#### Applied Geochemistry 63 (2015) 133-145

Contents lists available at ScienceDirect

**Applied Geochemistry** 

journal homepage: www.elsevier.com/locate/apgeochem

### Flood zone biogeochemistry of the Ob River middle course

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#### ARTICLE INFO

Article history: Received 2 April 2015 Received in revised form 4 August 2015 Accepted 6 August 2015 Available online 10 August 2015

Keywords: Siberia Flood Lakes Rivers Organic carbon Metals Colloids

#### ABSTRACT

The flood zone of the Ob River, the largest (in watershed area) river of the Arctic Ocean basin, is tens of km wide and, after the Amazon's Varzea, is the world's second largest flooding territory. To better understand the biogeochemistry of the Ob River and adjacent surface waters, we studied, in May and July 2014, the dissolved and colloidal organic carbon and trace metals in small rivers, lakes, and flooded water bodies connected and disconnected with the mainstream as well as the Ob River itself. All major and trace elements were distributed among two major categories depending on their pattern of dependence on the dissolved organic carbon (DOC) concentration. Dissolved inorganic carbon (DIC), Na, Mg, Ca, sulfate, Sr, Mo, Sb and U exhibited a general decrease in concentration with the increase of the [DOC]. The lowest concentration of these elements was observed in DOC-rich humic, acidic ( $4.9 \le pH \le 6.1$ ) upland lakes fed by surrounding bogs. These elements marked the influence of underground feeding in July during summer baseflow, which was most visible in flood lakes in the Ob riparian zone and the Ob River itself. In May, the flood lakes were statistically similar to the Ob River. The elevated concentration of DOC (up to 60 mg/L) in the upland lakes was not correlated with groundwater-related elements, suggesting a lack of significant groundwater feeding in these lakes. In contrast, insoluble, usually low mobile elements (Al, Fe, other trivalent hydrolysates, Ti, Zr, Hf) and some metals (Cr, Zn, Ni, Pb) demonstrated a steady increase in concentration with increasing DOC, with the lowest values observed in the Ob River and the highest values observed in small tributaries and organic-rich upland lakes in July. It follows that these elements are limited by their main carriers - organic and organo-ferric colloids, rather than by the availability of the source, peat and mineral soil or plant litter. While for the majority of non-colloidal, groundwater-fed elements with high mobility (DIC, Na, Mg, Ca, K, Sr...) the small tributaries can be used as representatives of the Ob main stream, this is not the case for low mobility "insoluble" elements, such as Fe, Al, trivalent and tetravalent hydrolysates, and metal micronutrients (Cu, Zn, and Mn). The low soluble elements and divalent metals exhibited a much lower concentration in the river mainstream compared to that in the flood lakes, upland lakes and small rivers. This difference is significantly more pronounced in the baseflow in July compared to the spring flood in May. Presumably, autochthonous processes, such as the photo-oxidation and bio-oxidation of organo-ferric colloids and phytoplankton uptake are capable decreasing the concentration of these elements in the river mainstream.

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#### 1. Introduction

Despite the importance of the Ob River, the largest river discharging to the Arctic Ocean in terms of watershed area, systematic seasonally resolved studies of this river's dissolved load (carbon

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http://dx.doi.org/10.1016/j.apgeochem.2015.08.005 0883-2927/© 2015 Elsevier Ltd. All rights reserved. and metals) are limited compared to those of the Lena, Yenisei and Mackenzie Rivers. A possible reason for this understudy could be the weak coverage of the Ob watershed by permafrost (only 30% of the basin compared to 75%, 90%, and 100% of the Mackenzie, Yenisei, and Lena watersheds, respectively, Environment Canada, 2015; McClelland et al., 2004), which is the object of attention of most "arctic" researchers. However, ongoing climate change in the boreal and subarctic region will likely cause not only permafrost degradation and a respective river flux change but will also affect







the precipitation regime and, in particular, the relative contribution of the spring flood versus summer and winter baseflow (Peterson et al., 2002; McClelland et al., 2006; Shiklomanov and Lammers, 2009; Rennermalm and Wood, 2010). Here, the importance of the Ob River is triple. First, the Ob River, exhibiting the second largest (after the Amazon's Varzea, Viers et al., 2005) flooding area, may become the largest contributor of dissolved carbon and related element transport from the land to the Arctic Ocean. Second, the majority of the Ob's watershed lies within the highly productive boreal taiga zone. The productivity of the terrestrial boreal biome is at its highest at the riparian zone and river banks, especially in the permafrost-free region (Huston and Wolverton, 2009). Because the degradation of plant litter is one of the major factors regulating the overall export of DOC and chemical elements from the boreal watersheds (Laudon et al., 2012; Pokrovsky et al., 2012) and because plant litter leaching is very fast (Aerts and Chapin, 1999), the spring flood period on the Ob River is especially important for the biogeochemistry of the western Siberia plain. Third, the Ob River watershed is likely to be most vulnerable to on-going climate change and permafrost thaw because the major part of its permafrost coverage is intermittent and sporadic permafrost (0-2 °C), rather than the continuous and discontinuous permafrost that is observed in other Arctic rivers (McClelland et al., 2004). The former is known to be most vulnerable to the ground temperature rise (Romanosvky et al., 2010).

The further importance of the Ob River and its watershed for the Arctic and subarctic region function stems from the very high dissolved Fe concentration in this river: the mean value for the period 1990–1996 is a factor of 5 higher than that of the Yenisey and the Lena rivers (Alexeeva et al., 2001). As a result, the Ob River provides almost 40% of the total flux of this important, potentially limiting micronutrient (i.e., Harrison and Cota, 1991; Schroth et al., 2014) and essential vector of metal transfer in surface waters (Hassellov and Von Der Kammer, 2008) from the land to the whole Arctic basin (Alexeeva et al., 2001). In the Western Siberia Lowland (WSL) rivers in general and in the Ob River watershed in particular, the elevated concentration of dissolved organic matter (DOM) linked to the abundance of peat bogs and wetlands is the main hydrochemical feature rendering this territory an important source of dissolved organic carbon (DOC) to the Arctic Ocean (cf., Lobbes et al., 2000; Frey and Smith, 2005; Dickens et al., 2011; Amon et al., 2012). The majority of divalent metals, trivalent and tetravalent hydrolysates are likely to be transported in the form of organic and organo-mineral colloids whose migration capacity and bioavailability depends on the nature of DOM. The DOM of terrestrial (peat and forest floor) or aquatic (phytoplankton and water plants exometabolites) origin may be subjected to photo- and biodestruction as it is fairly known for the boreal zone (Von Wachenfeldt et al., 2008; Hanson et al., 2011; Koehler et al., 2012; Ilina et al., 2014). These processes produce large variety of TEbearing colloids in western Siberia lakes and ponds of the permafrost-subjected zone (Pokrovsky et al., 2011; Shirokova et al., 2013). However, the degree of transformation of these organic colloids in small and large rivers, permanent and ephemeral lakes receiving different inputs from bogs, forests and flooded meadows of the Ob River floodplain, remains fairly unknown. Note that, while the effect of water discharge from the flood plain lakes is addressed in numerous hydrological studies of Western Siberia (Nikitin and Zemtsov, 1986; Yang et al., 2004; Zakharova et al., 2014) the effects of the flood zone of the main river hydrochemistry are totally unknown since no transect-like study on the Ob River watershed has been performed so far.

To better understand the mechanisms regulating the contemporary fluxes of carbon, trace metals and major nutrients at the Ob watershed and to predict possible future changes, the use of the time series only at the terminal gauging station (i.e., Cooper et al., 2008; Holmes et al., 2012) is not sufficient. Rather, detailed, seasonal studies of the different components of the watershed, such as the small tributaries, flooded water bodies and adjacent lakes, are necessary to reveal the variation of chemical composition, along a transversal flooding gradient.

To achieve this goal, we sampled small first order tributaries as well as upland and flooded zone lakes and the Ob River's middle course in the boreal taiga zone during the spring flood (May) and the summer baseflow (July). The chosen site is highly representative for the Ob River middle course (approx. 1000 km length) located within the permafrost-free zone. We addressed the following specific questions:

- (i) How variable is chemical composition of the main river, permanent and ephemeral lakes, secondary channels and small tributaries along a transversal flooding gradient?
- (ii) Can we distinguish the control of the groundwater versus surface runoff on the river and lake hydrochemistry during two contrasting seasons?
- (iii) How important is the control of the dissolved organic carbon on the TE concentration and colloidal forms in various surface water bodies?

We anticipate that understanding the main features of the dissolved load transformation between the feeding water bodies and the main rivers may help to predict the magnitude and direction of future changes of the Ob River's middle course hydrochemistry in response to the water flooding, river discharge regime and water temperature rise.

#### 2. Study sites and methods

The middle course of the Ob River, located within the boreal taiga biome (Fig. 1A), includes (i) isolated and interconnected water bodies that are flooded during the spring period but are persistent during baseflow (called herein "flood lakes"); (ii) the flooded area of the river valley and first terrace that is covered by the river during high flow in May and extends, via a system of interconnected shallow ephemeral lakes and primary and secondary water channels, over 5-10 km from the main water channel (called "flood zone"); (iii) permanent lakes located at the upper terraces of the river that are not flooded during the spring ("upland lakes"); and (iv) small, first order tributaries of the Ob River that have a watershed area of 10–100 km<sup>2</sup> and drain both the terraces and the flood zone ("small rivers"). Here, we operationally define an "upland" as the territory of the 1st to 3rd river terraces that are not subjected to flooding. The upland is at a higher elevation than the alluvial plain, which is considered to be "lowland" (see profile Fig. 1B). Note that upland lakes, typical water objects of the middle taiga zone of the WSL, serve as first source of DOC, metals and other solutes to the rivers and small streams reaching the Ob' River and can be considered as end-members subjected to maximal influence of bog feeding having minimal degree of groundwater discharge. To some degree, the normal transect of the Ob River middle course and its flooding zone is similar to that of the Mackenzie Delta lakes, comprising a significant flooding gradient (i.e., Squires et al., 2002; Tank et al., 2009).

The water residence time (WRT) in studied water bodies was evaluated based on the hydrological balance of the flood zone comprising the daily water flux at the nearest hydrological gauging station at Nikolskoe following the procedure recommended for western Siberia rivers (Nikitin and Zemtsov, 1986), the water volume of the lakes and in-field measurements of their inlet and outlet, or in the case of closed upland lake, the evaporation/



Clay

Fig. 1. A. Map of the Ob River flooding zone in its middle course with sampling points. B. A–B transect of the sampling region (Fig. 1A) showing the dominant water objects, vegetation, soils and lithology. The main autochtonous and allochthonous processes are discussed in the text (see Section 4).

precipitation balance of the territory. Given that the year 2014 was typical in terms of precipitation, flood and baseflow discharge, we used mean multi-annual hydrological data for these evaluations. In the absence of the gauging station at the river, we used either analogous river approach or mean values for the area-normalized discharge in the region, given highly homogeneous geographical and hydrological setting of the Ob River middle course. Similarly, for the evaluation of groundwater influence, we used available evaluations of the degree of groundwater feeding of WSL rivers based on previous hydrological works (Nikitin and Zemtsov, 1986).

These contrasting but representative water objects were sampled during two open water periods in 2014: the spring flood in May and the summer baseflow in July. Note that the access to some water bodies during flood was not possible and the whole water objects (secondary channels, lakes of the flood plain) could totally disappear being covered by the flood. We could not sample representative groundwaters of the area. The isolated lakes were sampled using a portable PVC boat, whereas the larger, interconnected water bodies, including the mainstream of the Ob River, were sampled from the motor boat using a submersible polycarbonate Aquatic Research<sup>®</sup> water sampler. Small parts of the river were sampled from the river bank or the middle of the flow. All of the sampling, storage and analytical procedures were identical to those described previously for boreal rivers and lakes (Shirokova et al., 2010, 2013; Pokrovsky et al., 2013), and they are explained in detail in the ESM-1. In addition to surface waters, we analyzed four integral (<0.45 um-filtered) snow samples collected in the end of the winter 2014 during our recent sampling campaign of snow particles and aerosols across the WSL (Shevchenko et al., 2015: Shevchenko et al., in preparation).

The TE-carbon concentration were analysed using best fit functions based on the least squares method, Pearson correlation and one-way ANOVA with STATISTICA version 10 (StatSoft Inc., Tulsa). The rang correlation coefficients were calculated to elucidate the relationships between the organic carbon and other dissolved components in the water objects. The ANOVA was carried out using Dunn's method because different aquatic systems comprised a different number of samples. In this method, a value of p < 0.05 indicates that the differences in the median values are important and are statistically significant.

#### 3. Results

# 3.1. Categories of major and trace elements exhibiting dependence on the DOC concentration

The list of sampled water bodies and their main hydrochemical characteristics is given in Table ESM-1. The lakes and rivers are clearly distinguished in terms of pH and DOC values (Fig. 2). The acidic and humic upland lakes exhibit the lowest pH values, being influenced by atmospheric feeding of surrounding bogs, peat and moss leaching. The flood lakes and the Ob River exhibited the pH above 7 most likely linked to groundwater feeding. Given a clear trend of DOC concentration decrease with pH increase in the pH – DOC plot, below we will use the DOC as best indicator of different water objects and main governing factor of TE migration.

Depending on their affinity to DOC, several groups of major and trace elements were distinguished. The 1st category comprised the dissolved inorganic carbon (DIC), specific conductivity, Na, K, Rb, Mg, Ca, sulfate, Cs, Sr, Mo, Sb and U. These elements exhibited a general decrease in concentration with an increase in the [DOC], achieving the lowest values in upland lakes, which are rich in DOC (Fig. 3 A–H). For the Ob River itself, the element concentration decreased with an increase in the DOC as well. Within this first category, various parts of the flooded zone sampled in May are



**Fig. 2.** DOC concentration in studied water objects as a function of pH. A decrease of [DOC] with the pH increase clearly marks the trend from acidic, humic, bog-fed upland lakes to ground-water-influenced rivers and flood lakes.

particular interesting as they presented a rather contrasting behaviour for different elements. First, the major (Ca, Mg, Na and DIC) and trace elements (Sr, Mo, Sb, U) were either independent of the DOC or their concentration decreased with the DOC (Fig. 3). On the other hand, K, Rb, and Si were correlated with the DOC in the flooding zone in May ( $0.58 \le R^2 \le 0.82$ , Fig. ESM-1). The ground water—fed elements are mostly pronounced in flood lakes during summer baseflow in July (Fig. 3A–E). Although most of them (DIC, Na, Mg, Ca, and Sr) are statistically independent of the DOC at p < 0.05, some clearly decrease as the DOC increases, marking an abrupt decrease of the groundwater influence (Mo, Sb, and U, Fig. 3F–H).

The 2nd category is composed of a few elements that are irrelevant to the DOC concentration, depicting no clear pattern in the concentration-DOC trend among various water objects. These are B, Cl, Si (except the flood zone in May) and V. Presumably, these elements present as neutral molecules or oxyanions that weakly interact with DOM and that may originate from atmospheric deposits (B and Cl) or surface flow (Si and V) rather than groundwater.

The 3rd category of elements comprises those that are controlled by organic and organo-mineral colloids, as follows from the results of the size fractionation described in the next section. These are insoluble, usually low mobile elements (Al, Fe, other trivalent hydrolysates, Ti, Zr, and Hf) and some metals (Cr, Zn, Ni, Ba, and Pb). They demonstrated a steady increase in concentration with an increase in the DOC, with the lowest values observed in the Ob River and the highest values observed in small tributaries and organic-rich upland lakes in July (Fig. 4A–L). Typically, the lithogenic elements of this category (Al, Fe, Ti, Zr, Hf, Th, and REEs) first increase their concentration by c.a. 2 orders of magnitude from 10 to 30 mg/L of DOC and then achieve a maximal concentration in most organic-rich rivers and upland lakes in July. At the same time, organic-rich upland lakes presenting c.a. 60 mg/L of DOC are not necessarily enriched in these elements relative to small rivers.

The analysis of the element concentration in the flood zone as a function of the distance from the main stream demonstrated statistically significant (p < 0.05) increase of the concentration of a number of elements, such as macro- (Si and K) and micro-nutrients (Mn), DOC and related metals (Fe, Ni, Co, and Cu), as shown in Fig. ESM-2. These elements are likely to be influenced by plant leaching (Si, K, Mn) and are present in the form of uncomplexed ions (Si, K, Rb) or organic and organo-ferric colloids (Fe, DOC, Cu, Ni, Co).

The divalent metals and micronutrients Mn, Cu and Zn should be considered separately from other elements (Fig. 5A–C). The



Fig. 3. Dissolved (<0.45 µm) concentration of DIC (A), Na (B), Mg (C), Ca (D), Sr (E), Mo (F), Sb (G) and U (H) as a function of dissolved organic carbon (DOC) for the Ob'river flood zone, rivers and lakes during baseflow and spring flood.

highest Mn concentrations are encountered in small rivers and upland lakes in July, in which Mn is independent of the DOC. The lowest concentrations of all three metals are observed in the Ob River in July. Zn exhibited the highest concentration in DOC-rich upland lakes and rivers in July, whereas Cu demonstrated the highest concentrations in the flood zone in May at the furthest distances from the main stream. It was highly correlated with DOC ( $R^2_{Cu, DOC} = 0.93$ ) in the flooding zone.



Fig. 4. Dissolved (<0.45  $\mu$ m) concentration of Al (A), Fe (B), Ti (C), Cr (D), Ni (E), Cd (F), As (G), Pb (H), Zr (I), La (J), Hf (K) and Th (L) as a function of dissolved organic carbon (DOC) for the Ob'river flood zone, rivers and lakes during baseflow and spring flood.



Fig. 4. (continued).

Given the large geographic coverage of samples from the spring flood zone, we tested whether the water objects of the flooded zone can be considered to be surrogates for the main river chemical composition. For this, we calculated the ratio of the element mean concentration in the Ob River and that in the flood zone in May (Fig. 6). Only a few elements deviate significantly from unity. These are U and Mo, which are enriched by a factor of 1.5–2.5 in the river relative to the flood zone water objects, and Zn, Fe and Mn, which are depleted by a factor of 3–10 in the Ob River. The other ~40 major and trace elements present in the flood zone waters fall within  $\pm 40\%$  of their riverine concentrations in May.

#### 3.2. Colloidal transport of the major and trace elements in the Ob River and upland lakes during summer baseflow and spring flood

The inorganic non-balanced charge  $((\Sigma^+ - \Sigma^-))(\Sigma^+ + \Sigma^-))$  calculated for most samples was  $\leq 0.1$ . Only the organic-rich upland lakes and humic river waters exhibited an important non-balanced anion deficit, with  $((\Sigma^+ - \Sigma^-))(\Sigma^+ + \Sigma^-)) = 0.1-0.6$ , which correlated ( $R^2 = 0.81$ ) with the concentration of DOC, typical for organic-rich boreal surface waters (Vasyukova et al., 2010). This strongly suggested the important role of organic ligands capable to complex major and trace elements in colloidal form.

The proportion of colloidal fraction was evaluated using in-situ dialysis in small, organic-rich upland lake and in the Ob river mainstream, in May and July (Fig. 7 and Fig. ESM-3). For the Ob River, proportion of colloidal form was <10–20% for anions and weakly complexed ions (Si, HCO<sub>3</sub>, K, Na, Ca, Mg, Rb, Cl, Cs, Li, SO<sub>4</sub>, Mo, Sb, V, W). Divalent metals (Cu, Ni, Zn, Co) exhibited a moderate proportion of colloids during both seasons. Trivalent and

tetravalent hydrolysates (Al, Fe, all REEs, Ti, Zr, Hf, Th) were strongly bound to organo-ferric colloids (>70%). There was an increase of the (Low Molecular Weight ligands) LMW<sub>< 1 kDa</sub> fraction in July relative to May for Fe, Cr, Ti and Cd. The presence of the small size suspended fraction of the size range from 1 kDa to 0.45  $\mu$ m containing lithogenic elements, such as Fe, Cr and Ti, may explain their high colloidal proportion in May. For the other elements, we observed a slight increase of colloids in July relative to May, probably because of the dominance of LMW forms from grass leachates, which are highly abundant in the flood zone in May (Fig. ESM-4).

Colloidal speciation in the upland lake is similar to that measured in the humic, organic-rich (30 mg/L), low-TDS lakes of western Siberia (i.e., Pokrovsky et al., 2013). The majority (>60%) of trace elements and alkaline-earth metals (Ca, Mg, Sr, and Ba) present as colloids, and only Cl, Si, Rb, Cs and Sb are present in a small proportion of the colloidal forms (<30%, as illustrated in Fig. ESM-3).

#### 4. Discussion

# 4.1. Previous studies of the Ob River watershed and element biogeochemistry in the flood zone

The geochemistry of the suspended matter of western Siberia's large river (Irtush, the largest tributary of the Ob River) was studied ten years ago (Gordeev et al., 2004) during the summer baseflow period; however, no data on the dissolved river water fraction were collected. Occasional data of some major element and nutrients (Gordeev et al., 1996) and trace metals, such as Fe, Cu and Zn (Dai and Martin, 1995; Telang et al., 1991; Shiklomanov and Skakalsky, 1994; and Alexeeva et al., 2001), are available for the mouth zone



Fig. 5. Dissolved (<0.45  $\mu m$ ) concentration of Mn (A), Zn (B), and Cu (C) as a function of dissolved organic carbon (DOC) for the Ob'river flood zone, rivers and lakes during baseflow and spring flood.

of the Ob River, Moran and Woods (1997) reported the Cd, Cr, Cu, and Ni concentration in the water column of the Ob and Irtush Rivers during summer baseflow. The range of metal concentrations reported in this previous study (0.001-0.015 for Cd, 0.06-0.34 for Cr, 1.8–4.8 for Cu and 0.8–2.8  $\mu$ g/L for Ni) is in good agreement with our baseflow and spring flood measurements (0.005, 0.2, 1.0-1.2 and 0.5–1.3 µg/L for Cd. Cr. Cu and Ni, respectively). Over the past decade, a significant amount of information on the major and trace element concentrations in the mouth zone of the Ob River was collected in the course of PARTNERS and ARCTIC GRO programs (Holmes et al., 2012). All of the aforementioned studies provided the major features of dissolved and suspended load chemical composition either at the terminal gauging stations or at the main river channel stations, without addressing the mechanisms controlling the element transport from the source (soil, peat, or litter) to the main stream via primary and secondary river channels and intermediate water bodies (lakes, small tributaries, and flood zones). The flood zone biogeochemistry was extensively studied in the European rivers, mainly with respect to pollution history and short-term events (i.e., Berner et al., 2012; Zachmann et al., 2013). The present study extends this knowledge towards the largest subarctic river allowing distinguishing between the contributions of the different sources and hypothesizing autochthonous processes in the water bodies during the two main open-water seasons by taking a "snapshot" of the spatial variability of all of the components of the flood zone and adjacent territories.

Highly soluble and mobile elements, such as major anions (DIC, sulfate), cations (Na, K. Mg, Ca), other alkali (Rb, Cs), alkaline earth traces (Sr), trace oxvanions (Mo, Sb) and U, marked the influence of underground feeding in July, as confirmed by an abrupt decrease of their concentrations with an increase in the DOC (Fig. 3F-H). In contrast, K, Rb, Si and Cu demonstrated a strong increase in concentration with the DOC in the flooding zone, with the maximal concentrations occurring within the flooded grass field (sample OB-9M, at the most remote sampling point). Most likely, these elements are controlled by leaching from the grass biomass which is strongly enriched in Si, K and Rb (Kovda, 1956). For example, Rb and K correlations with the DOC were the highest of the flood zone  $(R^2 = 0.82 \text{ and } 0.72, \text{ respectively})$ . While K is an essential component of grass and other ground vegetation that is covered by flood water in May, isomorphic Rb tightly follows this macronutrient, as is known from other environments (Stepanova et al., 2015; Kabata-Pendias, 2004).

Mn, Zn and Cu present a concentration-DOC dependence pattern, which was the opposite of the other elements. These potential micronutrients are known to be strongly linked to the dissolved organic carbon in temperate and subarctic rivers and lakes (Rember and Trefry, 2004; Pontér et al., 1992), as also follows from our dialysis results (Fig. 7). However, their concentrations do not follow the same general trend as that of the other insoluble traces. The lowest Mn concentration in the Ob River in July may be linked



Fig. 6. The ratio of the element concentration in the Ob' River to that in the flood zone in May. The error bars represent 2 s.d. (n = 10).



Fig. 7. Proportion of colloidal fraction in the Ob River in May and July.

to a strong insulation and the high residence time in this system, thus leading to Mn photo-oxidation, especially in the course of diurnal photosynthesis (Scott et al., 2002; Nimick et al., 2003; Pokrovsky and Shirokova, 2013). The elevated Mn concentration in certain flood lakes during baseflow (Fig. 5A) may be due to both underground discharge and sediment respiration (upward flux, Audry et al., 2011). Additionally, Mn may be mobilized from silt deposits from the RSM (Björkvald et al., 2008) because flood plains are known to play an important role in the storage of fine suspended sediment (Bradley and Cox, 1990). The river suspended matter transport is especially important for the Ob River (Smith and Alsdorf, 1998). Finally, in small humic rivers and organic-rich upland lakes, the influence of photo-oxidation and phytoplankton uptake is minimal, and the Mn concentration here is maximal. For Zn (Fig. 5B), the biouptake in the main river course in July (warm water) may decrease its concentration relative to the May flood (cold water) by approximately 5-fold. The highest concentrations of this element in the organic-rich upland lakes and small rivers in July ( $R^2_{Zn, DOC} = 0.71$  and 0.91, respectively) illustrate the importance of organic colloids but also the lack of uptake by the phytoplankton or biodegradation in these small humic water bodies. Cu has no visible link to the DOC in small rivers and flood lakes in July (p > 0.05) but exhibits pronounced control by the DOC in the flood zone in May and in the upland lakes in July ( $R^2_{Cu, DOC} = 0.93$  and 0.79, respectively, Fig. 5C). This result indicates the importance of the organic binding of this metal and its mobilization from surrounding peat deposits in lakes and ground vegetation in the flooding zone. By contrast, the mineral and underground feeding that are detectable for Zn in lowland flood lakes and small rivers during summer baseflow are virtually unimportant for Cu. The latter presumably originated from the organic (surface litter and grass of the riparian zone, Fig. ESM-4) horizon rather than the deep (mineral) horizon. Similarly, Zn and Si are also enriched in terrestrial vegetation and have concentrations superior by a factor of 2-3 in the flooded zone compared to the main stream because of their intensive leaching from the plant litter and grass.

The comparison of the Ob River's water dissolved load to the isolated and interconnected water bodies from the flooding zone in May demonstrated a similarity, within  $\pm 30-40\%$  of the dissolved element concentration in the flood zone and the main stream (Fig. 5). Significant enrichment (p < 0.05) of the Ob River in U and Mo may suggest pronounced underground feeding in the main water channel, which is virtually absent for the surface flood water bodies. The latter are likely to be fed from atmospheric precipitates containing non-negligible concentrations of these elements.

Given the lack of the rain water samples of the region, analyses of snow collected in the end the winter in the Tomskaya region (Ob's River middle course) allowed the assessment of the degree of possible influence of atmospheric feeding on the lake water chemistry. Comparison of average filtered snow samples (Table ESM-1) with the average concentrations of upland (permanent) lakes fed by surrounding bogs revealed two families of elements: (*i*) weakly (<30% which is within the variations of major and TE concentrations both in snow and in the lake water) affected by the snow melt: DOC, Na, Mg, K, Ca, Al, Si, Ti, V, Cr, Mn, Fe, Cu, Co, As, Ga, Rb, Sr, Zr, Ba, REEs, and (*ii*) significantly (30–100%) affected by the snowmelt: DIC, Cl, SO<sub>4</sub>, Zn, Mo, Cd, Sb, Cs, Pb and U. The flood lakes sampled in May, when these water bodies are likely to be fed by melt snow, demonstrated significant (>50% of lake water concentration) influence of the snowmelt for Cl, Al, Zn, Ga, Cd, Sb and Pb with weak effect for all other major and trace elements.

# 4.2. Role of the organic and organo-ferric colloidal transport of trace elements in the Ob watershed

The colloidal speciation of most major cations and all of the trace elements ( $\leq$ 80% in LMW<sub>< 1 kDa</sub>forms) in the humic, low TDS upland lake is consistent with the peat feeding of this lake. The majority of low-mineralized water bodies of western Siberia are very rich in colloids, with even major elements (Ca and Mg) often being present in a >50% colloidal form (Pokrovsky et al., 2013; Shirokova et al., 2013). This contrasts with the organic-rich boreal rivers, which rarely have more than 30% of colloidal Ca (i.e., Dahlqvist et al., 2004, 2007; Pokrovsky et al., 2010). Such rivers have a much higher TDS at an otherwise similar DOC and, as a result, lesser stability of the organic and organo-mineral colloids in solution because of the compacting of the electric double layer (see discussion in Pokrovsky et al., 2013).

Insoluble, usually low mobile elements (Al, Fe, other trivalent hydrolysates, Ti, Zr, and Hf) and some metals (Cr, Zn, Ni, Ba, and Pb) demonstrated a systematic increase in concentration with an increase in the DOC in all of the studied water objects. Presumably, similar to other boreal environments (Dahlqvist et al., 2007; Bagard et al., 2011; Pokrovsky et al., 2010), they are limited by the availability of their main carriers, organic and organo-ferric colloids, rather than the availability of the source, i.e., peat and mineral soil or plant litter. It is important to note that the majority of these trace elements significantly increase their concentration in the flooding zone, especially in the stagnant waters at a large distance from the river mainstream.

The role of the dissolved organic matter on rare earth elements' transfer in surface waters is evidenced by the positive correlation between the DOC and the REE concentration. Taking together, in all of the sampled water bodies, the correlation coefficient for DOC—heavy REEs was higher than 0.6, whereas the same coefficient for the DOC—light REE correlation was <0.6. This result confirms the relative affinity of HREE to organic ligands and LREE to iron colloids, which were established from several previous studies in boreal and temperate zones (Andresson et al., 2006; Sholkovitz, 1995; Leybourne and Johannesson, 2008). Consistent with that result, the percentage of colloids (essentially organo-ferric entities) was higher for LREE, and the low molecular weight fraction

(essentially organic ligands) was higher for HREE at p < 0.05 (see Fig. 7).

The existence of a certain limit on the concentration increase of Al, Fe, Ti, Zr, Hf, Th, and REs after a threshold of the DOC concentration (Fig. 5A–C and I–L) is evidenced in the organic-rich (c.a., 30 mg/L DOC) small rivers sampled in July, without a further increase in the concentration of TE in the upland lakes containing up to 60 mg/L of the DOC. This strongly suggests that in organic-rich (i.e., >20 mg/L) surface waters, the concentration of these elements is limited by their source (mineral soil or groundwater, most visible in small rivers during summer baseflow) rather than the availability of the carriers (soluble soil/peat humic and fulvic compounds).

In small rivers draining podzol mineral soils and peatlands during summer baseflow, the concentration increase of the insoluble elements (Fe, Ti, Pb, Zr, Th, REEs) ranges between 2 and 4 orders of magnitude for a ~3-fold increase in the DOC. The most likely mechanism of organo-ferric colloids generation, which is well established in other boreal zones (c.a., Pokrovsky and Schott, 2002), is TE coprecipitation with the Fe oxyhydroxide subjected to oxidation at the surface redox front. This most likely occurs within the riparian or hyporheic zone of the stream, where underground, partially anoxic water meets well oxygenated, organic-rich surface waters. Note that the enrichment of hyporheic sediments with Feoxyhydroxide is fairly well known in other pristine boreal rivers (cf. Siergieiev et al., 2014). Therefore, given the rather high DOC concentration in the surface western Siberian context, including Ob's flood plain/riparian zone, we suggest that the element source (including Fe) is of primary importance for colloid generation in the riparian zone of the small rivers. The limited underground feeding of small, organic rich upland lakes (~60 mg/L of DOC) precludes the further buildup of the trace element concentration relative to the flood lakes and organic-rich rivers, despite the doubling of the DOC from the surrounding peatlands.

## 4.3. Allochthonous and autochthonous processes controlling element transfer in the flood zone and in the main river

It can be hypothesized that the water residence time, which is known to be the main control of organic carbon (Algesten et al., 2003; Hanson et al., 2011; Köhler et al., 2013) and, presumably, related trace elements in the watersheds, is quite short in the flooded zone. This can strongly increase the relative impact of the surface (organic) source, such as fast plant litter leaching in the flood zone versus deep (groundwater) input related to slow mineral dissolution for rivers and permanent lakes. On the other hand, element removal from the water column of the river or lakes via phytoplankton uptake and heterotrophic and photo degradation of colloids, followed by precipitation to the bottom sediments, may also be tightly linked to the water residence time (WRT) in these water bodies. A preliminary evaluation of the hydrological balance of all of the studied water objects allowed them to be classified as follows in terms of the WRT: flood zone in May (days to 1-2 weeks)  $\leq$  small rivers in July < Ob River < flood lakes in July < upland lakes ( $\leq 1-2$  years). This order cannot be directly translated to the DOC and element concentration in various parts of the ecosystem measured in this study, as other enriching and depleting factors compete for the resulting concentration. The main processes affecting the surface bodies of the water chemical composition for various components of the lateral profile, from the main stream to the upland lakes, are shown in Fig. 1 B. The processes enriching the surface water bodies in various solutes are groundwater feeding, plant litter leaching, and peat (soil) leachate. The degree of groundwater feeding (visible only for the 1st group of highly labile elements) follows the order: flood zone in May < upland lakes < small rivers in July < Ob River in May < Ob River in July < flood lakes in July.

The factors depleting the element concentration are phytoplankton uptake and photo- and bio-degradation of colloids, leading to DOM and related element coagulation and precipitation, as shown in other studied continuums of the boreal watersheds (Agren et al., 2014; Ilina et al., 2014). Note that the vulnerability of the riverine DOC to bacterial mineralization is highly sensitive to the origin of organic matter, and it is the highest for forest carbon at high flow and the lowest for mire carbon (Berggren et al., 2009).

The influence of the processes removing the elements from the water column, such as plankton uptake and photo and biodegradation, is largest in flood lakes in July and the Ob River itself during baseflow and smallest in small rivers, the latter having the lowest water residence time. Note that even during few days of exposure of fresh peat-derived organic matter, it can be photo-oxidized with a rate of 10 mg C L<sup>-1</sup> day<sup>-1</sup> (Moody et al., 2013). However, we do not expect that the photo-oxidation and bacterial degradation will be significant in the organic-rich Ob's tributaries (samples OZE-4, 6, 7 and 14, Table ESM-1). In a similar boreal stream network, the loss of the DOC due to photo- and biodegradation from headwaters to the outlet was shown to be less than 1 mg L<sup>-1</sup> (Tiwari et al., 2014).

# 4.4. Projections of the element concentration and speciation in the Ob River watershed under a climate change scenario

The general picture of river water hydrochemistry in western Siberia under a climate warming scenario is that the relative role of groundwater feeding will increase as long as the thawing depth thickens and the permafrost degrades (Frey et al., 2007). Therefore, in the permafrost-bearing zone, the role of surface flow, peat leaching and plant litter degradation versus groundwater feeding will decrease. However, there is no current projection on the evolution of the permafrost-free boreal taiga zone, such as the majority of the Ob River watershed. Unlike European boreal and subarctic regions, which are currently recovering from a past acidification impact and demonstrating a Zn, Ni, and Cu decrease over the previous few decade(s) (Huser et al., 2011, 2012), western Siberia Lowland was only weakly affected by local atmospheric pollution, as also follows from the moss analyses across the WSL (Stepanova et al., 2015). As such, the evolution of the hydrochemical parameters in this region will be mainly linked to the natural factors.

In the middle course of the Ob River studied in this work, the main factors influencing the element input from the surrounding mineral and organic substrate to the Ob River are i) the groundwater influx during the baseflow and *ii*) plant and peat leaching, which depends on the water surface area coverage of the flooding zone during high flow. There is no reason to assume any significant modification of the groundwater chemical composition and discharge under climate warming; rather, the modification of the winter precipitation regime will influence the water discharge and flood area during the spring period. The exact projection of the precipitation change in western Siberia with sufficient seasonal resolution that is necessary to assess both small watersheds and the middle course of the main river is not available. By contrast, the main factors influencing element uptake from the water column and limiting their transport in the form of organic complexes and colloids can be evaluated. The DOC of the river water and small streams is believed to increase in response to on-going climate change in Western Europe and Canada (Oni et al., 2013; Vuorenmaa et al., 2006). However, the range of this increase is likely to be below 20 mg/L, whereas the most significant increase of the insoluble element concentration in the small rivers of the Ob region occurs at DOC >20 mg/L. Therefore, the mire-dominated feeding of the majority of the studied water bodies via peat leaching, which provides significant DOC concentration in headwater streams, are unlikely to be modified by the temperature rise.

The processes removing the TE from the water column are expected to be more sensitive to climate change. However, their influence will be mostly pronounced during the summer baseflow period. First, there will be an earlier onset of spring phytoplankton growth in temperate lakes in a warmer climate (Peeters et al., 2007). Second, the heterotrophic bacterioplankton degradation of colloids will increase as the water temperature rises, provided that the inorganic nutrients are not limited (i.e., Berggren et al., 2010). Finally, photodestruction should be enhanced at elevated temperatures (Leifer, 1988; Likens, 2010). The increase of both the primary productivity and heterotrophic mineralization of the DOM in the water column will certainly decrease the concentration of the total dissolved (<0.45 µm) DOC and trace elements in upland lakes, the Ob River and flood lakes, similar to what was reported during short-term water heating in other boreal lakes in European Russia (i.e., Shirokova et al., 2013) and western Siberia's thermokarst lakes (Pokrovsky et al., 2013).

#### 5. Conclusions

A hydro-chemical study of the Ob River's middle course, first order small tributaries, persisting and temporary flood lakes and upland lakes as well as the large flood zone in May and July established first-order factors controlling the dissolved organic carbon and related metal sources and sinks in this environmentally important ecosystem. Considering two contrasting seasons, spring flood and summer baseflow, helped distinguish the elements controlled by the groundwater influx (DIC, Na, Mg, Ca, SO<sub>4</sub>, Sr, Mo, Sb, and U) and those controlled by surface runoff via plant litter and topsoil leaching, notably during the spring flood (Si, K, Rb, Mn, Zn, and Cu). At the same time, Cl, SO<sub>4</sub>, Zn, Cd, Sb, Cs and Pb in upland lakes and flood lakes in May could be significantly influenced by aerosol deposition (snow melt).

The main carriers of many insoluble trivalent and tetravalent elements and some divalent metals (Cd, Pb, Cu) are organo-ferric colloids stabilized by dissolved organic matter. The main river stream's dissolved chemical composition can be approximated within  $\pm 30-40\%$  by that of the flood zone in May. It is hypothesized that the main autochthonous processes controlling the DOC and related TE transformation between different water bodies are phytoplankton uptake and the microbial heterotrophic and photodegradation of organo-mineral colloids, which in turn strongly depend on the water residence time. It is possible that under ongoing climate warming, these autochthonous processes will mostly affect the removal of colloidal TE from the water column of the flood lakes, large and small rivers and upland lakes of the Ob River's middle course watershed whereas the groundwater-influenced soluble elements will remain unaffected.

#### Acknowledgements

This work was supported by BIO-GEO-CLIM grant No 14.B25.31.0001 of Russian Ministry of Science and Education. LS and RM acknowledge partial (25%) support from an RSF grant No 15-17-10009.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2015.08.005.

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