

**Pokrovsky O.S.<sup>1</sup>, Viers J.<sup>1</sup>, Shirokova L.S.<sup>2,1</sup>, Shevchenko V.P.<sup>3</sup>,  
Dupré B.<sup>1</sup>, Filippov A.S.<sup>3</sup>**

(<sup>1</sup>Géochimie et Biogéochimie Expérimentale, LMTG, Université de Toulouse, CNRS-IRD-OMP, Toulouse, France, e-mail: [oleg@lmtg.obs-mip.fr](mailto:oleg@lmtg.obs-mip.fr); <sup>2</sup>Institute of Ecological Problems of the North, Russian Academy of Science, Arkhangelsk, Russia; <sup>3</sup>Shirshov Institute of Oceanology, Russian Academy of Science, Moscow, Russia)

## **Geochemistry of trace elements and dissolved organic carbon in Severnaya Dvina during different seasons**

Key words: trace elements, dissolved organic carbon, boreal zone, Severnaya Dvina River

Geochemistry of trace elements (TE) in boreal regions attracts large attention of researchers in view of on-going environmental changes that can affect both the fluxes of these elements to the ocean, their speciation and thus their bioavailability. High concentration of dissolved organic matter (DOM) and thus, organo-mineral colloidal status of most metals is the most important characteristic feature of European Russian Arctic zone biogeochemistry. Most trace elements in waters of boreal zone are transported via organic and organo-mineral colloids whose relative role changes during the year [1–3]. Except for a few studies of soil and river solute migration in Alaska [4] and occasional trace elements measurements in the Siberian Arctic [5–7], studies addressing colloidal vs. dissolved forms and transport of TE in organic-rich waters from pristine watersheds of the Arctic Ocean basin are scarce.

Specific feature of all boreal watersheds is an important flux of dissolved and particulate elements during relatively short high-level period of snowmelt in April to June. Concerning the boreal European Russian zone, all previous studies, similar to those of the Siberian Arctic and Canada dealt with analysis of samples collected during summer baseflow period [8]. Seasonally-resolved fluxes were assessed only for major elements in Karelia Region [9] and, with some smaller resolution, of the Mackenzie, Yukon, Kolyma, Lena, Yenissei and Ob rivers via the PARTNERS program in 2003–2004 [10]. However, the latter study dealt only with total dissolved (< 0.22 µm) and suspended fractions. At the same time, Swedish researchers devoted significant amount of efforts to understand the geochemistry of major and trace elements in small boreal catchments of the Baltic Sea basin, notably the Kalix river [1, 11]. It has been demonstrated that the main flux of usually insoluble elements occurs during the spring melt and that both organic and organo-mineral colloids exert strong control on TE speciation in the river water.

The main difference with Kalix river system, having similar climate conditions, is much larger size of Severnaya Dvina river watershed (348000 km<sup>2</sup> which is ~80% the territory of Sweden) and different lithological context: in case of Severnaya Dvina and Pinega watershed, the granitic till with spodosol soil profile is underlined, essentially by carbonate and partially by gypsum

sedimentary rocks (Fig. 1). Another important difference of Severnaya Dvina River with well studied small Scandinavian and Karelian watersheds is the weaker influence of lakes on the former river's hydrology and chemical composition; however, the effect of bogs and mires is quite important for Severnaya Dvina basin.



**Fig. 1.** Map of the studied area showing main lithological context and sampling locations in the Arkhangelsk region.

To summarize, except for the small river of the Baltic Sea basin and occasional measurements of total dissolved load of large arctic rivers, the seasonal flux and speciation of trace metals in rivers discharging to the Arctic ocean remain largely unknown. This study is aimed at extending this knowledge to the largest unregulated European river, Severnaya Dvina and its tributary (Pinega River).

The chemical status of major and trace elements (TE) and organic carbon (OC) has been studied in Severnaya Dvina and Pinega Rivers draining granitic moraine, carbonate and sedimentary deposits of the Arkhangelsk region (NW Russia). Sampling was performed during winter and summer baseflow seasons and during the spring flood (2007–2008) [12]. Altogether, 30 samples of Severnaya Dvina River in its mouth, 20 samples of Pinega River and its three tributaries, and a typical ombrotrophic bog feeding the large river in spring were sampled. Size separation procedure included on-site filtration through 5  $\mu\text{m}$ , 0.22  $\mu\text{m}$ , 100, 10 and 1 kDa and dialysis through 1 kDa and 10 kDa pore size membrane.

Organic carbon concentration in “truly” dissolved form (< 1 kDa) does not depend on rock lithology and season being in average equal to  $5.0 \pm 1.4$  mg/L (Fig. 2). Our observations indicate the presence of two pools of organic matter: allochthonous large-size colloids formed by lixiviation from upper soil horizons

and autochthonous (aquatic) small molecular-size substances, probably linked to bacterial and phytoplankton exudates. While the proportion of the formers is highly seasonally dependent, the contribution of the latter's remain relatively constant over the year. The total dissolved concentration of colloidal TE correlates with that of OC and Fe, being the highest during the spring flood and the lowest in winter time. There are two different patterns of TE colloidal status during different period of the year, depending on their association with organic or organo-mineral constituents of colloidal matter.

Trace and major elements concentration in the suspended matter of Severnaya Dvina River was measured during different seasons over 3 years of observation. Based on collected data, we evaluated, for the first time, the seasonal fluxes of all major and trace elements in the suspended ( $> 0.22 \mu\text{m}$ ), total dissolved ( $< 0.22 \mu\text{m}$ ) and colloidal (1 kDa –  $0.22 \mu\text{m}$ ) forms. On the annual basis, there is a significant contribution ( $\geq 30\%$ ) of conventionally dissolved ( $< 0.22 \mu\text{m}$ ) forms into overall flux of usually low mobile elements such as divalent transition metals, Cd, Pb, V, Y, all REEs, Zr, Hf, Th. The spring flood occurring in May provides between 30 and 60% of total annual dissolved and suspended flux of many insoluble trace elements (Fe, Co, Ni, Cr, Y, all REEs, Cd, Pb, Zr, Hf, Th). We argue that the typical feature of many trace element fluxes in the Arctic rivers is high proportion of total dissolved ( $< 0.22 \mu\text{m}$ ) compared to suspended pool due mostly to the high contribution of colloidal forms.

**Acknowledgements.** This work was supported by the French National Programme INSU (EC2CO, Environnement Côtier PNEC), by European Associated Laboratory "LEAGE", and by Project 17.1 of the Program 17 of Fundamental Studies of Presidium of Russian Academy of Sciences and Grant of President of Russia NSh-361.2008.5. We thank all colleagues who helps us in the field, Academician A.P. Lisitzin for useful discussions, V.B. Korobov and N.N. Zavernina for supplementary hydrological data.

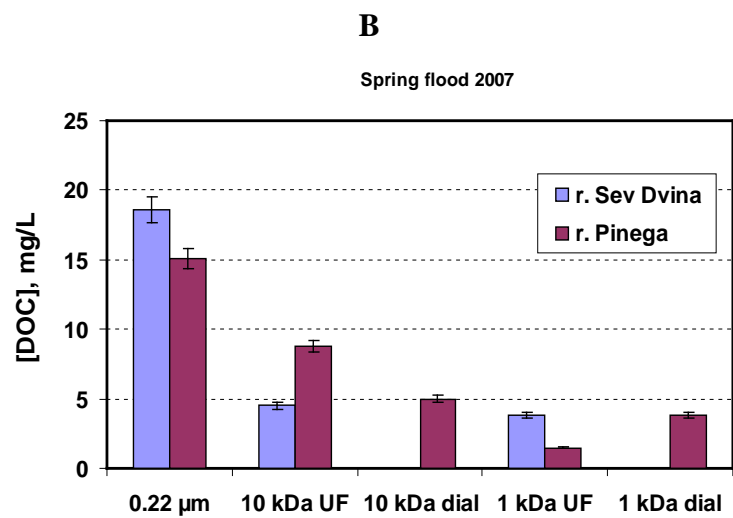
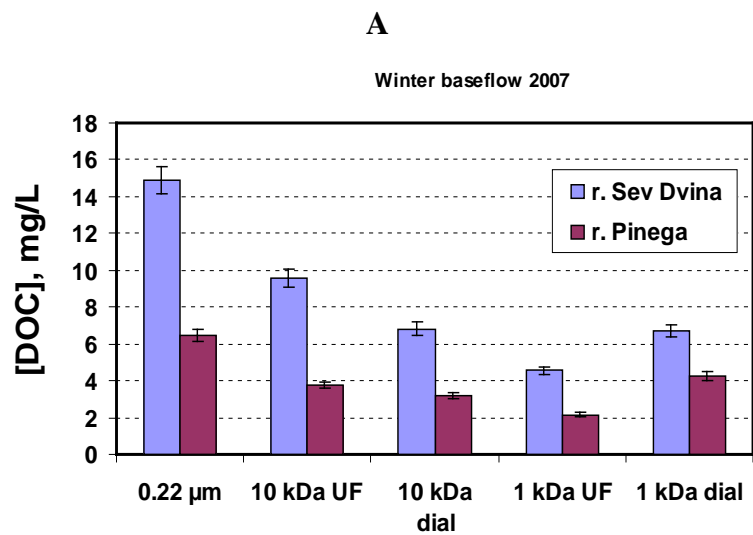


Fig. 2. DOC speciation during winter baseflow (A) and spring flood (B) as follows from results of UF and dialysis procedure.

### References

1. Ingri J., Widerlund A., Land M. et al. Temporal variations in the fractionation of the rare earth elements in a boreal river, the role of colloidal particles // *Chemical Geology*. 2000. V. 166. P. 23–45.
2. Pokrovsky O. and Schott J. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia) // *Chemical Geology*. 2002. V. 190. P. 141–179.
3. Dahlgvist R., Andersson K., Ingri J. et al. Temporal variations of colloidal carrier phases and associated trace elements in a boreal river // *Geochimica et Cosmochimica Acta*. 2007. V. 71. P. 5339–5354.
4. Rember R.D. and Trefry J.H. Increased concentrations of dissolved trace metals and organic carbon during snowmelt in rivers of the Alaskan Arctic // *Geochimica et Cosmochimica Acta*. 2004. V. 68. P. 477–489.
5. Dai M. and Martin J. First data on trace metal level and behaviour in two major Arctic river-estuarine systems (Ob and Yenisey) and in the adjacent Kara Sea, Russia // *Earth Planet. Sci. Lett.* 1995. V. 131. Nos. 3–4. P. 127–141.
6. Moran S.B. and Woods W.L. Cd, Cr, Cu, Ni and Pb in the water column and sediments of the Ob-Irtysh Rivers, Russia // *Mar. Poll. Bull.* 1997. V. 35. P. 270–279.
7. Pokrovsky O.S., Schott J. and Dupré B. Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basic terrain in Central Siberia // *Geochimica et Cosmochimica Acta*. 2006. V. 70. P. 3239–3260.
8. Pokrovsky O.S., Dupré B. and Schott J. Fe-Al-organic colloids control of trace elements in peat soil solutions // *Aquat. Geochem.* 2005. V. 11. P. 241–278.
9. Zakharova E.A., Pokrovsky O.S., Dupré B. et al. Chemical weathering of silicate rocks in Karelia region and Kola Peninsula, NW Russia: Assessing the effect of rock composition, wetlands and vegetation // *Chemical Geology*. 2007. V. 242. P. 255–277.
10. <http://ecosystems.mbl.edu/partners>
11. Ingri J., Malinovsky D., Rodushkin I. et al. Iron isotope fractionation in river colloidal matter // *Earth Planet. Sci. Lett.* 2006. V. 245. P. 792–798.
12. Pokrovsky O.S., Viers J., Shirokova L.S. et al. Trace element fluxes and colloidal speciation in large subarctic rivers during different seasons // *Chemical Geology*. 2009 (submitted).