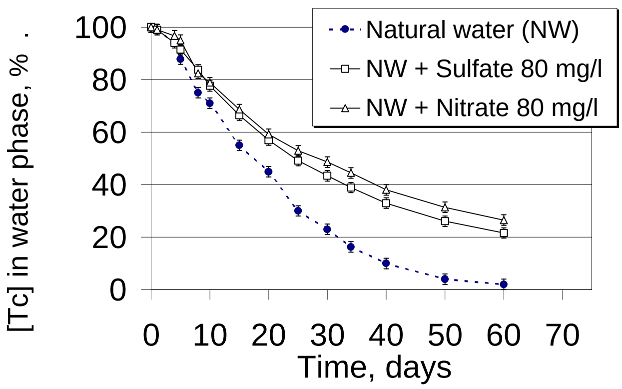

Fig.2. Substrates (additions of sulfate and nitrate) effect on the kinetics of Tc-99 uptake by eutrophic lake sediment (t = 20°C; $[Tc]_0 = 10^{-5}$M)

The kinetics' analysis of data from Fig.1 has shown that the half-time values of the initial content removal from the water-phase form 400h for Tc, 10h for Np and less than 1h for Pu. Two different uptake rates were characteristic for plutonium and neptunium sorption: fast uptake during the first hour when 60% and 50% of initial input was sorbed by sediment of eutrophic and dystrophic lakes, and a slow bioaccumulation period when neptunium uptake was completed in 1 and 2 months for eutrophic and dystrophic lakes respectively. Being added to water phase of dystrophic lake about 30% of Np were bounded in water-soluble complexes with natural humic acids (the latter were precipitating on acidifying the water to pH=1).

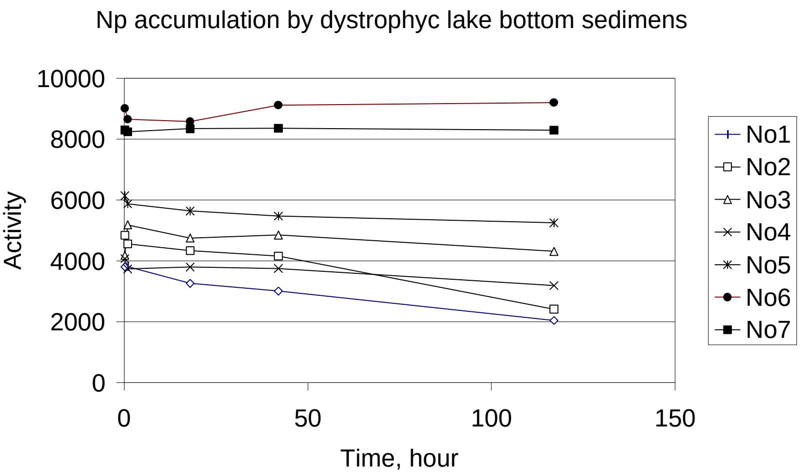

Fig. 3.

No 1	natural (silt+water), t=15^{o}C
No 2	natural (silt+water), t=15^{o}C
No 3	natural (silt+water), t=6^{o}C
No 4	natural (silt+water), t=6^{o}C
No 5	natural (silt+water), t=15^{o}C + 0.02 M H_2CO
No 6	humine water from the pond; t=15^{o}C
No 7	humine water from the pond + 0.02 M H_2CO; t=15^{o}C

As for Tc, the uptake rate was almost constant, the time of half-uptake being 1/2 and 1 month for eutrophic and dystrophic lakes. Concentration factors at 1550 hours of equilibration of Tc with sediments and natural water were 1700 ml/g for eutrophic lake and 56 ml/g for dystrophic lake. In case of natural water from dystrophic lake about 3 % of Tc(IV) was bounded to dissolved humic and fulvic acids while 95% was Tc(VII). The complete Tc accumulation by sediment took place after 1 and 2,5 months respectively. Speciation by centrifuging at 10000 rpm, ultrafilterfuging or filtration through 0.05 - 0.22 μm membranes, has shown that the Tc fraction remaining in water phase was present as truly ionic species up to 90%. The microflora of lake played important role in the accumulation and reduction of radionuclides. Some microorganisms being able of anaerobic respiration had competition relationships between SO_4^{2-} or NO_3^- and TcO_4^-. Addition of SO_4^{2-} or NO_3^- decreases the rate of Tc accumulation by sediment.

We suggest that reduction and sorption are the main mechanisms for Np, Pu and Tc accumulation in this biosystem. Kinetics study [4] indicates that at the actual TcO_4^- and S^{2-} concentrations the reduction of pertechnetate with hydrosulfide is inhibited. For this reason we suppose that Tc reduction and further uptake by the lake sediment is due to microbial activity of the sediment components, most probably to sulfate-reducing bacteria, that are known to reduce Tc [5]. The difference in the uptake rate is associated with the higher chemical stability of TcO_4^-. This mechanism is supported by Tc uptake rate slowing down when concurrent anions like sulfate or nitrate are injected into the water phase (firstly observed in [6]). For the alternative mechanism including reduction with hydrosulfide addition of sulfate would increase microbial hydrosulfide production and would effect on Tc behavior in the opposite way, increasing the uptake rate while addition of nitrate would not produce any effect. Significant difference in Tc bioaccumulation by the silts, taken in winter and summer periods, especially in the case of sterilized samples, was found out. Possibly the reason for this is the hydrosulfide concentration decrease in winter period due to the artificial aeration and the depression of metabolism at low temperatures.

Temperature effect was studied in the experimental set presented in Fig. 4.

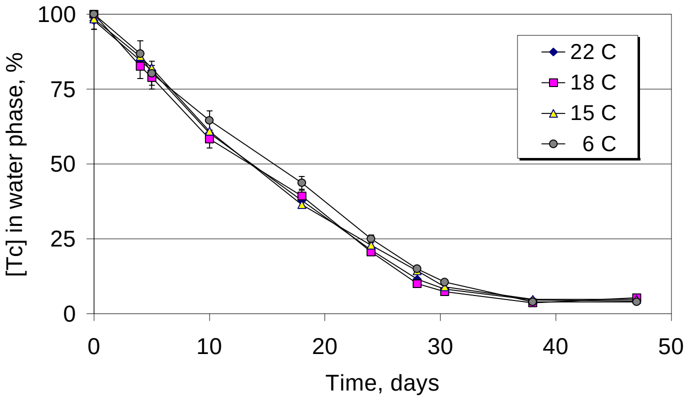

Fig 4. ^{99}Tc uptake by eutrophic lake sediment at different temperatures, $[Tc]_o=10^{-5}$M

Very small increase of uptake rate for contact time 10-20 days was found for cold weather. This observation correlates with the hypothesis that sulfate-reducing bacteria (dominating at this temperature if no artificial aeration was applied) are the most active microbial species toward Tc reduction among these present in the lake sediment.

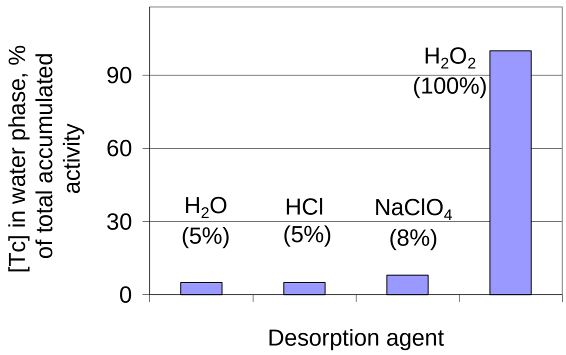

Fig. 5. Desorption of Tc-99 from the silt.

The sediments from freshwater lakes have a considerable sorption capacity. The consecutive sorption runs have demonstrated only small decrease of Tc uptake rate. The desorption of technetium was carried out with H_2O, 1M HCl, 1M $NaClO_4$ or 15% H_2O_2 and gave the desorption factors of 0.05, 0.05, 0.08 and more 0.99 thus indicating the reduction of technetium to be the main mechanism of its uptake.

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