THE CASCADE ULTRAFILTRATION AS THE METHOD OF STUDYING OF COMPLEXING OF MICROELEMENTS WITH NANOSCALE MOLECULES OF DOC IN NATURAL WATERS

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The study of transformation and regular differences in the dissolved and colloidal forms of the migration of certain metals with the organic matter (OM) are necessary in the natural waters for the problem solving of the balance of different elements in separate components of river flow.

Isolation in the migratory flow of the contributions, connected with the truly dissolved forms, colloids and suspensions under the rapid mutual transfers of the prevailing transport forms for the river current is complex problem. In the number of contributions the truly dissolved forms are characterized for the majority of inorganic ionic forms of metals by variable, but, as a rule, lowest concentrations. During the study of transformation dynamic of the forms of transfer the reliable determination of the concentrations of the dissolved substances, including the form of complexes of OM with metals and colloids, becomes fundamental task. It is known that certain metals can be connecting-link between the separate molecules of humus substances. It influences on the conditions and forms of their migration [1]. The humus substances play the notable position in the complexing in the surface water. They are: the badly dissoluble humic acid and metal-fulvic acid complex in the true solution, interaction with which has basic effect on the behavior of chemical elements in the natural waters.

The study of the problem of complexing micro- and the macroelements in river current with the dissolved organic matter (DOM) assumes the knowledge of the distribution the groups of the microelements between the molecules of humic and fulvic acids of different molecular weight and other low-molecular organic acids. The sampling of large volume (40 l) with sequential use of methods of stepped fractional filtration and ultrafiltration gives a possible to divide these groups on different types of filters and to study molecular-mass distribution of OM, what is the method of solution of the problem presented. Elements of this approach, for the first time developed in the works of B. Dupre and other [2], were adapted by us and augmented in connection with decided tasks. Our samples were underwented by stepped cascade filtration and ultrafiltration using different filters both membrane, and nuclear, through a progressively decreasing pore size (100; 0.45; 0.22; 0.1 mcm; 100 kDa (0.0064 mcm); 10 kDa (0.003 mcm) and 1 kDa (0.0014 mcm)), and dialysis through 1 kDa membrane.

The compositional analysis of the chosen fractions of filtrates and sediments was achieved consecutively and by separately different methods. All filtrates and dialyzates were analyzed for the wide spectrum of elements by the method ISP-MS, by three methods for determination of DOM: NPOC; spectrophotometrically in the range 400 to 590 nm (differential spectra of DOM), and also was measured ignition loss of dry solids. In a number of cases the defined differential values of the dry solids, ignition loss and method NPOC give the overstated values of DOM because of partial scavenging of the badly cross-linked matrix of cellulose filters. In this case we gave preference to spectrophotometric determinations under construction of calibration diagram of the DOM for not cellulose filters (fig. 1). Potentiometric and conductometric measurements were fulfilled and the content of dissolved oxygen was determined on the network of sampling.

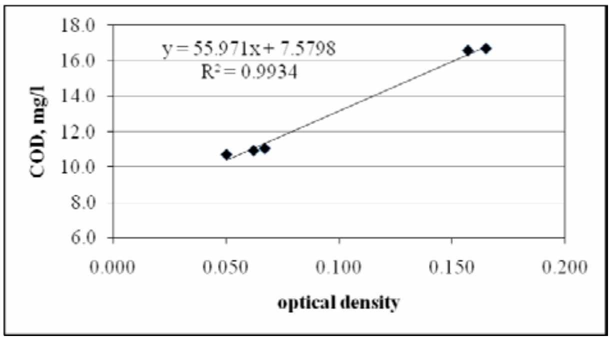


Fig.1. Calibration DOM-optical density diagram (according to filtrates 0,45 mcm, 0,22 mcm, 0,1 mcm of samples KAR-1 and KAR-2).

The small rivers of Russia were the objects of study (northern Karelia and the Vladimir province). The first is Paloyoki river of the background territory of northern Karelia. Water sampling was conducted in three fixed points: KAR-1 (average flow), KAR-2 (the swamp, which feeds Paloyoki river), KAR-3 (mouth reach, the zone of mixing river and Pyaozero lake). Waters are fresh; pH-rate is 7.3; in the swamp - 5.54). Second object is catchment basin of Senga river. The river is right tributary stream of Klyazma river, which drains background territories of the swampy part of the Meshchera lowland. The sampling was conducted in three points: Seng-1/08 (mouth reach of Senga river), Seng-2/08 (average flow of Senga river), Ign/08 (Ignatkovo lake, it is closed lake having swampy shores). The waters are fresh and alkalescent, but pH-rate in the Ignatkovo lake is 5.44. The specific contrast in the molecularly mass distribution of OM is observed for the river of boreal region (Paloyoki) and the river of midlatitudes of Russia (Senga), although there is a similarity in marsh feeding. In both cases there is a great portion of low-molecular DOM, but difference in the hydrological regime of the rivers cause occurrence of high portion high-molecular OM in the northern river, provided by the large contribution of planar washout (fig. 2).

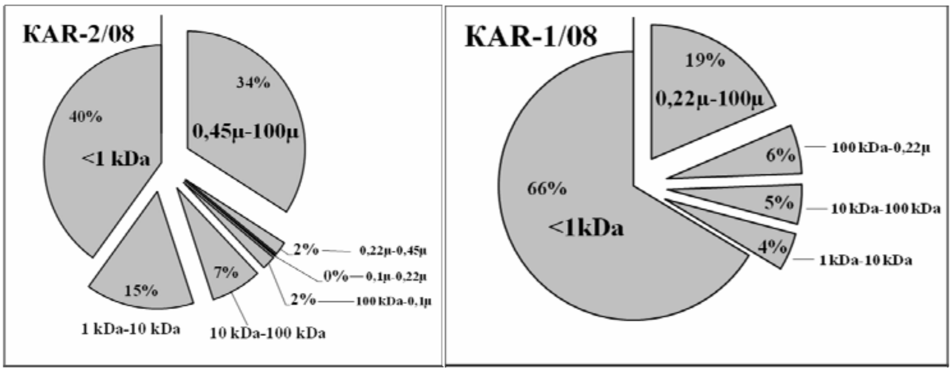


Fig.2. Distribution of Corg. on the chosen fractions of the samples: a) the swamp, which feeds Paloyoki river (KAR-2/08); b) average flow of Paloyoki river (KAR-1/08)

Initial samples after filtration through 100 mcm pore size predigitizing filter were underwent of 6-stage fractional filtration:

1) Through the FiTreM-1 filter (Dacron track diaphragm nonramming, g. Dubna) having a pore size of 0.45 mcm;

2) Through the FiTreM-1 filter (Dacron track diaphragm nonramming, g. Dubna) having a pore size of 0.22 mcm;

3) Under the pressure (1-2 atm.) through 0.1 mcm teflon membrane using a filter plant;

4) Under the pressure (0.7 atm.) through 100 kD ultrafiltration membrane “Millipore” (YM Of discs 100K NMWL of 90MM) using a filter plant “Amicon”;

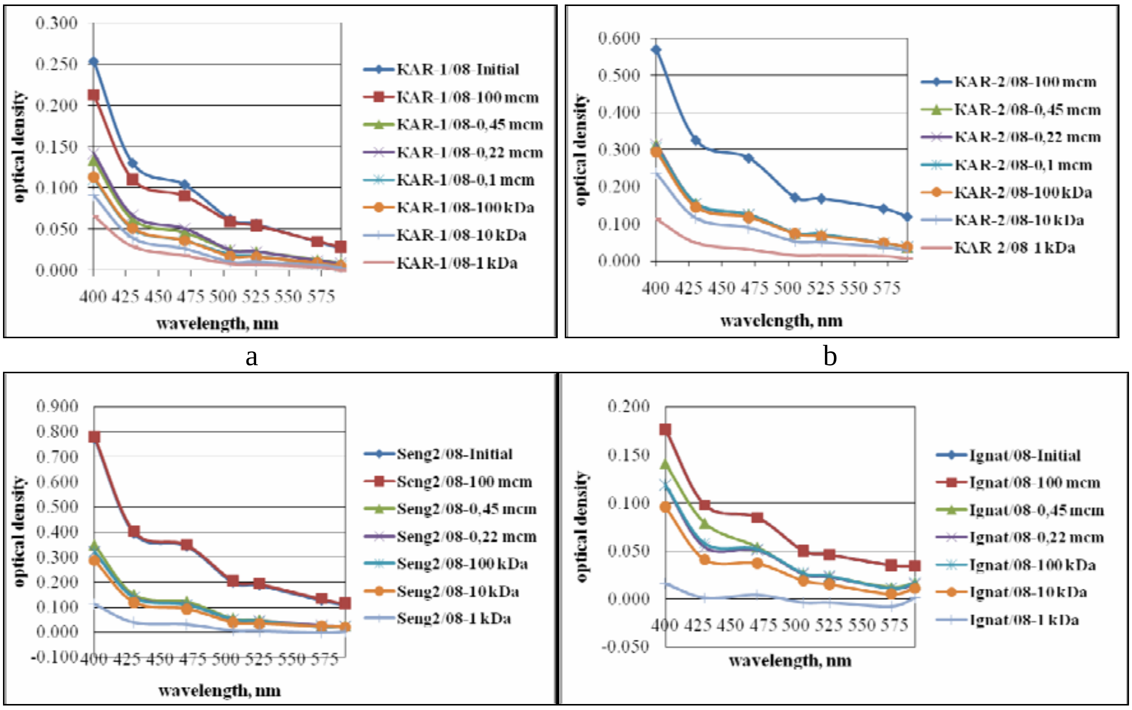
5) Under the pressure (3.7 atm.) through 10 kD ultrafiltration membrane “Millipore” (YM Of discs 10K NMWL of 90MM) using a filter plant “Amicon”

6) Under the pressure (3.7 atm.) through 1 kD ultrafiltration membrane “Millipore” (YM Of discs 1K NMWL of 90MM) using a filter plant “Amicon”

Cascade filtration using the filters 0.45 mcm, 0.22 mcm, 0.1 mcm makes it possible to obtain the more precise distribution of organic matter at the subsequent steps of the filtration, where the pore sizes (100 kDa, 10 kDa and 1 kDa) are compared with the molecular size of fulvic acids (0.0064 mcm, 0,003 mcm, 0.0014 mcm respectively), so does not occur the choking of filters by large particles. Although the molecule of humic acid can have the elongated form [3], having the sizes across flats of conditional rectangle from 0.0028 to 0.0049 mcm [4, 5], we conditionally assume molecule as a spherical in our calculated diameters of the molecules, passing through the steps of filtration. We realize, however, that the deformation of molecules during the extrusion through the small pore changing the valence angles is possible during the ultrafiltration.

This procedure makes it possible to study in detail the nature of OM distribution and the behavior of microelements in the natural waters, in particular, complexing with the fulvic acids.

The obtained spectrophotometric characteristics of initial samples and filtrates show regular difference between all spectral lines of filtrates. Decreasing of the optical density is observed from initial sample to last filtrate (fig. 3), which makes it possible to use spectrophotometry as a one of the methods of checking of the authenticity of data of OM under the field and laboratory conditions.



c d

Fig.3. Distribution of the absorption spectra of DOM during the cascade filtration (a – average flow of Paloyoki river, b – the swamp feeding Paloyoki river, c – average flow of Senga river, d – closed Ignatkovo lake)

The greatest quantity of organic matter in the swamp sample has size of particles from 0.45 to 100 mcm and <1 kDa, though the intervals of coarseness [0.45 – 100 mcm] and [0.0014 mcm (1 kDa) – 0.45 mcm] are comparable. There is a significant quantity of OM in the transition zone from humic to fulvic acids (from 1 to 10 kDa).

The sample of average flow of Paloyoki river has prevailing OM having size of the particles <1 kDa and it composes 66% of a total quantity of Corg. The fraction [0.22 mcm - 100 mcm] is second regarding the contribution to OM, where the part of OM is 19%.

It means that during the flowing from the swamp OM partially coagulates in the length with slow current, and also there is transformation and destruction of OM to particles of smaller size in the length with the rapid current.

Apparently, the basic contribution of organic matter of soils is low-molecular compounds, in essence it is fulvic acids, which are filtered with the ground food, and the ingress of high-molecular humic acid is connected with a planar washing.

The spectrophotometric monitoring of OM of the samples, which are kept in the dark during about 1 year, has shown the invariability of their optical density. It evidences about preservation of DOM. With regard to filtrates, which are standing under the daylight, it is observed the decrease of optical density to 20 - 40% in the first time, which testifies about the degradation of DOM. These studies make it possible to solve the problems of the kinetics of transformation of DOM in the river flow.

Three groups of elements are separated according to their correlation with OM. The distribution of elements in the filtrates is well correlated with the content of OM.

The first group includes the elements, complexed with high-molecular OM (Fe, Al, La- Gd, Y, V, Ti, Pb). During the filtration occurs their joint remain on the filters, i.e., their main part is connected with DOM, and the basic share of elements is connected with high-molecular OM adsorptively. About 80% of iron remains as a high-molecular form in the river and swamp water with the exception of Ignatkovo lake (fig. 4), where the low-molecular compounds of iron give a large contribution (about 80%). This is explained by the stagnant regime of the lake: ferrous colloids aggregate and gradual deposition occurs; therefore the content of iron is low in the initial sample.

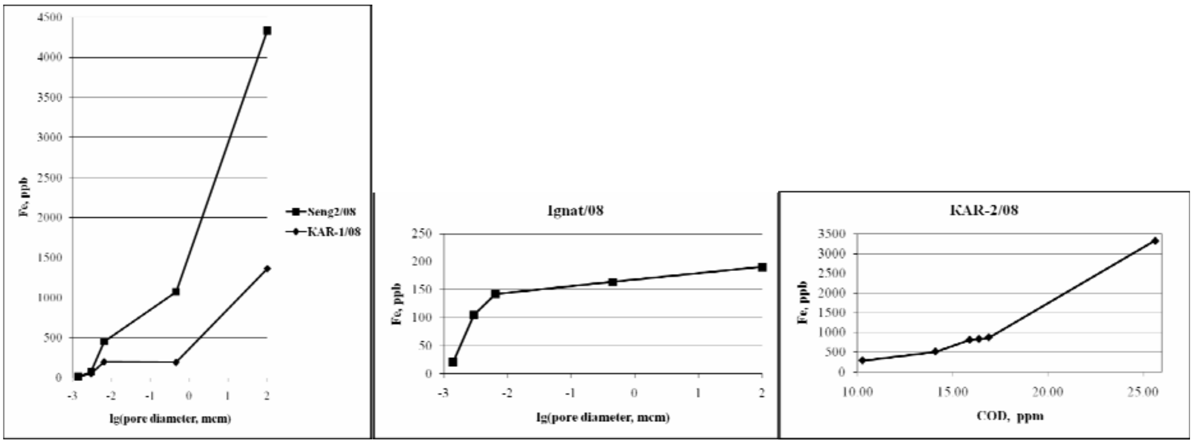
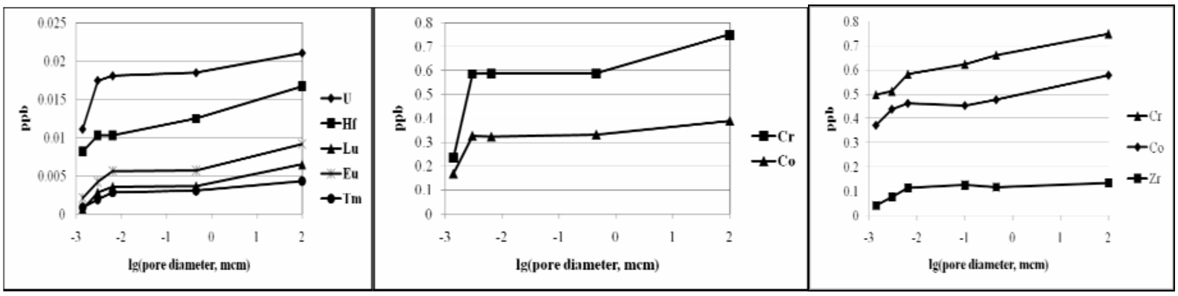


Fig.4. Distribution of iron for the filtrates of the samples of average current of Paloyoki river, Senga river and Ignatkovo lake

The second group contains the elements, having another type of filtrate distribution during the cascade filtration. They are complexed with low-molecular OM (Cr, Co, Hf, Lu, Eu, Tm, Th, U). Their deposition practically does not occur at first stages of filtration. The basic decrease of concentrations is observed in last filtrates (1- 10 kDa) (fig. 5). It means that the basic part of these microelements is located as the complexes with low-molecular OM (fulvic acid); however, adsorptive remain with the humic acid is observed for them.



a b c

Fig.5. Distribution of the elements for the filtrates of samples (a, b – average current of Senga river; c – the swamp feeding Paloyoki river)

The third group, undoubtedly, is more complex. It includes the elements, not complexed with OM (Na, K, Ca, Mg, Si, Zn) and complexes of low-molecular organic acids. We can see it according to schedule of calcium (fig. 6). It is sufficiently obvious that the remain of silica with OM on the filters does not occur, and the prevailing form is tdissolved non-polymerized flint acid (to 4.5 mg SiO_2/l).

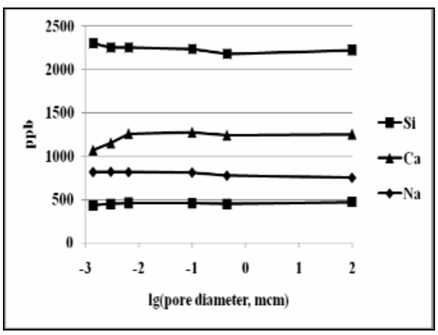


Fig.6. Si, Ca, Na and Mg concentrations in filtrates of the KAR-2/08 (swamp feeding Paloyoki river)

There are different approaches to a classification of fulvic acids and humic acid according to the molecular dimensions, and there is no strict boundary between the truly dissolved and colloidal forms of such eupolymer organic acids. It is customary to assume that the part of humic acids is not dissolved and sedimentation unstable, i.e., it gives hydrosols, which flow away by the current of river. All fulvic acids are soluble and form soluble organic complexes with metalls. The boundary of the sedimentation stability of OM of humic nature is determined by hydrological regime, but generically it corresponds to the interval from 0.1 to 1 mcm. It is possible to suggest that there is a transition zone from the processes of complexing with the soluble fulvic acids to the absorption on the hydrosols of organic matter, i.e., to complexing on the surface of humic acid.

For the investigated objects different distribution of DOM is observed on the coarseness of molecules with the significant predominance of the fractions of fulvic acids in the boreal zone and their more uniform distribution in the midlatitudes of Russia. Fraction of fulvic acids are predominant in the boreal zone (to 66%), in comparison with the waters of middle latitudes (where fulvic acids are below 20%). Degree of aggregation of OM correlates with the distribution of the certain groups of elements.

By significant variations in the concentration of DOM in different points of sampling the predominance of quantities of microelements, connected with adsorptive complexes with suspended OM, is observed. Majority it occurs for elements-hydrolyzates. Aggregation of DOM is the basic factor of transformation of the dissolved microelements to the suspension and determines their behavior in the river flow. These methodical elaborations and results lay the foundation for studying of transformation dynamics of the migration forms of the organic matter and distribution of the complexes of metals in the certain fractions of the river flow of different climatic zones.

Realized the methodical research makes it possible to validate the method of cascade filtration as foundation for studying the transformation dynamics of the migration forms of the OM, of delicate features of chain-length distribution of OM and distributing of the complexes of elements with OM in the certain fractions of the river flow of different climatic zones.

Fair investigation of the combined behavior of OM and microelements, in our opinion, needs in more depth analysis of processes their separation in the number of: soil - the DOM of soil solutions - the DOM of river waters - bottom sediments during the studying of the geochemistry problems of environment.

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