

# Impact of filtration artifacts on the seasonality of river waters chemical composition

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**Abstract.** The difference in concentration of filterable trace metals, macro ions, nitrate and dissolved organic carbon (DOC) after capsule and membrane 0.45  $\mu\text{m}$  filters was studied at the seasonal sampling of the typical medium size boreal Razdolnaya River, Far East of Russia. Trace metals showed notable decrease after membrane filtration compared with capsules, though concentrations of macro ions, nitrates and DOC were equal. Clogging of membranes with subsequent retention of coarse colloids was suggested as a reason for this difference. In summer the dissimilarity in concentration grew in order  $\text{Cu} < \text{Zn} < \text{Ni}$ ,  $\text{Cd} < \text{Mn} < \text{Fe}$  reflecting a significant role of coarse colloids in the pool of filterable forms for Fe and Mn. In winter, retention of Mn was declined due to input of ionic forms from redox cycle. Floods are the periods with the most notable increase of coarse colloids content and maximum bias in the determination of filterable trace metals if frontal membrane filtration is being used.

## 1 Introduction

Correct separation between particulate/colloidal and dissolved forms of chemical substances is necessary for the proper assessment of the water quality, fluxes with river runoff, and sorption processes in the water-suspended solids system. Filtration through the membranes or capsules with pore size 0.45  $\mu\text{m}$  continues to be the most often used technic, though several problems were raised at the separation of particulate, colloidal and dissolved forms of trace elements in river waters. Contamination of the dissolved phase has been overcome in general by the implementation of clean technic at the sampling and analysis [1]. Another issue connected with the separation of colloids and truly dissolved forms is successfully resolved by applying of ultrafiltration in combination with dialysis technic [2, 3].

Additional problem is a clogging of filters. Colloids smaller than 0.45  $\mu\text{m}$  are retained in this case and concentration of filterable forms are reduced by poorly predicted manner. This fact has attracted notable attention more than 20 years ago [4, 5]. According to the last review [6] the filtration artifacts due to clogging of filters 0.45  $\mu\text{m}$  continue to be a problem in obtaining reliable concentration of filterable forms of trace metals. The main reason of the pendency of this issue is a dependence of clogging not only from filters characteristics,

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but also from the influence of natural factors (content of suspended solids and coarse colloids) that are not under our control. General recommendation could be to use filters with high filtering capacity, such as capsules/cartridges, or to minimize the volume of samples at the filtration through the membranes [7].

It seems necessary to compare capsules and membranes with similar nominal pore size 0.45  $\mu\text{m}$  to obtain filterable forms of chemical substances at the different content of suspended solids. This is especially important for the study of seasonality of chemical composition of river waters, because suspended solids usually show distinct seasonal variability.

The objective of this paper is to assess the difference in filterable forms of trace metals (Fe, Mn, Zn, Cu, Ni, Cd) as well as macro ions ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ), nutrients ( $\text{NO}_3^-$ ), and dissolved organic carbon (DOC) in the filtrates of river water obtained after Pall® GWV capsules and Millipore® Durapore PVDF membranes. The study was carried out as part of a comprehensive research on the seasonality of chemical composition and fluxes of the Razdolnaya River – typical boreal medium size river with watershed 16.8\*10<sup>3</sup> km<sup>2</sup> and averaged annual runoff 2.3 km<sup>3</sup>. Second goal of this paper is to highlight the possible influence of the filtration on the assessment of seasonal variability of concentration and fluxes of filterable chemical compounds including trace metals in the rivers of boreal zone.

## 2 Materials and methods

### 2.1 Sampling and processing

The Razdolnaya R. drains the watershed located in China, North Korea (DPRK) and Russia territory with mouth and estuary situated in Russia at the northwestern coast of the Sea of Japan (Lat. 43°17', Long. 131°49'). Water regime of the Razdonaya R. is characterized by low discharge in winter during ice cover period (5-10 m<sup>3</sup>/s), spring floods (250-350 m<sup>3</sup>/s) in April-May, and monsoon floods in August-September (with monthly average up to 440-510 m<sup>3</sup>/s), and decreasing discharge down to 20-30 m<sup>3</sup>/s in October-November. The seasonal variability of suspended solids is also very high: from 3-6 mg/l in winter to 30-70 mg/l during regular runoff in summer, and up to 300-400 mg/l at high discharge.

Samples were taken biweekly or monthly from May 2015 until November 2017 at the downstream, but outside the seawater influence. Sampling was carried out from the riverbank using plastic 4 m pole with attached HDPE bottle. All precautions were done to avoid contamination (duly prepared bottles, double plastic bags, repeated rinsing by samples, plastic gloves). Within several hours 1 L subsample was filtered through the Pall GWV capsule filter, and another 1 L – through the preweighted 47 mm diameter Millipore Durapore membrane. Both filters have nominal pore size 0.45  $\mu\text{m}$ , but capsule has filtration area 700 cm<sup>2</sup>, and membrane – ca. 15 cm<sup>2</sup>. MasterFlex® peristaltic pump was used with capsules, and Sartorius filter holders for filtration through Millipore membrane under vacuum. Filtration was carried out at the clean bench with all precautions to avoid contamination.

### 2.2 Analysis

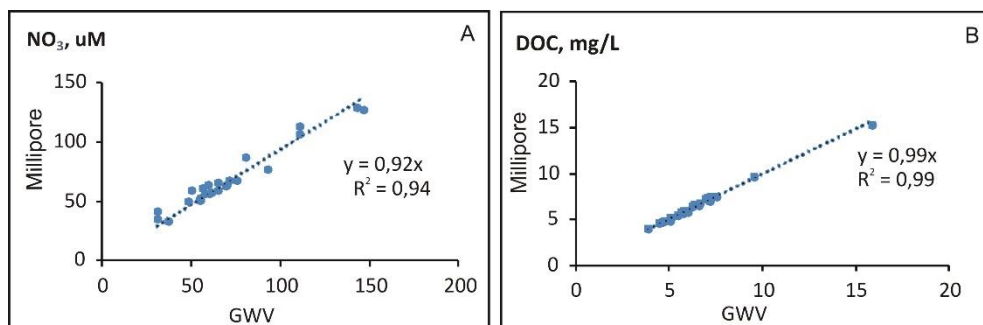
Analysis of cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) was carried out by flame atomic absorption spectroscopy.  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  were analyzed by ion-chromatography, and DOC – by thermocatalic oxidation (Shimadzu TOC-Vcpn). Suspended solids content was evaluated by the weighting of Millipore membranes after filtration and drying at 80°C. Analysis of filterable forms of trace metals was carried by atomic absorption after pre-concentration 50-

100 times. Good compatibility with difference less than 15% has been shown for the simultaneous determination of dissolved metals in the river waters by this method and direct analysis of the metals in the same samples by ICP-MS [8].

### 3 Results and discussion

#### 3.1 Effect of the filters on the concentration of filterable chemical components

Concentration of macro ions, nitrates and DOC in the filtrates obtained after capsules and membranes are equal within the accuracy of analytical methods along the entire range of seasonal variability regardless of the water regime or suspended solids content (Fig. 1 as example for nitrates and DOC). This means that all these substances do not depend on the possible clogging of membrane filters even at the high content of suspended solids. The main reason is a dominance of truly dissolved forms for macro ions and small colloids for DOC in the water of Razdolnaya R. all year around. It is not a surprise for macro ions [2], and supported by detailed studies of colloidal forms for DOC with evidence of prevailing small colloidal forms [3, 9] passing through even clogged membranes with pore size 0.45  $\mu\text{m}$ .



**Fig. 1.** Concentration of nitrates ( $\mu\text{M}$ ) and DOC (mg/L) in filtrates obtained after GWV capsules (X-axis) and Millipore membranes (Y-axis).

Concentration of filterable forms of some trace metals after capsules was notably higher than after membranes (Table 1). It is especially true for filterable Fe with concentration after capsules significantly increased during all seasons (Table 1). Maximum excess was observed in the summer and minimum in the autumn. For other trace metals, the significant difference (Mann-Whitney test  $p < 0.05$ ) was detected in spring and summer only (Table 1). In autumn, the surplus of filterable forms after capsules observed for Fe, and Cd, and in winter excess was registered for Fe, only (Table 1). Such trends in seasonal variability of the difference between filterable forms of the trace metals after capsules and membranes indicate two features of trace metals speciation in river waters. First one is a prevalence of coarse colloids, retained by clogged membranes, in the pool of conventionally dissolved ( $< 0.45 \mu\text{m}$ ) Fe forms. Dominance of coarse colloids for the dissolved Fe was observed for many other rivers [2, 6, 10]. Secondly, for all trace metals studied, maximum difference in concentration, and consequently the most significant role of retained coarse colloids was observed in summer when content of suspended solids is elevated as well.

Dissolved Mn is the only metal showing significantly elevated concentration of filterable forms in winter, when difference between Mn after capsules and membranes is

absent (Table 1). This means that in winter Mn does not associate with coarse colloids and therefore is not retained by clogged membrane. On the other hand in summer filterable Mn demonstrates similar to other trace metals excess after capsules indicating association with coarse colloids retained by clogged membranes (Table 1). Seasonality of dissolved Mn is explained by the influence of Mn release at the redox processes in bottom sediments as ionic compounds [5].

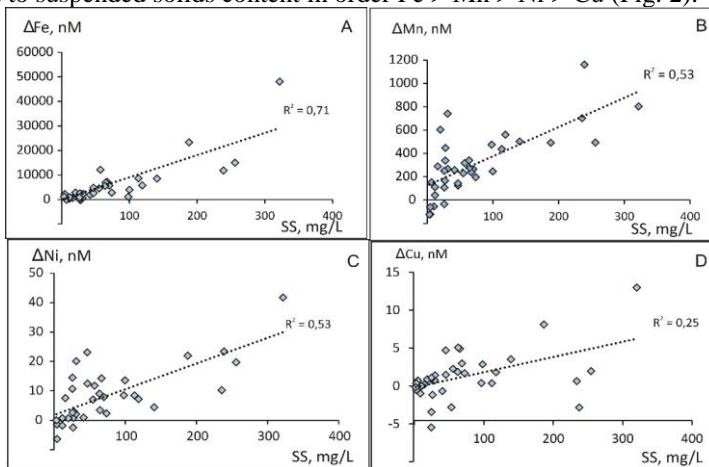
**Table 1.** Concentration of trace metals (nM) obtained after capsule GWV and membrane Millipore filters in the waters of the Razdolnaya R. in different seasons.

Season	Fe		Mn		Zn		Cu		Cd		Ni	
	GWV	Milli	GWV	Milli	GWV	Milli	GWV	Milli	GWV	Milli	GWV	Milli
<b>Spring-Summer, n=20</b>												
<b>med</b>	<b>6318</b>	<b>665</b>	<b>646</b>	<b>282</b>	<b>17</b>	<b>13</b>	<b>22</b>	19	<b>0.017</b>	<b>0.007</b>	<b>28</b>	<b>18</b>
<b>aver</b>	9866	282	707	321	23	17	22	20	0.023	0.014	31	20
<b>std</b>	10443	396	423	256	14	12	7	5	0.017	0.017	17	9
<b>Fall, n=8</b>												
<b>med</b>	<b>1207</b>	<b>604</b>	754	<b>798</b>	8	10	12	13	<b>0.024</b>	<b>0.014</b>	21	18
<b>aver</b>	1169	684	916	751	7	11	11	12	0.030	0.018	20	17
<b>std</b>	411	321	558	450	3	13	3	4	0.017	0.009	4	6
<b>Winter, n=5</b>												
<b>med</b>	<b>2557</b>	<b>896</b>	3170	<b>3294</b>	18	18	<b>13</b>	13	0.020	0.018	<b>21</b>	21
<b>aver</b>	2339	899	3863	3773	18	19	13	13	0.022	0.018	21	22
<b>std</b>	1198	343	3242	3423	7	7	4	3	0.006	0.010	3	5

Med – median, aver – average, std – standard deviation, n – number of samples; concentrations are significantly differing by Mann-Whitney test ( $p < 0.05$ ) are marked as bold italic.

### 3.2 Suspended solids as a factor controlling the difference in filterable trace metals

Content of suspended solids is the most obvious factor determining clogging of the filters. Higher quantity of suspended matter during the floods provides faster clogging. Amount of coarse colloids is also elevated at the seasonal increase of suspended solids. As a result, difference in concentration of filterable trace metals due to retention by clogged membranes is correlated to suspended solids content in order  $Fe > Mn > Ni > Cu$  (Fig. 2).



**Fig. 2.** Difference of filterable forms of metals after capsules and membranes ( $\Delta Me = Me_{\text{capsule}} - Me_{\text{membrane}}$ , nM) against concentration of suspended solids (SS, mg/L).

### **3.3 Influence of filters clogging on the assessment of seasonality of dissolved and particulate trace metals concentrations and fluxes in river waters**

Underestimation of filterable “dissolved” forms of trace metals during summer floods is most obvious consequence at the use of standard 47 mm membranes with pore size 0.45  $\mu\text{m}$ . The impact of the retention of coarse colloids at the clogged membranes declines in late autumn and in winter in accordance with seasonally diminished level of suspended solids in river waters of studied northwest Pacific region.

Underestimation of filterable trace metals has an impact on the assessment of their fluxes to the sea. Most pronounced bias coincides with elevated water discharge in floods, when obvious multiplicative effect takes place. Calculation of fluxes of particulate and filterable forms shows that variation of water discharge is a major factor controlling fluxes. The strong prevalence of particulate Fe forms diminishes influence of significant variability in filterable Fe forms on the total flux to the sea. Role of coarse colloidal forms of Mn in summer flux is more important, despite the concentration of filterable Mn is much higher in the winter (Table 1). For other trace metals with less significant difference between “capsule” and “membrane”, the changes of fluxes are proportional to the quota of coarse colloids.

## **4 Conclusions**

Concentration of filterable forms of some trace metals (Fe, Mn, Zn, Ni, Cd) in the boreal Razdolnaya R. was higher after capsule compared to membrane filters 0.45  $\mu\text{m}$ . Macroions, nitrates and DOC do not show any notable difference. The clogging of membranes with retention of coarse colloids is the reason. The retention was minimal for Cu (10%), and increased for Zn (27%), Ni (37-53%), and Cd (35-61%) with higher difference at the flood regimes, and in accordance with the role of large colloids in the pools of these metals in river waters. For Mn difference was notable (~60%) in summer floods, but negligible in winter due to increased role of truly dissolved Mn released from sediments. Most substantial difference was observed for Fe: during the floods concentration after membranes could be 10-30 times less than after capsules, in accordance with prevalence of coarse colloids in the pool of conventionally dissolved Fe. Besides using of capsules with high filtering capacity and minimizing of sample volume, the check of possible bias at the floods could be recommended for the more accurate assessment of filterable forms of Fe, Mn and other trace metals attracted to coarse colloids.

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## **References**

1. G. Benoit, K.S. Hunter, T.F. Rozan, *Anal.Chem.* **69**, 1006 (1997)
2. O.S. Pokrovsky, J. Schott, *Chem. Geol.* **190**, 141 (2002)
3. O.S. Pokrovsky, J. Viers, L.S. Shirokova, V.P. et al., *Chem. Geol.* **273**, 136 (2010)
4. Horowitz, K. Elrick, M. Colberg, *Wat. Res.* **26**, 753 (1992)
5. M. Morrison, G. Benoit, *Env. Sci. & Tech.*, **35**, 3774 (2001)
- A. J. Horowitz, *Env. Sci. & Tech.*, **47**, 2471 (2013)
6. A.M. Shiller, *Env. Sci. & Tech.*, **37**, 3953 (2003)
7. V.M. Shulkin, N.N. Bogdanova, V.I. Kiselev, *Geochem. Intr.*, **45**, **1**, 70 (2007)

8. O.S. Pokrovsky, L.S. Shirokova, J. Viers, V. V. Gordeev, V. P. Shevchenko, A.V. Chupakov, T.Y. Vorobieva, F. Candaudap, C. Causserand, A. Lanzasova, and C. Zouiten, C., *Ocean Sci.*, **10**, 107 (2014)
9. D. Vignati, J. Dominik, *Aqua. Sci.*, **65** (2), 129 (2003)